



EurJIC

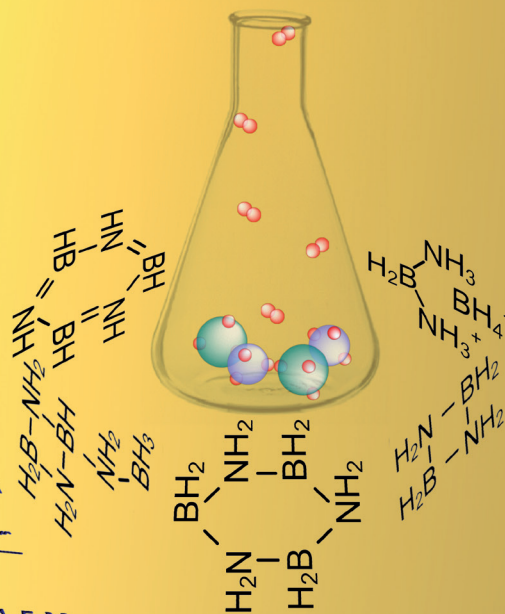
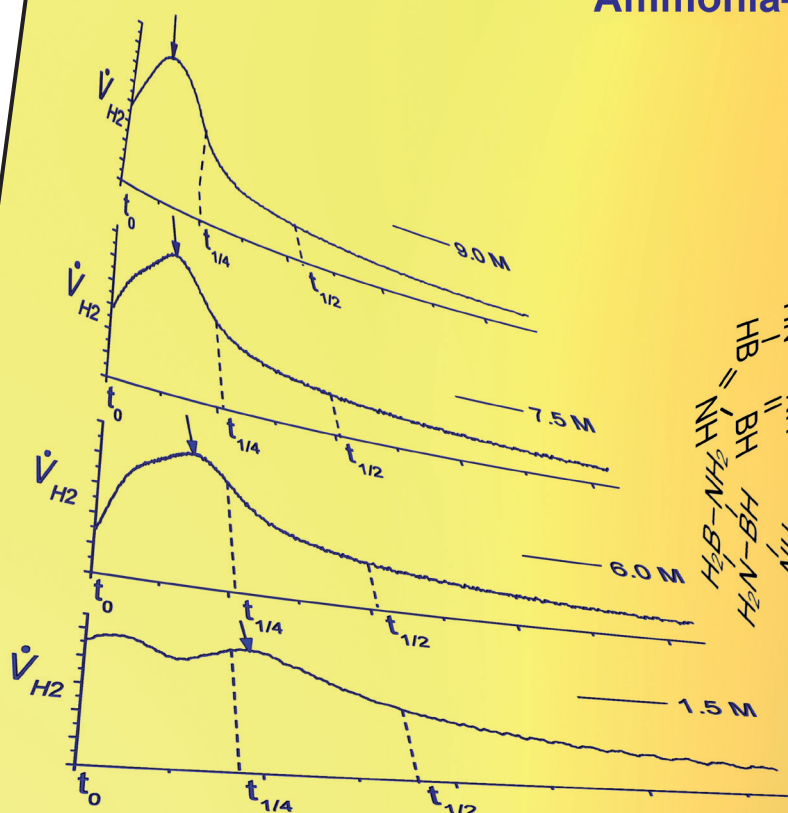
European Journal of
Inorganic Chemistry

1/2012

1st January Issue

Hydrogen Release from

Ammonia–Borane in Glyme



Cover Picture

Florian Mertens et al.

Dehydrogenation of Ammonia–Borane/Triglyme Mixtures

Microreview

Angela K. Crane and Mark J. MacLachlan

Porous Structures Based on Metal Salen Complexes

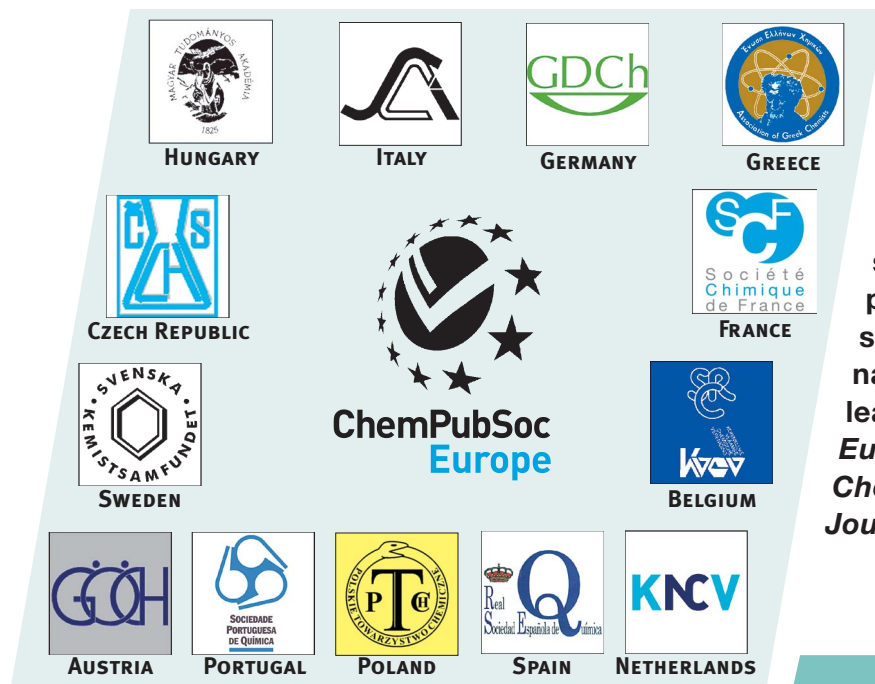
WILEY-VCH

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A Journal of



ChemPubSoc
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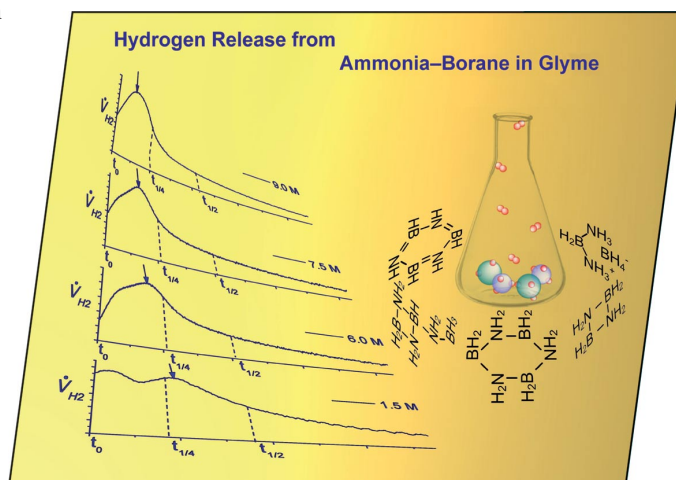


EurJIC is a journal of ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem*, *ChemCatChem*, *ChemPlusChem* and *ChemistryOpen*.

COVER PICTURE

The cover picture shows a graph of the hydrogen release rate from ammonia–borane dissolved in glyme solutions (left). On the right, the compounds formed during the decomposition of ammonia–borane under these conditions as detected by NMR spectroscopy are depicted. The increase of the hydrogen release rate during the course of the reaction as well as the spectroscopic analysis indicate the presence of a complex process governed by multiple pathways. Similarly to the hydrogen release from solid ammonia–borane and in contrast to the low concentration case, the analysis of the decomposition of ammonia–borane in highly concentrated glyme solutions demonstrates that the diammoniate of diborane (DADB) plays a vital role in the overall decomposition scheme. Details are discussed in the article by F. Mertens et al. on p. 49ff.





ChemPubSoc Europe – Serving the needs of the chemical community



Karen Hindson, Editor, EurJIC



International Year of
CHEMISTRY
2011

The past year stood under the star of the International Year of Chemistry (IYC) and therefore was characterized by a look back to the heroes, and particularly the heroines in the emphasis on the contributions by women to our discipline, as well as to

a look forward not only to the possibilities in Chemistry to solve the present worldwide problems, but also to the education of those who will take over the task in years to come. All chemical societies played an intensive role in filling the year with stimulating activities for interested laymen and professional chemists alike. A coordinated effort worldwide is an excellent focus for our public relations effort and I hope that it also serves to remind us that positive publicity starts with us.

In line with the IYC emphasis on women, ChemPubSoc Europe, the union of 16 European chemical societies that own EurJIC, selected the birthplace of Marie Curie, now

the headquarters of the Polish Chemical Society, for its discussions on publishing activities to suit the needs of their members and the chemistry community in general. An emerging concern was the requirement of some funding bodies that the research they funded should be freely accessible to all. All the ChemPubSoc Europe journals including EurJIC offer “OnlineOpen”, a system whereby an author may pay for an article in the journal to be available to non-subscribers from the time it appears in Wiley Online Library as an EarlyView paper. This program, however, does not satisfy all funding agencies, some of whom insist that the journal must be a dedicated open-access publication. ChemPubSoc Europe felt that, in general, the perception amongst the chemistry community was that no open-access journal catered to their research as well as the subscription journals. Certainly, no chemical society offered a journal to suit their needs for open access. The societies therefore decided to fill this gap with a ChemPubSoc Europe gold-road, open-access journal, *ChemistryOpen* (<http://www.chemistryopen.org>). The new journal joins the



Representatives of ChemPubSoc Europe and Wiley-VCH in front of the Maria Skłodowska Curie museum and Headquarters of the Polish Chemical Society.

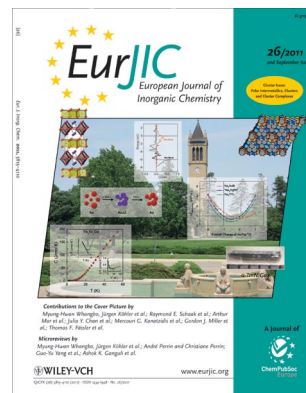
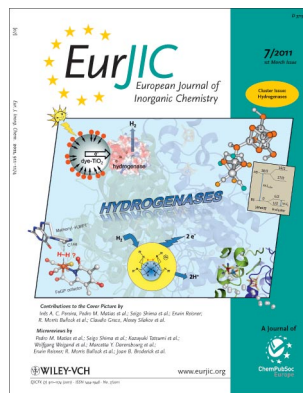
portfolio that includes *EurJIC*, *EurJOC*, *Chemistry – A European Journal*, and the interdisciplinary journals *Chem BioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem* from the beginning of 2012. The societies selected editors who have gained experience in these journals to guide the new *ChemistryOpen*. Haymo Ross, Editor of *EurJOC*, and I were appointed Co-Editors and Natalia Ortuzar of *ChemMedChem* accepted the position of Deputy Editor.



Following the tradition of consolidating their publishing activities under the umbrella of ChemPubSoc Europe, one of the member societies offered a national journal, the Collection of Czechoslovak Chemical Communications, to be the basis of another relaunched journal in the portfolio. *ChemPlusChem* (<http://www.chempluschem.org>) is set to become the platform for research exploring the interfaces of traditional disciplines, which often does not fit into any existing publication. Again, ChemPubSoc Europe appointed an editor of an existing journal, Neville Compton, to give this multidisciplinary journal a good start.

This year two anniversaries have a special interest for inorganic chemistry. Fifty years ago the synthesis of XePtF_6 ^[1] challenged the accepted belief that the noble gases were unreactive. And in 1912 a discovery that has had far-reaching repercussions for inorganic chemistry was reported at the Physikalische Gesellschaft of Göttingen: the diffraction of X-rays by crystals.^[2] Two years later Max von Laue was awarded the Nobel Prize in Physics for this research. Today most issues of every inorganic chemistry journal contain many single-crystal X-ray structures. Last year, in acknowledgement of this fact and on the advice of an Advisory Board member, *EurJIC* sends the CIF files with an article for peer review to facilitate and speed up the work of our peer reviewers, whose time we value highly. We, therefore, wish to remind all authors of papers that include X-ray crystal structures to send the CIF files by mail to EurJIC@wiley-vch.de when they upload their manuscript.

These two anniversaries underline once again the complexity of inorganic chemistry. As a journal that aims to cover all areas that are included in this broad discipline, *EurJIC* now publishes Cluster Issues that draw together papers



from major players in fields of inorganic chemistry that may not be represented in every issue. Last year issue 7 clustered excellent papers on all aspects of hydrogenase research. The second cluster issue was prompted by the 85th birthday of the best known proponent in the field – “Corbett chemistry” was covered in issue 26 on Polar Intermetallics, Clusters and Cluster Complexes. Watch out for *EurJIC*’s next Cluster Issue on the highly topical theme of redox-active ligands and open-shell reactivity. Others will follow at irregular intervals.

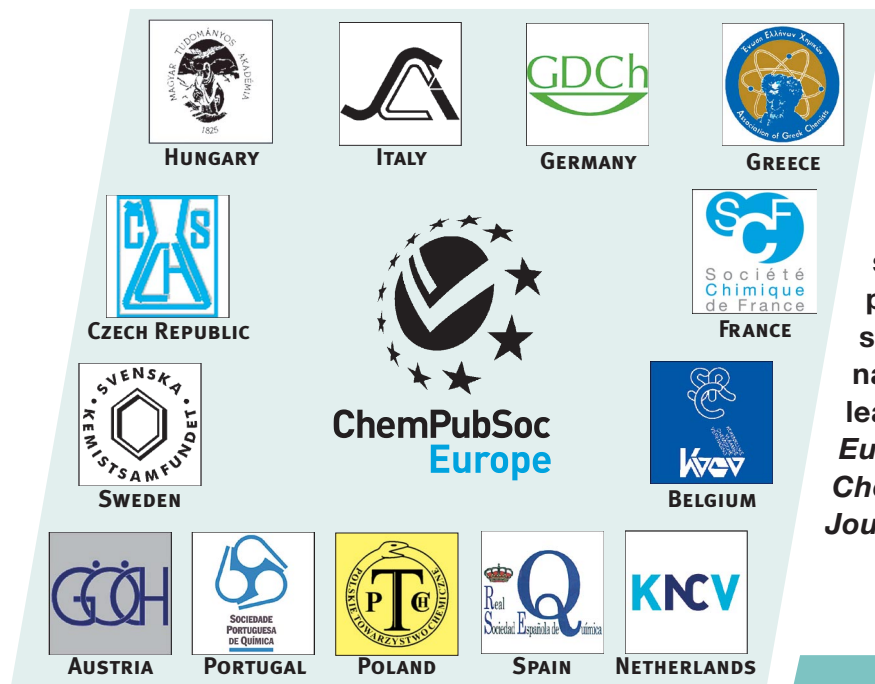


All in the Editorial office wish the authors and readers of *EurJIC* a stimulating and successful “Personal Year of Chemistry 2012”!

Karen J. Hudson

[1] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218.

[2] http://en.wikipedia.org/wiki/Max_von_Laue.

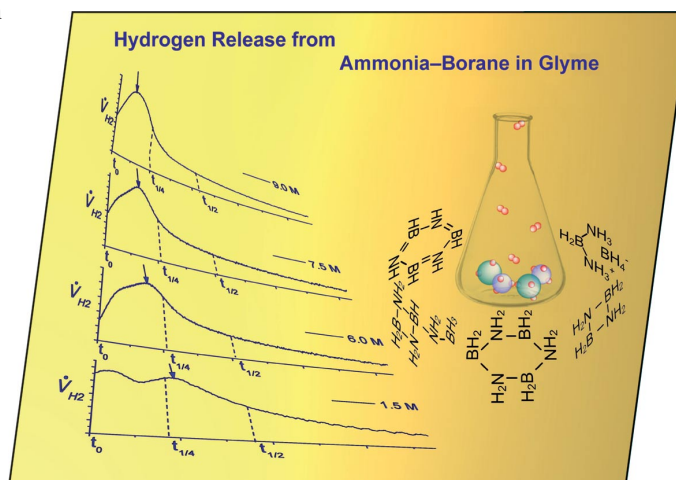


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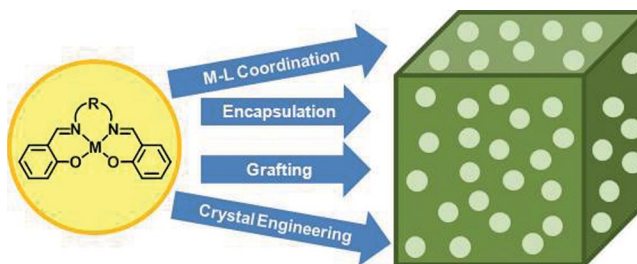
MICROREVIEW

Immobilized Salen Complexes

A. K. Crane,
M. J. MacLachlan* 17–30

Portraits of Porosity: Porous Structures Based on Metal Salen Complexes

Keywords: Schiff bases / Microporous materials / Supramolecular chemistry / Salen complexes



By integrating metal salen complexes into new porous architectures, chemists are developing exciting new materials that com-

bine the shape- and size-specificity of the porous structure with the catalytic activity and sensing ability of the metal complex.

SHORT COMMUNICATIONS

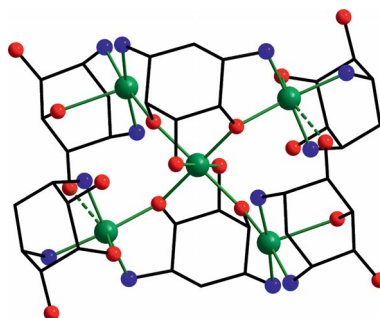
Supramolecular Microporous Networks

G. J. Merten, C. Neis, S. Stucky,
V. Huch, E. Rentschler, H. Natter,
R. Hempelmann, K. Stöwe,
K. Hegetschweiler* 31–35



The Interplay of Hydrogen Bonding and Multiple Metal Binding – A New Cyclic Polyaminopolyalcohol Ligand as Building Block for the Construction of Microporous, Supramolecular Networks

Keywords: Coordination modes / Bridging ligands / N,O ligands / Amino alcohols / Chelates / Hydrogen bonds



$[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}$ cations (daci = 1,3-diamino-1,2,3-trideoxy-*cis*-inositol) and SO_4^{2-} form a porous network with a crystalline, hydrated (30 °C) and an amorphous, dehydrated (150 °C) phase. Although this transition is a complex multi-step reaction, it is entirely reversible.

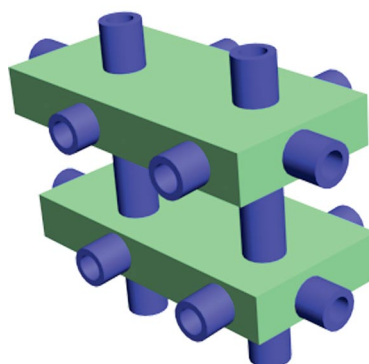
Unusual Layered Frameworks

Y. Han, Y. Li,* J. Yu, Q. Pan,
R. Xu 36–39



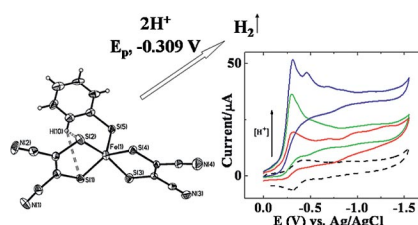
A Zinc Phosphate Structure with Unusual Double-Sheet Layers Templated by a Cobalt Hexaammine Complex

Keywords: Layered compounds / Microporous materials / Template synthesis / Cobalt / Zinc phosphate



A new zinc phosphate compound, $[\text{Co}(\text{NH}_3)_6]_3[\text{Zn}_8(\text{HPO}_4)_8(\text{PO}_4)_2](\text{PO}_4)$, with unusual double-sheet layers has been synthesized. Within the layered host framework, 8-ring apertures along the thickness and in the plane of each layer are interconnected to form an 8^6 cavity, the shape of which is directly affected by the guest cobalt hexaammine complex cation.

The iron(III) dithiolene complex $[\text{PPh}_4]_2\text{[Fe(mnt)}_2(\text{SPh})]$ (**1**) has a highly distorted square-pyramidal geometry and an intermediate spin ferric ion, which catalyzes electrochemical H_2 evolution at the lowest achievable reduction potential known to date: $E_p = -0.309$ V in CH_3CN and $E_p = -0.53$ V in H_2O .



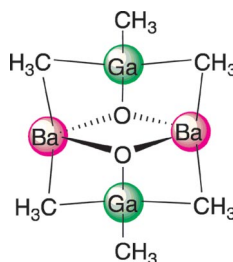
A. Begum,* S. Sarkar* 40–43

An Iron(III) Dithiolene Complex as a Functional Model of Iron Hydrogenase

Keywords: [Fe] hydrogenase / H_2 evolution / EPR spectroscopy / Cyclic voltammetry / Dithiolenes / Iron

Soluble BaO

The reaction of $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ with the chelating Lewis base 1,10-phenanthroline (Phen) gave the dibarium complex $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{Phen})]_2$, whereas its treatment with the Lewis acid GaMe_3 afforded the soluble molecular barium oxide $[\text{Ba}(\mu_4\text{-O})(\text{GaMe}_3)_2(\text{toluene})]_2$.



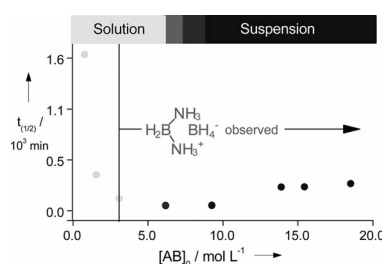
O. Michel, K. W. Törnroos,
C. Maichle-Mössmer,
R. Anwander* 44–47

Barium Bis(dimethylsilyl)amide – Adduct vs. Oxo Formation

Keywords: Barium / Amides / Molecular oxides / 1,10-Phenanthroline / Agostic interactions

FULL PAPERS

Ex situ ^{11}B NMR spectroscopic studies and gas volumetric analysis of the thermolysis reaction of ammonia–borane (AB) dissolved in triglyme (TG) reveal an unexpected but favourable concentration dependence of its dehydrogenation behaviour. In concentrated solutions of AB in TG, diammoniate of diborane was found in significant amounts similar to the solid state, yet the mechanism of AB decomposition differs.



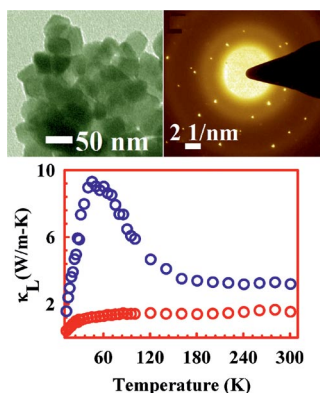
J. F. Kostka, R. Schellenberg, F. Baitalow,
T. Smolinka, F. Mertens* 49–54

Concentration-Dependent Dehydrogenation of Ammonia–Borane/Triglyme Mixtures

Keywords: Ammonia borane / Dehydrogenation / Hydrogen storage / Kinetics / Reaction mechanisms / Thermolysis

Nanocrystals for Thermoelectrics

High-yield 40 nm $Pnmm$ FeSb_2 nanocrystals were synthesized by a low-temperature ethanol-mediated solvothermal process. Polycrystalline FeSb_2 obtained by densifying the nanocrystals by means of spark plasma sintering resulted in a large reduction in the thermal conductivity (red) as compared to that of the bulk (blue) due to nanoscale grains.



A. Datta, G. S. Nolas* 55–58

Synthesis and Characterization of Nanocrystalline FeSb_2 for Thermoelectric Applications

Keywords: Antimony / Iron / Nanostructures / Crystal growth / Thermoelectricity / Thermal conductivity

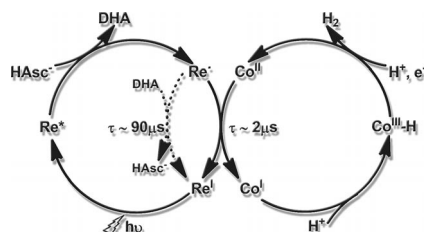
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Photocatalytic Hydrogen Evolution

M. Guttentag, A. Rodenberg, R. Kopelent,
B. Probst, C. Buchwalder, M. Brandstätter,
P. Hamm,* R. Alberto* 59–64

Photocatalytic H₂ Production with a Rhenium/Cobalt System in Water under Acidic Conditions

Keywords: Hydrogen / Photochemistry / Green chemistry / Cobalt / Homogeneous catalysis



Ascorbic acid was used as electron donor in a homogeneous rhenium/cobalt-based system for photocatalytic hydrogen evolution to lower the pH of the reaction solution. The system showed higher stability in terms of turnover numbers and reaction times than similar systems that work under basic conditions with triethanolamine as electron donor.

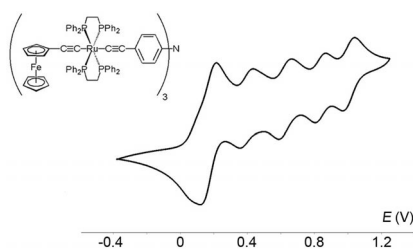
Molecular Optical Switches

G. Grelaud, M. P. Cifuentes, T. Schwich,
G. Argouarch, S. Petrie, R. Stranger,
F. Paul,* M. G. Humphrey* 65–75



Multistate Redox-Active Metalated Triarylamines

Keywords: Metallocenes / Sandwich complexes / Ruthenium / Iron / Alkyne ligands / Electrochemistry



Modular construction of complexes that contain ferrocenyl, bis(bidentate diphosphane)ruthenium, and triarylamine units linked through ethynyl groups has afforded species stable in up to six reversibly interconvertible redox-active states with distinct linear optical properties.

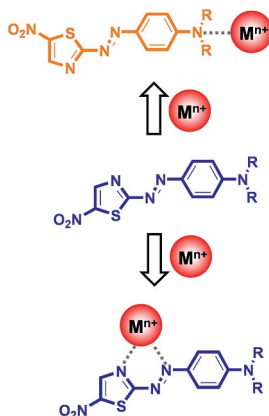
Chromogenic Cation Sensors

T. Ábalos, M. Moragues, S. Royo,
D. Jiménez, R. Martínez-Mañez,* J. Soto,
F. Sancenón, S. Gil, J. Cano 76–84



Dyes That Bear Thiazolylazo Groups as Chromogenic Chemosensors for Metal Cations

Keywords: Chemosensors / Cation sensors / Lead / Mercury / Density functional calculations / Dyes / Azodyes



A family of dyes that contain a thiazolylazo group and several macrocyclic cavities with different ring sizes and type and number of heteroatoms has been synthesised and characterized. Studies of protonation and coordination behaviour in the presence of metal cations have been carried out. The interaction was also studied by using density functional theory quantum mechanical calculations.

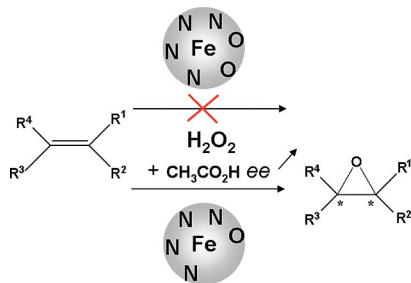
Biomimetic Iron Catalysts

F. Oddon, E. Girgenti, C. Lebrun,
C. Marchi-Delapierre, J. Pécaut,
S. Ménage* 85–96



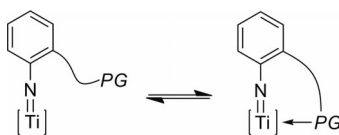
Iron Coordination Chemistry of N₂Py₂ Ligands Substituted by Carboxylic Moieties and Their Impact on Alkene Oxidation Catalysis

Keywords: Bioinorganic chemistry / Biomimetic synthesis / Asymmetric synthesis / Homogeneous catalysis / Epoxidation / Oxidation / Iron



The substitution of N₂Py₂ ligands with carboxylic functionalities affects the catalytic properties of a series of iron complexes. Selective epoxidation catalysis with H₂O₂ was obtained only when one carboxylic group was present in the ligand. The moderate (up to 40%) enantioselectivity of the reaction with electron-rich/poor alkenes was also tuned by the presence of exogenous acids.

A variety of new titanium imido complexes with different pendant groups have been synthesized from $\text{Ti}(\text{NMe}_2)_4$. The nature of the donor atom in the pendant group and the length of the side arm influence the coordination to the metal center. These compounds were evaluated as ethylene polymerization precatalysts.

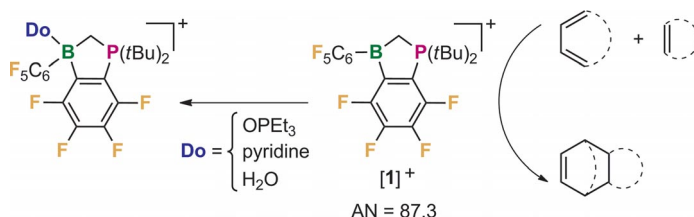


V.-H. Nguyen, L. Vendier,
M. Etienne, E. Despagne-Ayoub,
P.-A. R. Breuil, L. Magna,
D. Proriot, H. Olivier-Bourbigou,
C. Lorber* 97–111

Titanium–Imido Complexes with Pendant Groups – Synthesis, Characterization, and Evaluation of Their Role as Precatalysts for Ethylene Polymerization

Keywords: Titanium / Imido ligands / N ligands / Coordination chemistry / Polymerization

Boron Lewis Acids



The very strong cationic Lewis acid $[1]^+$ (Gutmann acceptor number $\text{AN} = 87.3$) forms adducts with different uncharged do-

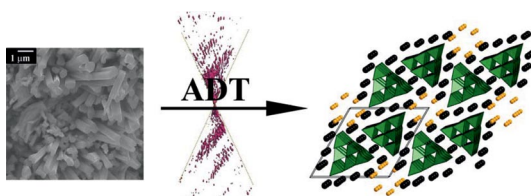
nors and catalyzes the $[4+2]$ cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene.

A. Schnurr, M. Bolte, H.-W. Lerner,
M. Wagner* 112–120

Cyclic Phosphonium Bis(fluoroaryl)boranes – Trends in Lewis Acidities and Application in Diels–Alder Catalysis

Keywords: Boron / Homogeneous catalysis / Lewis acids / Perfluoroarenes / Phosphorus

Structure Elucidation



Triangular columns: By applying automated electron diffraction tomography to a multiphase nanocrystalline sample, the exceptional phosphate structure of $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ has been solved (see

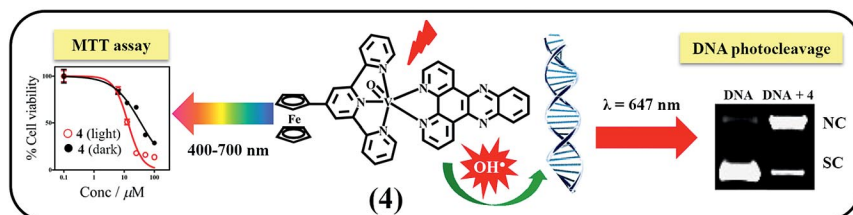
Figure). The structure comprises 1D, column-shaped $\frac{1}{\infty}\{(\text{P}_{12}\text{N}_{17}\text{O}_9)^{9-}\}$ ions that are built from $\text{P}(\text{O},\text{N})_4$ tetrahedra with 3-rings, three-coordinate nitrogen atoms and Ba^{2+} and Br^- ions.

E. Mugnaioli, S. J. Sedlmaier, O. Oeckler,
U. Kolb, W. Schnick* 121–125

$\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ – A Column-Type Phosphate Structure Solved from Single-Nanocrystal Data Obtained by Automated Electron Diffraction Tomography

Keywords: Solid-state reactions / Barium / Structure elucidation / Automated electron diffraction tomography / Silicate analog / Phosphates / Oxonitrides

Photodynamic Therapy



A ferrocene-conjugated VO^{2+} complex of dipyrrophenazine as a potent bioorganometallic agent for photodynamic therapy (PDT) shows significant red-light-induced

DNA photocleavage activity and cytotoxicity in HeLa cells. Nuclear staining data suggest apoptotic cell death.

B. Balaji, B. Banik, P. K. Sasmal,
B. Maity, R. Majumdar, R. R. Dighe,
A. R. Chakravarty* 126–135

Ferrocene-Conjugated Oxidovanadium(IV) Complexes as Potent Near-IR Light Photocytotoxic Agents

Keywords: Medicinal chemistry / Ferrocene / Vanadium / DNA cleavage / Photodynamic therapy

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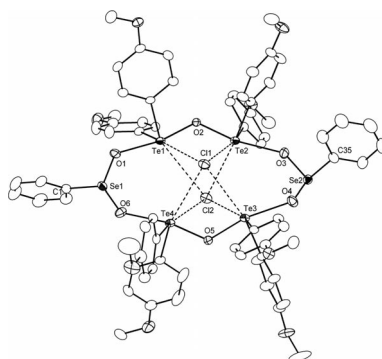
Te–O–Te and Se–O–Te Macrocycles

N. K. Srungavruksham,
V. Baskar* 136–142



12-Membered Macrocycles Containing Di-
telluroxane and Selenotelluroxane Units

Keywords: Macrocycles / Tellurium / Sel-
enium / π interactions / Halogen capping



12-Membered macrocycles that comprise $\text{Te}_4\text{Se}_2\text{O}_6$ frameworks have been isolated and characterized. Halogen atoms, which are stabilized by Te–X interactions, cap both sides of the macrocycle to provide charge neutrality. Macrocycles **1–4** are the first structurally characterized examples of compounds that contain Te–O–Te and Se–O–Te units and belong to a unique class of macrocycles.

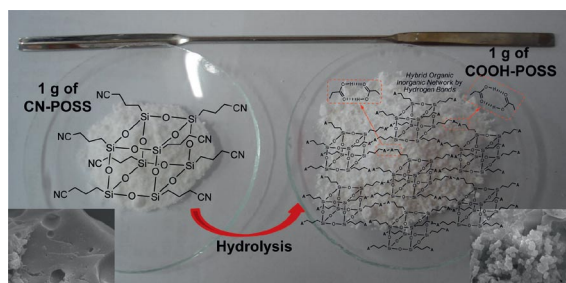
Hybrid Materials

A. Boullanger, G. Gracy, N. Bibent,
S. Devautour-Vinot, S. Clément,
A. Mehdi* 143–150



From an Octakis(3-cyanopropyl)silses-
quioxane Building Block to a Highly
COOH-Functionalized Hybrid Organic–
Inorganic Material

Keywords: Organic–inorganic hybrid com-
posites / Sol-gel processes / Hydrogen
bonds / Ion chelation / Nanostructures /
Silsesquioxanes / Silicon / Solid-state
NMR spectroscopy



A nanostructured COOH-functionalized hybrid material based on polyhedral oligomeric silsesquioxane (POSS) has been synthesized. The nanostructuring of **HOOC-POSS** was induced by noncovalent

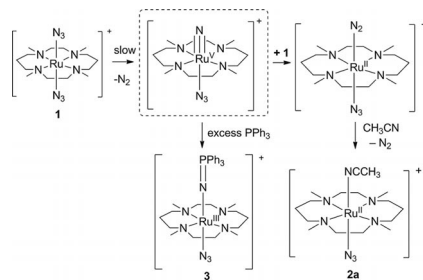
hydrogen bonding between the COOH units. An investigation of the chelating properties of this hybrid material has revealed its potential for extraction chemistry.

Azidoruthenium Complexes

C.-M. Ho, H.-C. Leung,
S. Wu, K.-H. Low, Z. Lin,
C.-M. Che* 151–159



Thermal and Photochemical Reactions of
Azidoruthenium(III) Complexes of
Macrocyclic Tertiary Amines and the
Structure of the (Phosphoraniminato)-
ruthenium(III) Complex $\text{trans}[\text{Ru}(\text{14-TMC})(\text{N}_3)(\text{NPPH}_3)]^+$



Azidoruthenium(II) and (III) complexes that are supported by macrocyclic tertiary amine ligands were synthesized and characterized. ESI-MS results, kinetic measurements and a trapping experiment confirm that an electrophilic ruthenium(V) nitride species has been generated.

Keywords: Ruthenium / N ligands / Macro-
cyclic ligands / Azides / Nitrides

* Author to whom correspondence should be addressed.



Supporting information on the WWW (see article for access details).



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If not otherwise indicated in the article, papers in issue 36 were published online on December 14, 2011



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computer, click on any of the items to read the full article. Otherwise please see the DOIs for easy online access through Wiley Online Library.

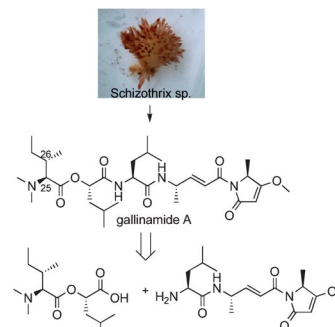


Total Synthesis

T. Conroy, J. T. Guo, R. G. Linington, N. H. Hunt, R. J. Payne*

Total Synthesis, Stereochemical Assignment, and Antimalarial Activity of Gallinamide A

Naturally active: The total synthesis of gallinamide A, a cyano-bacterium-derived depsipeptide, is described. Four N-terminal diastereoisomers of gallinamide A were prepared by using two key fragments (see scheme). Spectroscopic comparison to the isolated natural product enabled the absolute configuration of the *N,N*-dimethylated isoleucyl residue to be determined as 25*S*, 26*S*. Gallinamide A (and its diastereoisomers) were also shown to possess potent antimalarial activity.



Chem. Eur. J.
DOI: 10.1002/chem.201102538

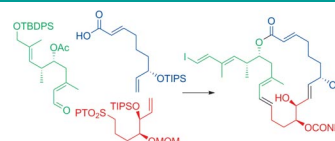


Total Synthesis

S. A. Pujari, P. Gowrisankar, K. P. Kaliappan*

A Shimizu Non-Aldol Approach to the Formal Total Synthesis of Palmerolide A

Total Recall: A convergent and efficient formal total synthesis of palmerolide A has been achieved. This synthetic approach involves a coupling of three fragments involving Julia–Kocienski, Yamaguchi esterification, and ring-closing metathesis (RCM) reactions as key steps.



Chem. Asian J.
DOI: 10.1002/asia.201100429

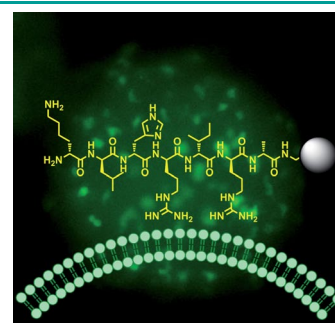


Cell Proliferation

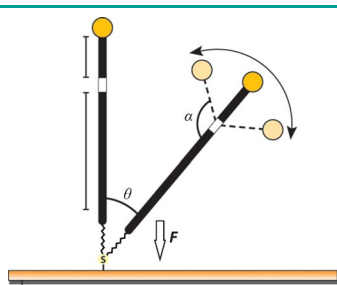
M. Meldal,* B. Wu, F. Diness, R. Michael, G. Hagel

Metabolically Stable Cellular Adhesion to Inert Surfaces

Novel adhesion peptides for the growth of cell monolayers on inert surfaces were identified by screening D-amino acid split-mix combinatorial libraries. Peptide adhesion was superior to that of poly D-lysine and allowed a monolayer of nonadhesive HEK293 cells to be established on the surface of PEG-based polymer beads for on-bead cellular screening.



ChemBioChem
DOI: 10.1002/cbic.201100382



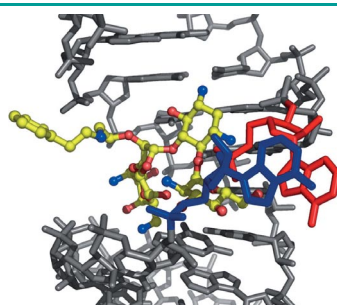
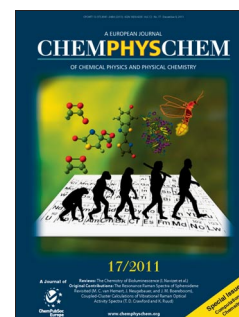
ChemPhysChem
DOI: 10.1002/cphc.201100578

Electron Transfer

N. Hüsken, M. Gębala, A. Battistel, F. La Mantia, W. Schuhmann,* N. Metzler-Nolte*

Impact of Single Basepair Mismatches on Electron-Transfer Processes at Fc-PNA-DNA Modified Gold Surfaces

Mismatches in nucleic acids: A single-mismatch-induced enhancement of the bending elasticity of nucleic acid duplexes is derived from the electron-transfer kinetics at Fc-PNA-DNA modified gold surfaces.



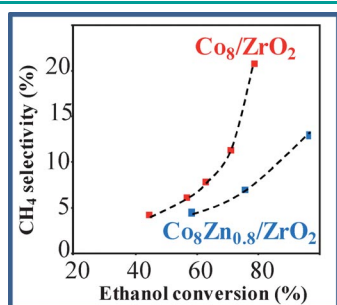
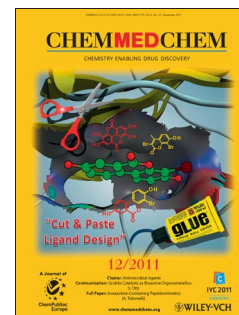
ChemMedChem
DOI: 10.1002/cmdc.201100346

Antibacterial Agents

J. Szychowski, J. Kondo, O. Zahr, K. Auclair, E. Westhof, S. Hanessian,* J. W. Keillor*

Inhibition of Aminoglycoside-Deactivating Enzymes APH(3')-IIIa and AAC(6')-II by Amphiphilic Paromomycin O2'-Ether Analogues

Paromomycin analogue activity: Novel amphiphilic aminoglycosides are shown to inhibit clinically relevant deactivating enzymes, without undergoing significant deactivation themselves.



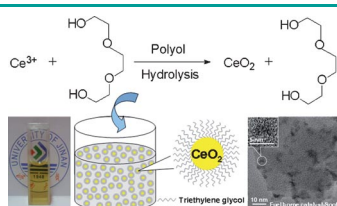
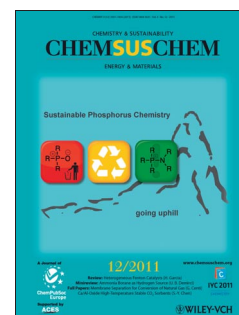
ChemSusChem
DOI: 10.1002/cssc.201100240

Ethanol Reforming

V. M. Lebarbier, A. M. Karim, M. H. Engelhard, Y. Wu, B.-Q. Xu, E. J. Petersen, A. K. Datye, Y. Wang*

The Effect of Zinc Addition on the Oxidation State of Cobalt in Co/ZrO₂ Catalysts

State of oxidation leads the way: The effect of zinc addition to the catalyst 8Co/ZrO₂ is examined in the steam reforming of ethanol. Higher ethanol conversion and lower CH₄ selectivity are observed for the Co/ZrO₂ catalyst promoted with Zn.



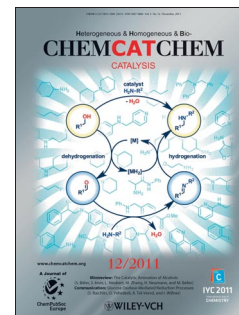
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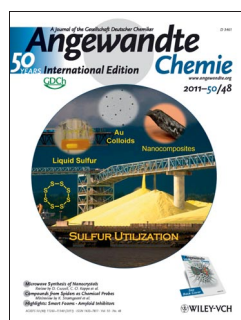
Quantum Dots

Y. Xin, X. Yang, P. Jiang, Z. Zhang,* Z. Wang, Y. Zhang*

Synthesis of CeO₂-Based Quantum Dots through a Polyol-Hydrolysis Method for Fuel-Borne Catalysts

Dots for diesel: Transparent colloidal solutions of (Fe doped) CeO₂ quantum dots (QDs) were prepared by heating a triethylene glycol solution of Ce(NO₃)₃·6H₂O (and Fe(NO₃)₃·9H₂O) at 180 °C. The QDs show improved activity for soot combustion compared with their nanometer counterparts. The high surface area and especially small particle size of QDs result in a large number of contact points between the catalyst and the soot.



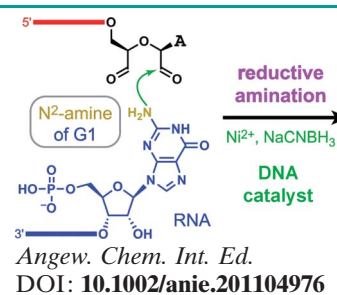


Catalytic DNA

O. Y. Wong, A. E. Mulcrone, S. K. Silverman*

DNA-Catalyzed Reductive Amination

A new reaction for DNA: DNA is shown to catalyze Ni^{2+} -dependent reductive amination involving the N^2 -amine of a guanosine nucleobase (see picture). This finding expands the repertoire of nucleic acid catalysis to include reductive amination, an important natural biosynthetic reaction that has practical synthetic utility.

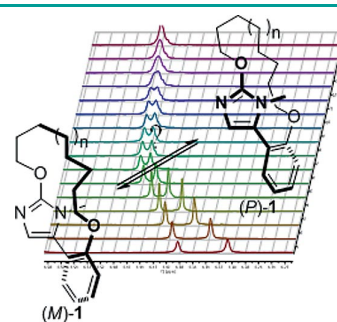


Planar Chirality

E. Van Den Berge, J. Pospíšil, T. Trieu-Van, L. Collard, R. Robiette*

Planar Chirality of Imidazole-Containing Macrocycles – Understanding and Tuning Atropisomerism

The synthesis and characterization of imidazole-containing macrocycles displaying planar chirality has been achieved. HPLC and NMR studies combined with computational calculations allowed us to understand the mechanism and the interactions involved in the conformational equilibrium between the two atropoisomers, which revealed the crucial role of the alicyclic chain length.



Chemistry of the Christmas Candle

Klaus Roth

Chemistry of the Christmas Candle

A burning candle seems far removed from the suspenseful world of chemistry, since it would appear to amount to nothing more than combustion of an organic compound. But the chemistry involved is not only especially beautiful, but also especially complex.



ChemViews magazine
DOI: 10.1002/chemv.201000133

Portraits of Porosity: Porous Structures Based on Metal Salen Complexes

Angela K. Crane^[a] and Mark J. MacLachlan^{*[a]}

Keywords: Schiff bases / Microporous materials / Supramolecular chemistry / Salen complexes

Metal complexes based on the salen ligand are highly versatile compounds that have many interesting properties, including magnetism, catalysis, and reversible oxygen binding. The marriage of complexes of salen with porous materials is a promising way to combine the attractive properties of the

salen complex with those of the porous structure. In this Microreview, we discuss several recent examples of published research that illustrate the power of combining these two disparate areas of research. Approaches based on supramolecular chemistry are emphasized.

1. Introduction

It is not surprising that Schiff base ligands have grown to be among the most widely explored ligands for coordination complexes – they are relatively easy to prepare and their modular design makes them versatile and readily tunable.^[1] Prepared through the condensation of an aldehyde or ketone with an amine, Schiff base ligands can provide metal-binding pockets with controllable denticity and electronic properties. The salen family of ligands (Figure 1) is a popular group of Schiff base ligands that includes two imines. Salen [*N,N'*-ethylene-bis-(salicylimine)] is the simplest ligand in the family and is formed by reacting two equivalents of salicylaldehyde with one equivalent of ethylenediamine. The resulting coordination site, an N₂O₂ binding pocket, is capable of bonding to metals in a tetradentate fashion. Salen-type ligands have been used extensively to

stabilize metals for catalysis (e.g. manganese in Jacobsen's catalyst for enantioselective alkene epoxidation^[2] and cobalt in the O₂ carrier and oxidation catalyst Salcomine^[3]). Furthermore, by using the salphen derivative, rigid, shape-persistent scaffolds can be produced as a monomeric ligand with one N₂O₂ binding pocket,^[4] as a binding pocket subunit in an extended polymer,^[5] or in a macrocyclic arrangement with 3, 4 or 6 salphen units.^[6] These macrocycles can

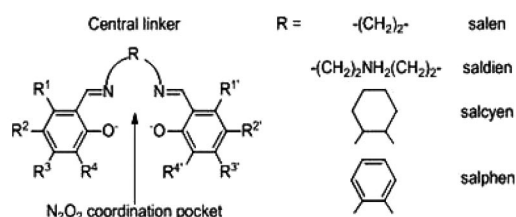


Figure 1. General structure of salen family ligands. Substituents on the phenyl rings (R¹–R⁴ and R^{1'}–R^{4'}) are readily modified and may be used for immobilization and easy control over the ligand properties.

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Angela Crane received her B.Sc. in Chemistry and Applied Mathematics from Memorial University in St. John's, Newfoundland Labrador in 2008. During her undergraduate years she studied metal complexes of amine bis(phenolate) ligands with Dr. Chris Kozak, numerical solutions to the Hartree–Fock equations with Dr. Ray Poirier, and analytical methods of monitoring RCM reactions with Dr. Deryn Fogg at the University of Ottawa. She then moved to the University of British Columbia to join the MacLachlan Lab for her Ph.D. studies. She is currently working on the synthesis of metal–organic frameworks using self-directing, shape-persistent ligands.



Mark MacLachlan received his B.Sc. degree from the University of British Columbia in 1995 and his Ph.D. from the University of Toronto in 1999, where he studied inorganic materials with Dr. Ian Manners and Dr. Geoff Ozin. After 2 years as an NSERC Post-Doctoral Fellow with Dr. Timothy Swager at the Massachusetts Institute of Technology, he returned to UBC as a faculty member in 2001, where he is now a Professor. His research interests span several areas of supramolecular materials chemistry, including the development of porous materials based on nanocrystalline cellulose, ptycenes and shape-persistent Schiff base macrocycles.

then undergo further aggregation into supramolecular assemblies, such as nanofibers^[7] and metallocavitands.^[8] By considering the ease of structural modification, and known applications for many monomeric metal salen complexes, it is intriguing to use these complexes as building blocks for constructing new materials, such as porous materials.

Porosity in materials can lead to many exciting research directions and potential applications: host–guest chemistry, molecular sensing and separation, gas storage, and heterogeneous catalysis, for example.^[9] Advances in synthetic techniques have led to many methods for introducing porosity into materials, such as the use of templates or crystal engineering at the molecular level. Moreover, once a porous system has been achieved, further chemical modification and reactivity can be observed. Examples include covalent grafting to the pore surface or incorporated heterogeneous catalytic sites, respectively.^[10] By developing porous materials that incorporate versatile metal salen complexes, enhanced activity and applications can be observed.

In this Microreview, the evolution of methodologies to introduce porosity into metal salen systems is explored with recent examples from the literature. We use the term “metal salen systems” to refer to any complex (such as those in Figure 1) that has the same basic structure as salen at the core, with an N_2O_2 binding pocket. Emphasis is placed on the structure and application of materials based on the use of external porous media, further self-assembly through non-covalent coordination, and intrinsic porosity inherited through molecular structure.

2. Porosity Introduced Through External Media

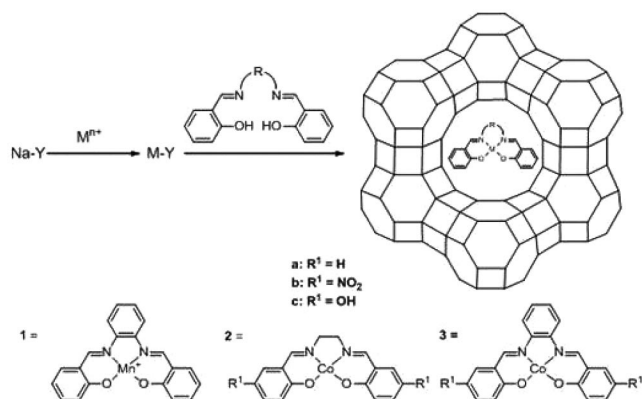
Creating porous materials with metal salen complexes first arose in an effort to introduce known homogeneous catalysts into heterogeneous systems.^[11] Most commonly, metal salen systems have been well developed for use in catalytic reactions, such as alkene epoxidation,^[12] asymmetric syntheses of cyanohydrins and amino acids,^[13] and oxidation of heteroatom-containing compounds.^[14] Non-covalent encapsulation or covalent grafting of metal complexes to porous media such as zeolites,^[15] pillared clays (PILCs),^[16] or silica substrates,^[17] allows increased catalyst stability, separation, and recyclability. Catalyst poisoning may also be prevented, as constraints placed on the complexes within the media inhibit the formation of catalytically inert oxo- and peroxo-bridged products.^[18]

2.1 Encapsulation Within Zeolites

Metal salen systems have been encapsulated within the micro- and mesopores of zeolites. By using a “ship-in-a-bottle” technique,^[19] metal ions and ligands that react within the pores of a zeolite form a metal complex that is too large and rigid to diffuse out of the pore. Applying only steric confinement to the metal complex allows the chemical properties of the complex to remain unchanged.^[20] Hence, the appropriate zeolite must be selected for a given

metal complex to facilitate diffusion of the individual components and prevent leaching of the assembled product. Zeolite-Y,^[21] a synthetic zeolite isostructural to the natural zeolite faujasite (FAU), has a large pore channel (7.4 Å in diameter) that serves as an entrance way to a larger pore cavity (12 Å in diameter), and is most often used for metal salen encapsulation.

Synthesis of encapsulated metal salen complexes follows a stepwise procedure (Scheme 1).^[22] First, metal ion exchange of sodium (present in the parent zeolite-Y) for the desired transition metal occurs by suspension of Na-Y in an aqueous solution of the transition-metal salt. The metal-exchanged zeolite, M-Y, is then impregnated with a solution of excess salen ligand by using the flexible ligand method, which allows complexation to occur. Excess ligand and unencapsulated complex are removed by Soxhlet extraction and uncoordinated transition-metal ions are removed by ion-exchange with an aqueous NaCl solution, which results in the encapsulated system [M(salen)]-Y. By using this method, several zeolite-encapsulated salens have been synthesized with first-row transition metals such as manganese, cobalt, nickel, and copper.

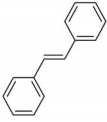
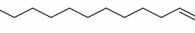


Scheme 1. General procedure for the flexible ligand method, “ship-in-a-bottle” encapsulation of metal salen complexes in zeolite-Y. Highlighted systems **1**, **2**, and **3** are shown.

Mirkhani and co-workers^[20] have shown that a zeolite-Y encapsulated Mn^{III} -salphen (**1**) is an effective biomimetic catalyst for both alkene epoxidation and alkane hydroxylation in the presence of $NaIO_4$. When compared to the homogeneous analogue, both conversion of alkene substrates to the desired epoxide and overall epoxide yield generally increased, despite lower turnover frequency (TOF) (Table 1). In some cases (e.g. *trans*-stilbene and 1-dodecene), both conversion of substrate and epoxide yield showed twofold improvement. With respect to hydroalkylation catalysis, **1** again showed lower TOFs than the homogeneous catalysts, yet exhibited greater selectivity for alkane conversion to either the desired ketone or alcohol (Table 2). Lastly, **1** showed enhanced stability in recovery and reuse, with no evidence of Mn leaching or decomposition, while maintaining a high level of activity.

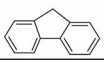
Li et al.^[23] showed that various Co(salen)-Y and Co(salphen)-Y systems are active catalysts for green processes,

Table 1. Selected examples of epoxidation of alkenes with NaIO₄ catalyzed by **1** and Mn^{III}-salphen.^[a]

Entry	Alkene	Conversion [%] ^[b] /Time [h]		Epoxide yield [%] ^[b]		TOF [h ⁻¹]	
		1	Homogeneous	1	Homogeneous	1	Homogeneous
1		85/10	41/0.5	85 (81) (<i>trans</i> -epoxide) ^[c]	41 (<i>trans</i> -epoxide) ^[c]	1.81	8.2
2		91/10	58/0.5	68 (<i>cis</i> -epoxide) ^[c] 23 (<i>trans</i> -epoxide) ^[c]	36 (<i>cis</i> -epoxide) ^[c] 22 (<i>cis</i> -epoxide) ^[c]	1.94	11.6
3		51/12	29/0.7	51	29	0.90	4.14
4		40/12	18/0.7	40	18	0.71	2.57
5		99 ^[d] /10	92 ^[d] /0.5	89 (85)	74	2.11	18.4
6 ^[e]	—	97/—	—	85	—	—	—
7 ^[e]	—	96/—	—	85	—	—	—
8 ^[e]	—	94/—	—	83	—	—	—

[a] Data originally reported in ref.^[20] [b] GLC yield based on starting alkene, and the yields in parenthesis refers to isolated yields. [c] Both ¹H NMR and GLC data approved the reported yields. [d] The byproduct is acetophenone. [e] The results of catalyst recovery (**1**) in the epoxidation of α -methylstyrene for 2–4 runs.

Table 2. Selected examples of hydroxylation of alkanes with NaIO₄ catalyzed by **1** and Mn^{III}-salphen.^[a]

Entry	Alkane	Conversion [%] ^[b] /Time [h]		Ketone [%] ^[b]		Alcohol [%] ^[b]		TOF [h ⁻¹]	
		1	Homogeneous	1	Homogeneous	1	Homogeneous	1	Homogeneous
1		55/12	38/0.7	42	20	13	18	0.98	5.43
2		34/12	16/0.7	24	13	10	3	0.6	2.29
3		51/12	39/0.7	51	39	44	—	0.90	5.57

[a] Data originally reported in ref.^[20] [b] GLC yield based on starting alkane.

such as the oxidative carbonylation of aniline and methanol (MeOH) to produce methyl-*N*-phenylcarbamate (MPC) and dimethyl carbonate (DMC), respectively. For the conversion of aniline to MPC, substituted salen **2** and salphen systems **3** were studied alongside the homogeneous analogues (Table 3).

In all cases, an increase in aniline conversion, MPC yield, MPC selectivity, and TOF were observed in the heterogeneous encapsulated system; system **3c** provided the highest activity. In testing the recyclability of this catalyst, a slight decrease in activity was observed from the fresh catalyst to the first recovered run (Table 4). This was attributed to a lowered Co content in the recovered catalyst, and the authors suggested that this loss resulted from leaching of excess Co²⁺ and ligand that was unable to diffuse from the original zeolite structure because of blockages by the Co complexes in the cages. After the initial run, the catalytic

Table 3. Selected examples of oxidative carbonylation of aniline (AN) to MPC^[a,b] and MeOH to DMC.^[c,d]

Catalyst	Substrate conversion [%]		Product selectivity [%]		Product yield [%]	
	AN	MeOH	MPC	DMC	MPC	DMC
1 Co(salen)	45.4	16.7	70.3	99.5	32.8	16.6
2 2a	65.7	19.6	70.7	99.5	45.8	19.5
3 Co(salphen)	46.7	21.2	73.7	99.5	34.4	21.1
4 3a	64.0	25.4	70.9	99.5	45.4	25.3
5 Co(salphen)(NO ₂) ₂	39.5	—	28.8	—	11.4	—
6 3b	45.5	—	28.8	—	13.1	—
7 Co(salphen)(OH) ₂	51.6	—	75.2	—	38.8	—
8 3c	67.1	—	77.3	—	51.8	—

[a] Data originally reported in ref.^[23a] [b] Reaction conditions: 0.5 g catalyst, 0.365 g KI, 11 mmol AN, 25 mL MeOH, *P*(CO) = 3.6 MPa, *P*(O₂) = 0.4 MPa, 170 °C, 3 h. [c] Data originally reported in ref.^[23b] [d] Reaction conditions: 1.0 g catalyst, 40 mmol MeOH, 25 mL CH₃CN, *P*(CO) = 2.0 MPa, *P*(O₂) = 1.0 MPa, 120 °C, 4 h.

activity of the encapsulated system remained exceptionally high and stable. The same system can be used for the conversion of MeOH to DMC. Enhanced catalytic activity, stability, and recyclability were also observed for the encapsulated systems (**2a** and **3a**) when compared with the homogeneous analogues; Co leaching remains a problem during the first run.

Table 4. Oxidative carbonylation of aniline (AN) to MPC catalyzed by the recovered catalyst **3c**.^[a,b]

Entry	Run	Co content [wt.-%]	AN conversion [%]	MPC selectivity [%]	MPC yield [%]
1	Fresh	1.35	67.1	77.3	51.8
2	1st	1.24	53.1	70.4	37.4
3	2nd	1.22	50.1	72.4	36.3
4	3rd	1.21	48.2	74.9	36.1
5	4th	1.21	47.8	74.8	35.8
6	5th	1.21	47.7	74.8	35.7

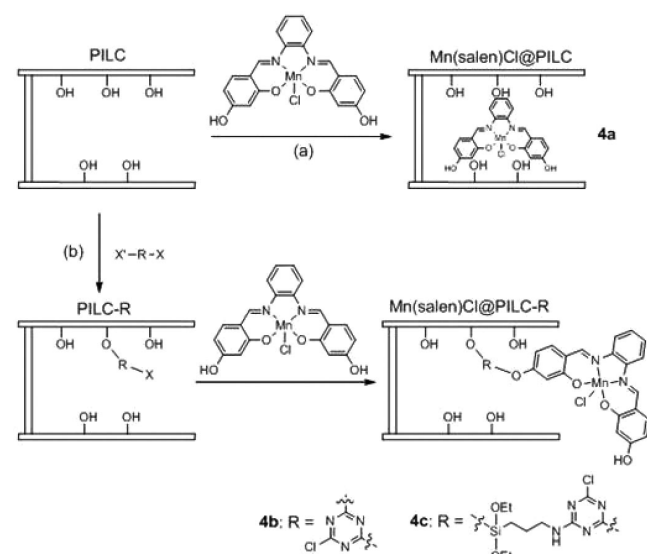
[a] Reaction conditions: 0.5 g catalyst, 0.365 g KI, 11 mmol AN, 25 mL MeOH, $P(\text{CO}) = 3.6 \text{ MPa}$, $P(\text{O}_2) = 0.4 \text{ MPa}$, 170°C , 3 h.

[b] Data originally reported in ref.^[23a]

2.2 Intercalation and Anchoring Within PILCs

Pillared clays (PILCs) are a family of porous materials prepared by the calcination of a clay that has undergone exchange of interlayered cations with bulky polyoxo- and polyoxy- cations.^[24] The spaces between the remaining metal oxide clusters within the layers create a well-defined pore system for both intercalation of metal salen complexes and functionalization leading to covalent anchoring of complexes to the surface.

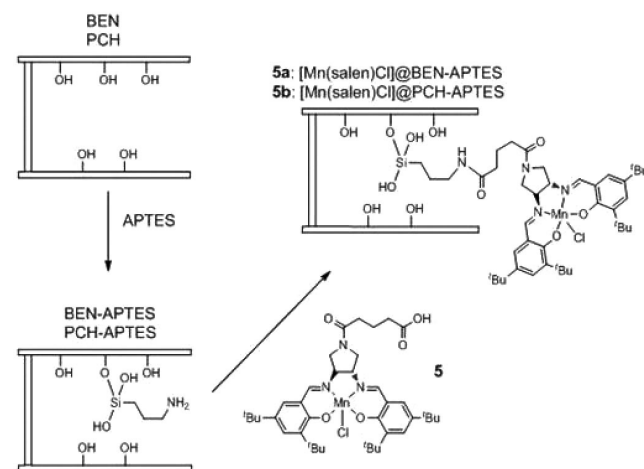
The choice of preparation methodology is extremely important for metal-salen-loaded PILCs, as it can dictate the catalyst immobilization within the composite material.



Scheme 2. General procedures for preparing metal-salen-loaded PILCs by (a) non-covalent encapsulation and (b) covalent anchoring.

Moreover, dependency on the desired interaction between the PILC and metal complex must be considered (Scheme 2). For intercalation compounds in which the metal salen is not covalently bound, encapsulation can be achieved by the flexible ligand method used for zeolites, where a transition-metal functionalized PILC is suspended in a solution of the ligand for in situ complexation.^[24] Alternatively, the prepared metal complex may be diffused into the layers of the PILC in solution. Covalently anchored metal salen complexes, however, must be coupled to a PILC that has been functionalized with an organic linker. For example, hydroxy groups on a salen complex can react with a tethered cyanuric chloride through Williamson ether synthesis, while PILCs functionalized with 3-aminopropyltriethoxysilane (APTES) have amino groups that can react with carboxylic acid groups to link complexes by amide tethers.^[25]

Freire and co-workers have worked extensively on both immobilization through intercalation and covalent anchoring of Mn^{III} -salen epoxidation catalysts to several PILCs. Initial studies compared the encapsulating and grafting of the catalyst on an aluminum PILC (Al-WYO) support.^[25] It was found that non-covalent encapsulation of complex **4a** yielded the highest catalyst loading of the PILC (0.40% Mn), as well as the highest immobilization efficiency (37.5%). Grafted materials constructed with different organic linkers contained significantly less catalyst (0.11% Mn and 0.06% Mn for **4b** and **4c**, respectively) and showed a drastic decrease in immobilization efficiency (7.4 and 8.7% for **4b** and **4c**, respectively). Nonetheless, there appeared to be no significance of the size and rigidity of the organic linker chosen. In later studies, the inorganic Al-WYO was substituted for a natural clay (BEN) and a porous clay heterostructure (PCH).^[26] After functionalization with APTES, BEN-APTES was observed to have a higher efficiency for catalyst loading (through amidation coupling of the catalyst to the APTES functionality; Scheme 3) than PCH-APTES (0.1 and $\approx 0.03\%$ Mn for **5a** and **5b**, respectively).



Scheme 3. Preparation of $\text{Mn}(\text{salen})\text{Cl}$ anchored on PILC through amidation.

The catalytic activity of these materials was tested towards the epoxidation of styrene in the presence of an oxidant (PhIO and *m*-CPBA/NMO for **4** and **5**, respectively; Table 5). When compared to the homogeneous analogue, the non-covalently encapsulated system **4a** performed the best, showing similar conversion and selectivity, though a decreased TOF. The covalently anchored systems **4b** and **4c** showed a significant reduction in catalytic activity. Decreases in catalytic behavior were attributed to restricted diffusion of the substrate within the pores, as well as electronic changes to the ligand and, hence, metal center where the catalysis takes place. This may hold particularly true for the anchored systems, where both effects can be seen. With respect to system **5**, it was found that changing the scaffold to BEN or PCH produced competitive catalysts to the homogeneous analogue. In the case of **5b**, a significant increase in TOF was observed, while conversion and selectivity remained comparable. This is particularly remarkable when the low catalyst loading is considered.

Table 5. Epoxidation of styrene using Mn(salen) catalysts immobilized on PILCs with PhIO^[a,b] and *m*-CPBA/NMO^[c,d] as oxidants.

Entry	Catalyst	% Mn ^[c]	Conversion [%] ^[d] /Time [h]	Epoxide selectivity [%] ^[f]	ee [%]	TOF
1	homogeneous 4	0.5	89/42	92	—	0.5
2	homogeneous 4	1.7	49/3	90	—	2.7
3	4a	1.8	35/48	80	—	0.1
4	4b	0.4	38/48	29	—	[g]
5	4c	0.3	46/72	18	—	[g]
6	homogeneous 5	1.6	30/1	—	4	20
7	5a	0.4	14/6	71	5	3
8	5b	0.1	33/9	84	6	119

[a] Data for Entries 1–5 originally reported in ref.^[25] [b] Reaction conditions: CH₃CN at room temperature, molar ratio styrene/PhIO = 2:1. [c] Data for Entries 6–8 originally reported in ref.^[26] [d] Reaction conditions: CH₂Cl₂ at 0 °C, molar ratio styrene/*m*-CPBA/NMO = 1:2:5. [e] Mol-% relative to styrene. [f] Determined by GC-FID against internal standard (chlorobenzene). [g] Not calculated because of the significant change in Mn% during catalytic cycles.

2.3 Grafting Onto Porous Silica Scaffolds

Surfactant-templated mesoporous silicates, MCM-41 and MCM-48, have highly uniform and tunable pore sizes

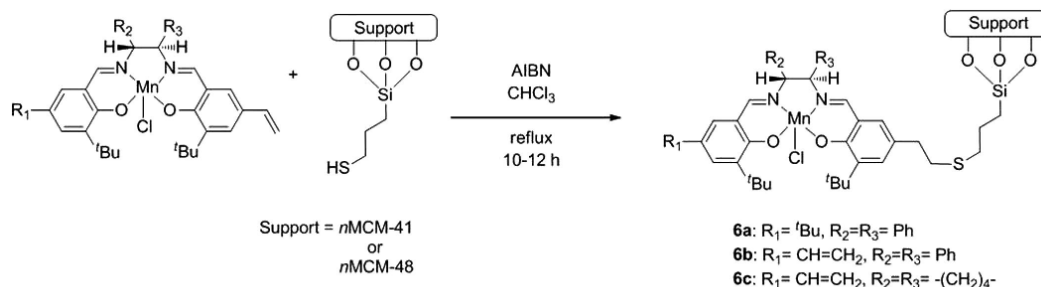
that are attractive environments for catalysis. As the pore dimension may be varied without affecting their composition, these materials may be used to examine the relationship between pore size confinement and catalytic activity. Furthermore, functionalization of the terminal hydroxy groups available on the surface of these silica substrates allows grafting of the complex onto the scaffold.^[27]

Liu et al. have examined the effect of pore size on the catalytic activity of metal salen catalysts immobilized within mesopores of MCM-41 and MCM-48.^[28] Specifically, they studied the catalytic epoxidation of styrene using systems

Table 6. Epoxidation of styrene using Mn(salen) catalysts immobilized on silica scaffolds with *m*-CPBA/NMO as an oxidant.^[a]

Entry ^[b]	Catalyst	Pore diameter [Å] ^[c]		Conversion [%] ^[d] /Time [h]	ee [%] ^[e] (<i>R</i>)
		Before grafting	After grafting		
1	6a	—	—	>99.9/2	66.9
2	18MCM-41- 6a	33.3	27.4	56.1/8	26.0
3	16MCM-41- 6a	27.5	24.4	55.1/8	15.8
4	14MCM-41- 6a	21.8	19.2	52.9/8	6.2
5	12MCM-41- 6a	18.1	17.2	52.2/8	5.0
6	16MCM-48- 6a	21.3	19.0	57.7/8	40.6
7	14MCM-48- 6a	19.3	17.7	48.9/8	6.7
8	12MCM-48- 6a	17.8	17.2	45.6/8	3.4
9	6b	—	—	99.5/2	66.0
10	18MCM-41- 6b	31.7	27.1	64.7/8	30.1
11	16MCM-41- 6b	27.9	24.2	64.5/8	25.7
12	14MCM-41- 6b	21.9	19.0	59.9/8	24.1
13	12MCM-41- 6b	18.9	17.5	54.3/8	14.6
14	16MCM-48- 6b	26.0	21.1	76.9/8	41.2
15	14MCM-48- 6b	23.2	17.4	53.9/8	16.4
16	12MCM-48- 6b	18.6	17.0	47.4/8	11.4
17	6c	—	—	99.8/2	47.0
18	18MCM-41- 6c	31.7	27.0	71.8/8	24.2
19	16MCM-41- 6c	27.9	24.4	62.4/8	20.9
20	14MCM-41- 6c	21.9	19.1	60.1/8	18.5
21	12MCM-41- 6c	18.9	17.3	49.4/8	8.0
22	16MCM-48- 6c	26.0	19.0	69.3/8	29.6
23	14MCM-48- 6c	23.2	18.9	45.5/8	11.9
24	12MCM-48- 6c	18.6	17.3	45.3/8	16.6

[a] Data for Entries 1–8 originally reported in ref.^[28b] data for Entries 9–24 originally reported in ref.^[28a] [b] Reaction conditions: CH₂Cl₂ (10 mL) at room temperature, molar ratio styrene/*m*-CPBA/NMO = 1:2:5, 2 mol-% catalyst for **6a** and 1.5 mol-% catalyst for **6b** and **6c**. [c] As calculated from N₂ adsorption experiments. [d] Determined by GC against internal standard (toluene). [e] % ee determined by GC with RESTEK RT-BetaDEXse chiral column and was calculated by $|([R] - [S])| / ([R] + [S]) \times 100\%$.



Scheme 4. Preparation of Mn(salen)Cl anchored on silica scaffold through hydrothiolation.

6a, **6b**, and **6c** (Scheme 4; Table 6). For these materials, substrate conversion and selectivity increased as the pore size was increased. Furthermore, it was found that MCM-48, which has a cubic structure with interconnected pores, was better suited for the immobilization of the Mn(salen) catalyst as it showed superior activity to the MCM-41 systems. MCM-41 has a 2D hexagonal lattice of isolated cylindrical channels. Both of these results can be attributed to diffusion of substrate and products throughout the porous networks of the silica scaffold, enhanced by both increased pore sizes and interconnectivity of the pores.

3. Porosity Achieved Through Metal–Ligand Interactions

In discrete salen complexes, the metal is bound within the N_2O_2 pocket of the ligand. Extended structures can be formed by axial coordination of ditopic ligands to the bound metal ion. Alternatively, the salen-type complex may be functionalized with peripheral groups that can function as ligands. By using these two approaches, porous supramolecular assemblies and multidimensional structures (coordination frameworks) can be produced.^[29]

3.1 Supramolecular Box Assemblies from Bridged Metal Salen Complexes

Metal salen complexes aggregate into dimers or larger structures.^[30] In Zn(salen) systems, for example, dimeric species have been observed by X-ray diffraction studies,^[31]

while alkoxy-derived Zn(salen) derivatives may further aggregate to yield 1D nanofibers and gels.^[32] Multinuclear metal salen systems, formed from ligands containing more than one N_2O_2 binding site, can also aggregate through stacking or head-to-tail polymerization.^[6c,33] Extension of such aggregation can be performed with the use of a bridging ditopic ligand, to give rise to self-assembled molecular boxes.^[34] For Zn(salen) systems, ligands containing pyridyl moieties have predominately been applied to create supramolecular structures.

Kleij et al. have worked extensively on Zn(salen) systems with pyridyl linkers. Early attempts to extend Zn(salen) dimerization included the use of 4,4'-bipyridine (bipy) and its analogues to form higher-order supramolecular structures.^[34] First, the bridging bipy was used to disrupt dimerization of Zn(salen) complexes (Figure 2a). Additionally, bis-Zn(salen) complexes were studied in the hope of preparing neutral box assemblies (Figure 2b). The binding of bipy in a 1:2 and 2:2 fashion [Zn(salen): bipy for **7** and **8**, respectively] in solution was confirmed by UV/Vis spectroscopy in titration experiments and by ^1H NMR spectroscopy, and by X-ray diffraction in the solid state (Figure 3). The diameter of the molecular boxes (13.9 and 15.5 Å for **8a** and **8b**, respectively) was determined by measuring the Zn–Zn distance within the bis-Zn(salen) building block (8.1 Å) and the distance between the nitrogen donors of the ditopic bipy unit (11.3 and 13.5 Å for **8a** and **8b**, respectively). The stacked packing of these molecular boxes in the solid state leads to parallel channels. As these complexes are neutral, the channels are not blocked by counterions, but create solvent-accessible void spaces that suggest potential applications in molecular separation, heterogeneous catalysis, and storage.

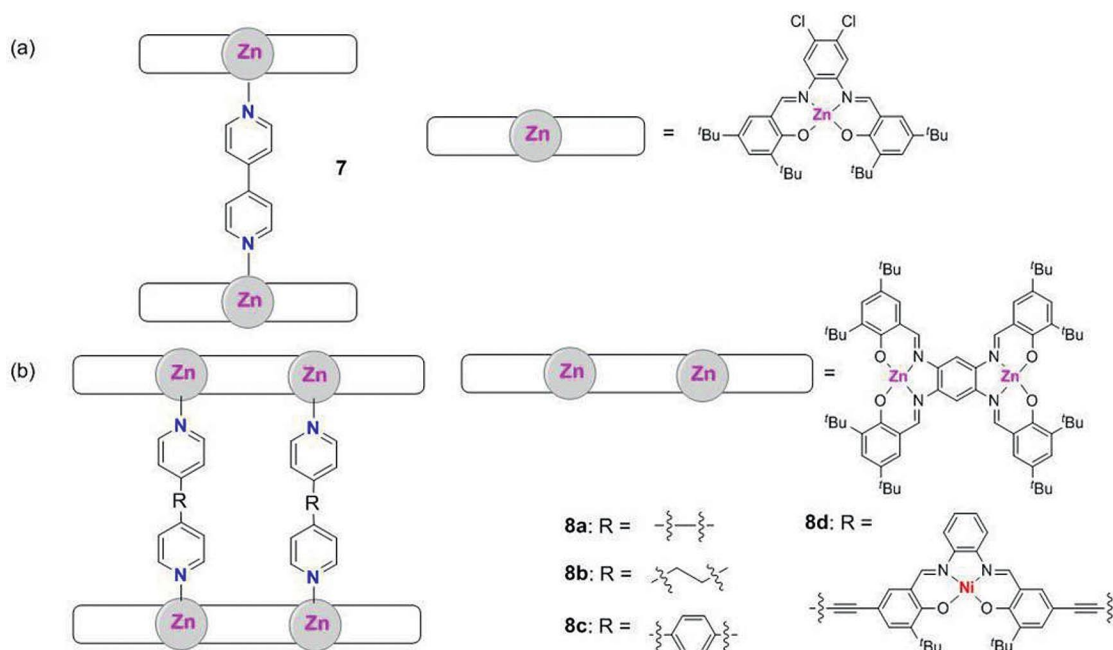


Figure 2. Bridging of Zn(salphen) and bis-Zn(salphen) complexes with 4,4'-bipyridine analogues.

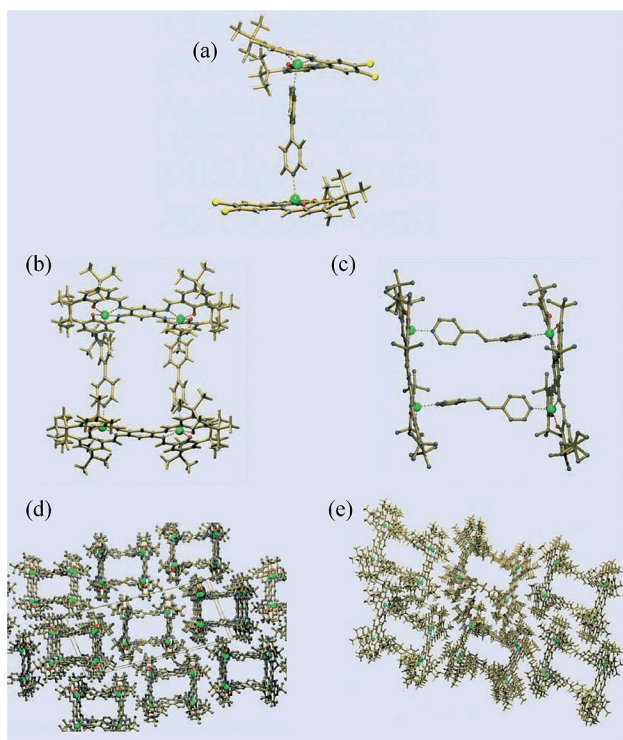
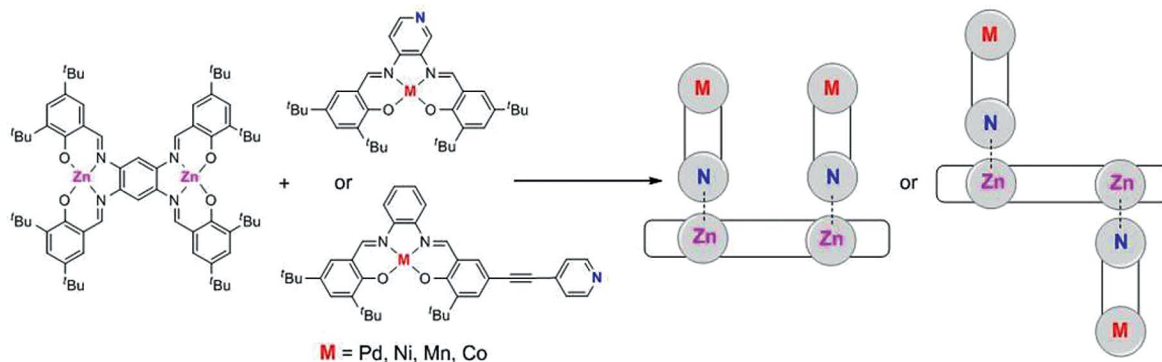


Figure 3. Molecular structure of (a) 2:1 assembly **7**, (b) 2:2 assembly **8a**, (c) 2:2 assembly **8b**. Packing of 2:2 assemblies into channels are shown for (d) **8a** and (e) **8b**. Reprinted with permission from ref.^[34] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA.

In an effort to examine assemblies containing two or more metal ions in active sites separated by a fixed distance, as observed in enzymatic systems, Kleij and co-workers also constructed hetero-multimetallic salen complexes.^[35] This required the construction of metal salen complexes with a pyridyl-functionalized salen, as in **8d**, or in which the pyridyl functionality resides in the salen backbone (known as salpyr ligands). Open-box templated assemblies **9** consisting of monodentate pyridyl-functionalized M(salen) complexes and bis-Zn(salphen) or bis-Ru(salphen) complexes show co-operative binding at both metal sites and the steric effects associated with addition to either the same or different faces of the bis-salphen complex (Scheme 5). By extending



Scheme 5. Templated “open box” assemblies **9** with coordination motifs between a bis-Zn(salphen) acceptor and metallosalen donor complexes.

to the molecular box assembly **8d**, the construction of the supramolecular system was observed by variable-temperature ¹H NMR spectroscopy. In solution, only one species corresponding to the fully formed 2:2 molecular box ($r_{\text{calcd.}} = 11.8 \text{ \AA}$, $r_{\text{exp.}} = 12.7 \text{ \AA}$; Figure 4) is observed by diffusion-ordered spectroscopy (DOSY). This assembly is disrupted by the addition of [D₅]pyridine, which competitively binds to the bis-Zn(salphen) complexes, and “opens” the pre-formed molecular box. Such a dynamic system in solution may be useful for creating novel catenanes and rotaxanes.

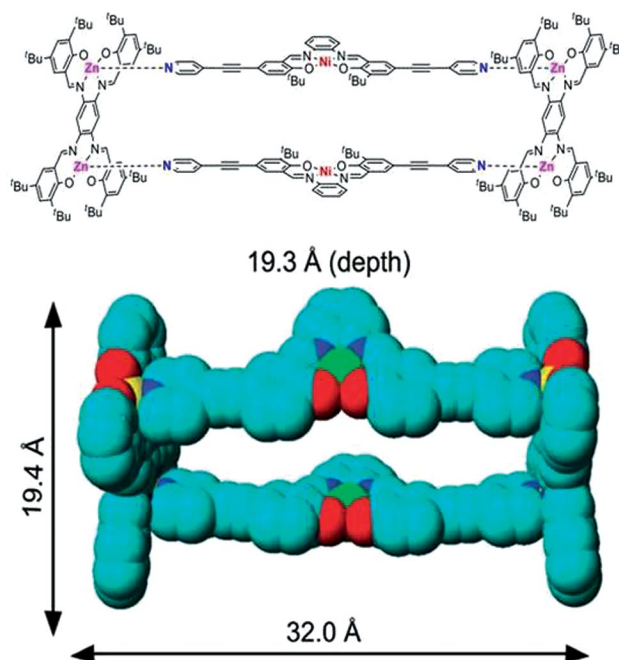


Figure 4. Proposed structure of the 2:2 assembly **8d** and the energy-minimized modeled structure. Reprinted with permission from ref.^[35] Copyright 2008 American Chemical Society.

3.2 Self-Assembled Metallosalen Polymers

As illustrated in the supramolecular box assemblies, co-ordination through pyridyl linkers to metal salen complexes is an easily accessible means of creating extended self-as-

sembled systems. By incorporating the pyridyl moiety into a metal salen complex, reversible assembly of a single metal salen complex into an extended structure can be achieved. Furthermore, the pore size can be tuned on the basis of the helical pitch of the assembly, which itself is based on the size and coordination mode of the pyridyl group to a neighboring complex, as well as on the choice of metal ion.

Cui et al. have studied helical, flexible self-assembled metallosalen complexes for molecular separation (Figure 5a).^[36] The first system involved the assembly of Zn(salen-py₂) complexes in a self-complementary fashion by heating a solution containing the ligand and Zn salt [Zn(NO₃)₂·6H₂O] in DMF and CH₃CN (**10**). This affords a porous 3D structure based on tetrameric [Zn₄L₄] building units that have four hydrophobic pockets occupied by guest solvent (CH₃CN) molecules. Packing of this building unit in a crystalline lattice occurs in the tetragonal chiral space group *P*₄₂. The position of each [Zn₄L₄] building unit is based on π - π stacking interactions with the extended π -conjugated portions of each individual [ZnL] component (interplanar separation ca. 3.37 Å). The structure has two different channel systems: zigzagging equilateral triangular channels, each side measuring 7.0 Å, and rhombus-shaped channels with dimensions of 4.0 × 5.5 Å. This structure is an example of a rare nanoscale chiral molecular container, and hence was tested for enantioselective separation of racemic 2-butanol and 3-methyl-2-butanol mixtures. After soaking **10** in a neat racemic mixture of 2-butanol at 40 °C for 2 days, single-crystal analysis showed that only (*R*)-2-butanol is included into the porous framework. Furthermore, desorption of the included 2-butanol molecules, followed by chiral GC analysis gave an *ee* value of 99.8% for the absolute *R* configuration. Similar experiments with racemic 3-methyl-2-butanol gave an *ee* value of 99.6% for the absolute *R* configuration. This material could be recycled, but selectivity significantly decreased from the first to second cycle (91.6% *ee* for the second cycle with 3-methyl-2-butanol). This can be overcome by dissociating the framework with dilute HCl, then regenerating the material. By using 4-ethynylpyridyl groups on the metal salen complex, a flexible, stretchable metallosalen coordination network **11** was prepared in a similar way (Figure 5b).^[37] Single-crystal X-ray diffraction studies showed that the material is arranged in a chiral space group, *C*₂, with [Zn₂L₂] repeat units organized into infinite zigzag 1D chains. Strong π - π interactions observed between extended π -conjugated portions of each individual [ZnL] component (interplanar separation ca. 3.44 Å) generate a neutral rhombohedral 2D grid. Further interlamellar interactions between acetylene groups in each 2D sheet create a 3D supramolecular structure with two 1D open channels (3.49 × 3.77 Å and 0.87 × 1.17 Å) for guest occupation. When the desolvated crystalline material was exposed to benzene vapor at 100 °C for 2 days, crystals of the same symmetry were obtained, but the unit cell showed expansion along the *c*-axis (19.5%) and contraction along the *a*- and *b*-axes (7.2 and 11.6%, respectively). The stretching was caused by significant twisting around the Zn metal centers. Upon removal of benzene from the material,

the structure reverted to its original dimensions, which demonstrates reversibility. Toluene and cyclohexane adsorption were also examined. Both benzene and toluene show high adsorption (118 and 132 mg/g of **11**), whereas cyclohexane shows only minimal adsorption ($\approx$ 20 mg/g of **11**). The authors attribute the difference to the strong non-covalent interactions between the aromatic systems and the hydrophobic pore surface that act as a driving force for the guest to enter the channels; these interactions are not observed with cyclohexane. After desolvated crystals of the substance were immersed in 1:1 mixtures of aromatic and aliphatic solvents, molar ratios of the desorbed guests were 97:3, 98:2, and 94:6 for benzene/cyclohexane, toluene/cyclohexane, and toluene/*n*-heptane mixtures, respectively. These materials show promise for separation of aliphatic and aromatic compounds.

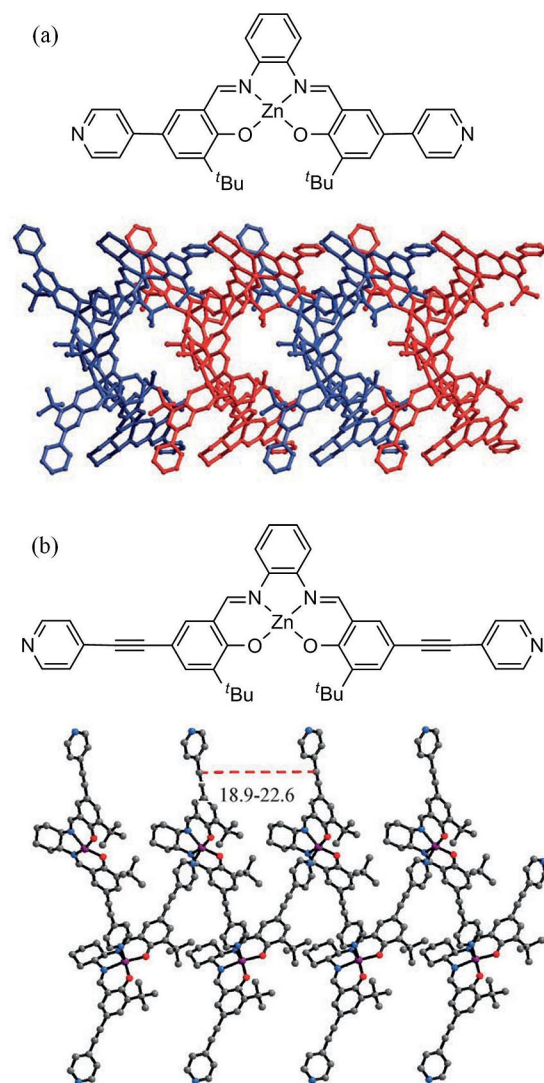


Figure 5. 1D metallosalen polymer chains, (a) **10** and (b) **11**, with peripheral 4-pyridyl coordination motifs. (a) Reprinted with permission from ref.^[36] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Reproduced^[37] by permission of the Royal Society of Chemistry.

Most recently, Cui and co-workers showed that these homochiral helical coordination polymers have easily tun-

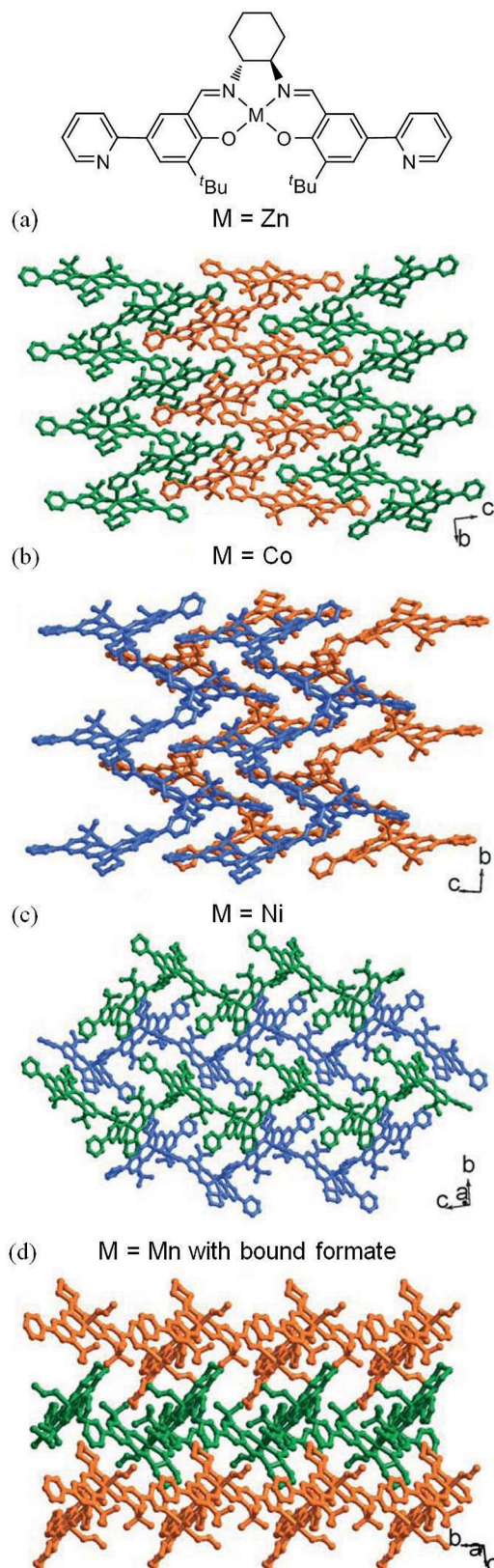


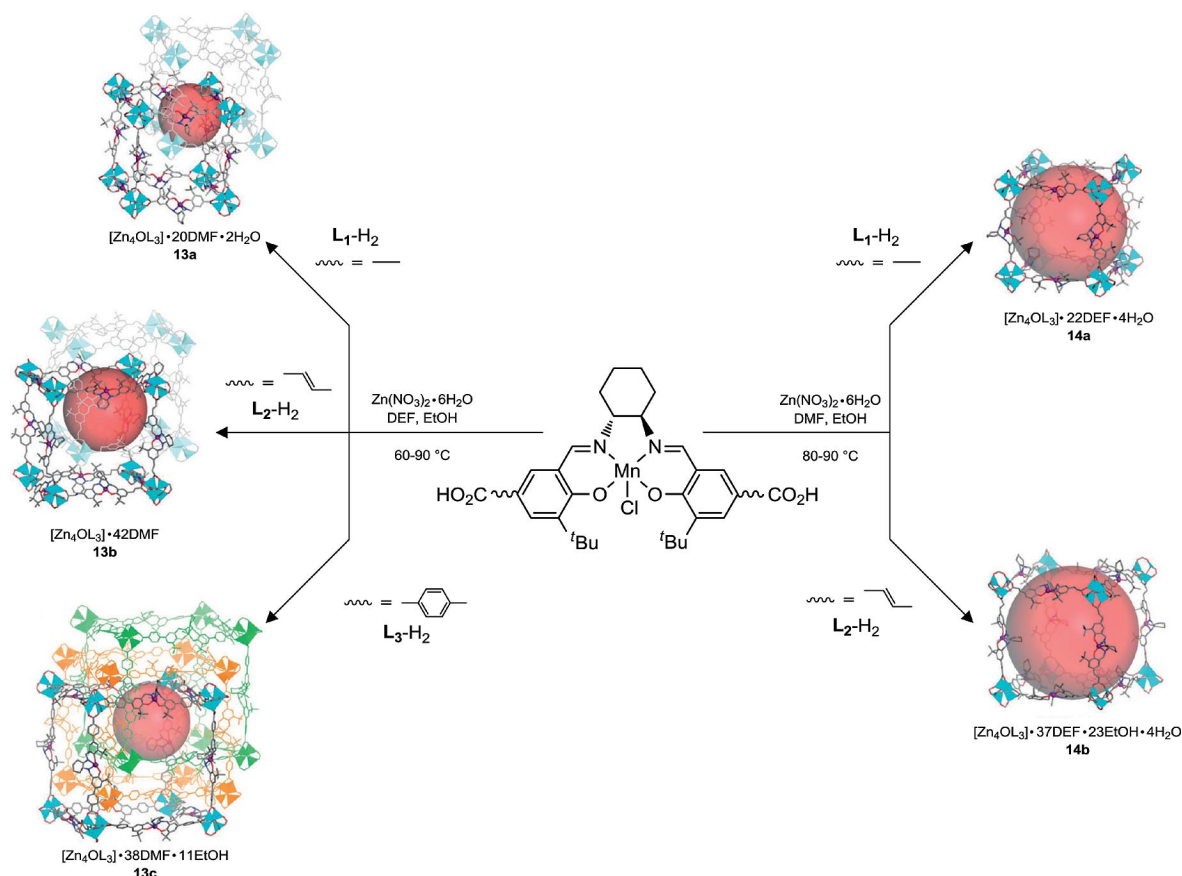
Figure 6. Homochiral helical 1D metallosalen polymers (a) **12a**, (b) **12b**, (c) **12c**, and (d) **12d** packed as 2D grids.^[38] Reproduced by permission of the Royal Society of Chemistry.

able pitches based on the choice of metal ion used.^[38] By using a 3-pyridyl unit for intermolecular binding of the metal salen complexes, metallosalen polymers of zinc, cobalt, nickel, and manganese formate were prepared (**12**; Figure 6). These polymers take on a very similar structure to that of **11**, in that a repeating $[\text{M}_2\text{L}_2]$ unit is observed in the chiral space group $P2_1$. Polymers **12a** and **12b** exhibit a 1D left-handed helical structure, **12d** exhibits a 1D right-handed helical structure, and **12c** exhibits a 1D zigzag chain structure. The structural difference between **12c** and **12d** is most likely due to the presence of uncoordinated pyridyl groups and the presence of the formate adduct bound to the Mn^{3+} center. From the solid-state structures determined by X-ray diffraction, the helical pitch of the 2_1 screw axis was calculated to be 10.430(1) Å for **12a**, 12.656(2) Å for **12b**, 18.798(6) Å for **12c**, and 12.191(5) Å for **12d**. As with the other systems presented, strong π - π interactions between the $[\text{ML}]$ extended π -conjugated components of the metallosalen polymer lead to packing of the 1D chain polymers into 2D sheet-like frameworks.

3.3 Formation of Metal–Organic Frameworks (MOFs)

There has been a great deal of interest in the production of metal–organic frameworks (MOFs) where the properties of the materials may be tuned by modifying the properties of the precursor components. With a wide variety of applications – gas storage, chemical sensing, catalysis, biomedical imaging, and drug delivery,^[39,40] – incorporation of functional systems into MOFs has been used to elucidate structure–property relationships. Furthermore, the use of a solvothermal synthetic route leads to highly reproducible materials where framework topology can be controlled with pore and channel sizes as a variable. This is achieved by linking ligands of varied sizes to metal-coordinated secondary building units (SBUs). Several SBUs have been observed in MOF synthesis; the $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$ or $[\text{Zn}_4\text{O}]^{6+}$ SBU, however, has shown versatility in metal salen systems and produce cubic MOFs with the overall composition $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CR})_6]$.

A series of isorecticular Mn(salphen)-containing MOFs has been synthesized and characterized by Lin et al. to demonstrate the molecular tuning of pore sizes within a hetero-multimetallic catalytic system.^[41] The Mn(salphen) core unit was functionalized with carboxylic acid groups to coordinate to a $[\text{Zn}_4\text{O}]^{6+}$ SBU (Scheme 6). Upon solvothermal synthesis with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 80–90 °C in *N,N'*-dimethylformamide (DMF) and ethanol (EtOH), the interpenetrated catalytic MOFs (CMOFs) **13a**, **13b**, and **13c** were produced. In an effort to discourage interpenetration of the framework nets, DMF was replaced by its larger analogue, *N,N'*-diethylformamide (DEF). This yielded CMOFs **14a** and **14b**, while a network with benzenecarboxylate linkers analogous to **13c** was never obtained, even with more sterically demanding solvents such as *N,N'*-diisopropylformamide and *N,N'*-dibutylformamide. X-ray diffraction analysis of the CMOF series showed that all of the materi-



Scheme 6. Series of synthesized CMOFs. Different cavity sizes shown as red balls in CMOF series: **13a** = 1.4 nm, **13b** = 2.0 nm, **13c** = 1.8 nm, **14a** = 2.6 nm, and **14b** = 3.2 nm. Reprinted with permission from ref.^[41] Copyright 2008 American Chemical Society.

als, including the triply-interpenetrated system **13c**, exhibited pore and channel sizes suitable for diffusion through the crystalline material, although negligible surface areas were measured by nitrogen adsorption experiments. Subsequently, the first example of a heterogeneous system with direct incorporation of a catalytic component accessible through porosity was produced.

To investigate the catalytic activity of the CMOF series, epoxidation of 2,2-dimethyl-2*H*-chromene was examined. Interestingly, the rate of conversion of the alkene substrate depends strongly on the channel size in the CMOF. The conversion rates increase with channel size – **13a** < **13c** < **13b** < **14a** < **14b** – which suggests that diffusion of the substrate, oxidant, and product through the CMOF is a significant factor for determining reaction rates of these CMOF-catalyzed systems. Relative to the homogeneous complex, $\text{L}_3\text{-Me}_2$, **14a**, and **14b** showed comparable conversion and selectivity. These results indicate that CMOFs containing metal salen moieties can be effective heterogeneous catalysts. The appeal of the CMOF system is further increased by noting other metal salen systems that rely on cooperative bimetallic catalysts, as seen in many of the metal salen systems developed by Jacobsen.^[42]

As with other heterogeneous systems that have been highlighted, catalyst leaching, recyclability, and stability must be considered. In the CMOF series, control experi-

ments examined the heterogeneity and stability of the catalyst. By testing the CMOF-free supernatant liquid towards epoxidation with fresh substrate and oxidant, no catalytic activity was observed. This confirms that the catalyst is bound to the CMOF and that the catalytic activity does not originate from the leached catalyst or from decomposition. Recyclability studies on **14a** and **14b** were performed by using recovered CMOF catalyst for subsequent catalytic runs (Table 7). Powder X-ray diffraction (PXRD) of the fresh and recovered catalyst show the same pattern as predicted from a pristine solid sample. Furthermore, only a

Table 7. Recycling of CMOF materials for the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene.^[a,b]

Catalyst	Run	Conversion [%] ^[d]	ee [%] ^[e]
14a ^[c]	1	76	76
	2	80	72
	3	79	71
	4	72	69
14b	1	72	86
	2	70	81
	3	68	80

[a] Data originally reported in ref.^[41] [b] Reaction conditions: 0.5 mol-% catalyst and 0.5 equiv. oxidant. [c] Substrate: 2,2-dimethyl-2*H*-chromene-6-carbonitrile. [d] Determined by GC. [e] Determined by chiral capillary column Supelco β -DEX 120.

slight deterioration in catalytic conversion and selectivity is observed within 3–4 runs. Instability of the catalyst was observed, however, depending on the choice of oxidant. For more typical oxidants, such as *m*-CPBA and bleach, the CMOFs were found to be unstable under the required reaction conditions. This problem arises as MOFs containing the $[\text{Zn}_4\text{O}]^{6+}$ SBU are known to be hydrolytically unstable.^[43]

4. Intrinsic Porosity in Molecular Structure

There has been extensive growth in the field of crystal engineering, where non-covalent interactions are used to create new crystalline solids. By employing hydrogen bonding or metal–ligand bonding in the assembly, researchers have constructed diverse porous frameworks. Recently, there has been interest in creating porous structures from molecules that are not physically interconnected.^[44] By using bulky molecules that cannot pack efficiently, for example, it is possible to create porous molecular solids.

Iptycenes, which are shape-persistent molecules with arene planes attached to [2.2.2]bicyclooctatriene bridgehead systems, offer intrinsic “internal molecular free volume” (IMFV). For example, triptycene, the smallest of the iptycene family, is a rigid three-bladed rigid propeller-shaped molecule with 120° angles between each arene ring that hinders efficient packing in the solid state.^[45] Polymers containing triptycene and pentiptycene exhibit porosity, which gives rise to enhanced properties useful for molecular sensing and adsorption.^[46,47]

MacLachlan and co-workers have probed the effect of introducing triptycene functionalities to Ni(salphen) systems (Figure 7) for the purpose of creating amorphous, po-

rous solids for H_2 uptake.^[48] By comparison of complexes containing up to six triptycene functionalities with simple Ni(salphen) structures, it was found that the addition of a triptycene moiety greatly enhanced the observed surface areas of the materials. This alone, however, was not the only factor to be considered; addition of Ni(salphen) units also produced a large increase in the accessible surface area. Interestingly, the N_2 adsorption isotherms for these materials did not match any of those outlined by IUPAC recommendations. Instead, large hysteresis is observed, which is characteristic of capillary condensation in mesoporous materials (Figure 8). As these solids show pore sizes in the microporous regime, it is likely that this hysteresis is caused by the swelling of the solid as the adsorbate pushes the individual molecules apart. In this system, where no significant interactions are expected between the individual molecules, such hysteresis could prove beneficial for gas storage applications. The solid-state structure of **19a** (Figure 9) confirms that large void spaces are present (occupied by free solvent

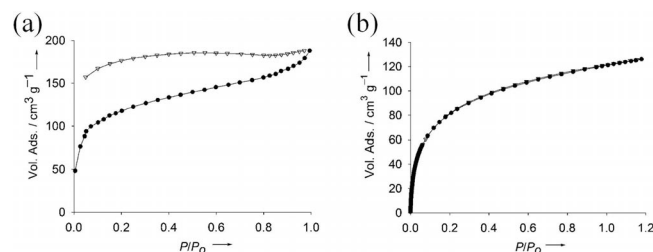


Figure 8. (a) N_2 adsorption/desorption isotherm and (b) H_2 adsorption/desorption isotherm for **20**. ●: adsorption; ▽: desorption. Reprinted with permission from ref.^[48] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA.

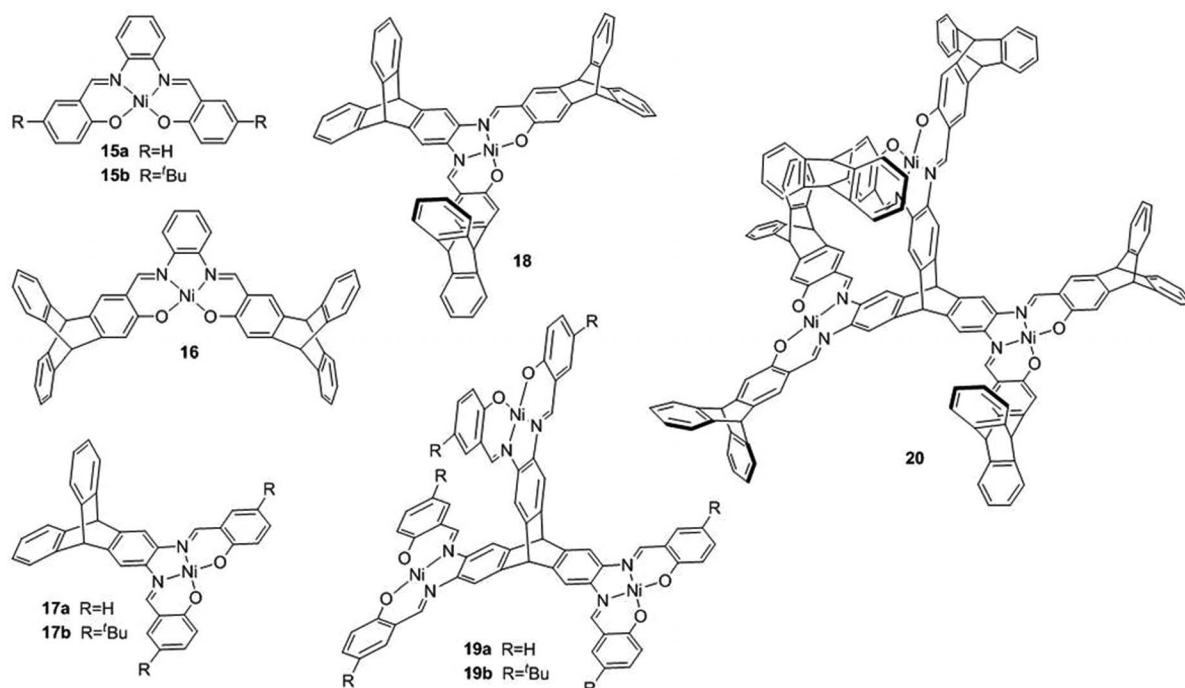


Figure 7. Ni(salphen) complexes prepared to model the effect of introduction of shape-persistent moieties on bulk solid samples.

Table 8. Structure summary and properties of Ni-salphen complexes.^[a]

	# Salphen units	# Triptycene units	IMFV [%] ^[b]	Surface area ^[c] [m ² g ⁻¹]	H ₂ adsorption [cm ³ g ⁻¹] ^[d]	Weight H ₂ adsorbed [%] ^[e]
15a	1	0	46.5	Null ^[d]	—	—
15b	1	0	67.7	Null ^[d]	—	—
16	1	2	76.5	40, 61	6.7	0.1
17a	1	1	79.6	Null ^[d]	—	—
17b	1	1	76.4	146, 233	21.2	0.2
18	1	3	74.2	216, 311	52.4	0.5
19a	3	1	72.5	174, 253	49.8	0.4
19b	3	1	74.6	499, 725	84.3	0.8
20	3	7	84.6	403, 592	121.0	1.1

[a] Data originally reported in ref.^[48] [b] Calculated by using CPK models with idealized geometry from PM3 calculations. [c] BET and Langmuir surface areas, respectively, determined from N₂ adsorption at 77 K. [d] Measured at 1 atm, at 77 K. [e] N₂ isotherm shows that the error is disproportionately high because of low adsorption and, consequently, the surface area data is unreliable.

molecules). Further, close packing is prevented because of the presence of the triptycene functionalities with no significant interactions between individual molecules.

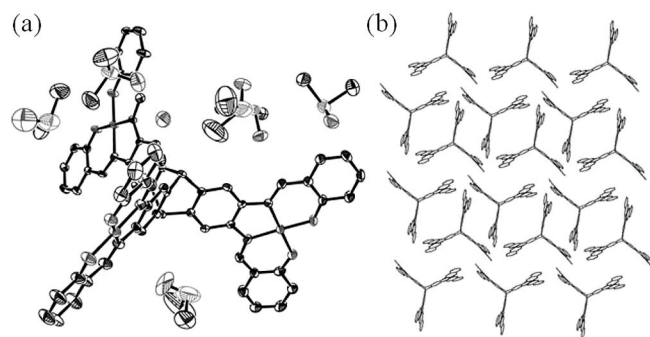


Figure 9. Solid-state structure of **19a** showing (a) free solvent in the IMFV of the molecule and (b) the packing of individual molecules. Reprinted with permission from ref.^[48] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA.

Surprisingly, the surface areas determined by N₂ adsorption were not effective predictors as to which solids would show the highest H₂ adsorption (Table 8). For example, compound **19b** showed the largest surface area, while compound **20** had the highest H₂ adsorption, 1.1 wt.-%, which is competitive with primitive MOF systems studied for H₂ storage.^[49] One possible explanation for this result is the size difference between N₂ molecules and H₂ molecules, i.e. H₂ molecules can access more void spaces than N₂ molecules. Another possible explanation is that the increased H₂ adsorption is associated with the increased number of arene rings in compound **20** (21) when compared with compound **19b** (9). Increasing the density of arene rings in a system has previously been shown to have a large effect on the ability of a material to adsorb H₂.^[50]

5. Conclusions and Perspectives

In this Microreview, we have illustrated numerous ways in which salen complexes are being integrated with porous materials. By introducing porosity into metal salen systems, exciting new materials can be obtained. These materials are promising for gas storage and sensing, and especially for

heterogeneous catalysis, where the chemical reactivity of salen complexes can be harnessed inside a pore of controlled dimensions. Furthermore, they enable fundamental studies of diffusion control and stereocontrol in confined spaces of porous materials. With advances in crystal engineering, a shift from non-covalent encapsulation and covalent grafting on an external porous media to self-assembled networks based on metal–ligand interactions or intrinsic porosity based on molecular packing has occurred.

There are many new opportunities for studying systems that combine salen-type complexes with porosity. Already in 2011, while this review was in preparation, several references have appeared that we have not been able to incorporate.^[27h–27j,51] We are hopeful that the future of this field will bring many intriguing developments, particularly in the area of gas adsorption for the purpose of gaseous fuel storage.

Acknowledgments

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The Interplay of Hydrogen Bonding and Multiple Metal Binding – A New Cyclic Polyaminopolyalcohol Ligand as Building Block for the Construction of Microporous, Supramolecular Networks

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Cyclohexane-based polyaminopolyalcohols (PAPAs) such as 1,3-diamino-1,2,3-trideoxy-*cis*-inositol (daci) have been prepared by hydrogenation of suitable aromatic precursors. The pentanuclear complex $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2](\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (**C3**) revealed antiferromagnetic and ferromagnetic interactions between the Cu^{II} centers with an $S = 3/2$ ground state.

The microporous structure of **C3** exhibited a dehydration/rehydration reaction with an entirely amorphous dehydrated phase at 150 °C and a completely reversible rehydration process at 30 °C. The potential of PAPA ligands for forming polynuclear complexes and supramolecular, hydrogen-bonded networks is discussed.

Introduction

The design and synthesis of microporous solids has become a prominent research topic in solid-state chemistry.^[1] The components currently used are, however, often limited to a few structure types, and an extension to other classes of compounds would be a worthwhile task.^[2] With this focus, some of us have shown that aliphatic or alicyclic molecules comprising a linear $(\text{CHX})_n$ chain furnished with functional groups X such as NH_2 or OH ($n > 3$) represent promising scaffolds for multiple metal binding, since for steric reasons it is not possible to bind more than three of these groups to the same metal center.^[3] Polyaminopolyalcohols (PAPAs) are of particular interest, because the amino groups can either be coordinated directly to the metal centers or can act as internal bases, facilitating the coordination of the hydroxy groups by accepting their protons.^[4] PAPA ligands are not only versatile metal-complexing agents, they are also potent sources for the construction of hydrogen-bonded networks, and the interplay of hydrogen bonding vs. multiple metal binding represents a particularly fascinating aspect of their chemistry.

Cyclohexane-based PAPA ligands have not received wide attention, although they can be readily obtained by stereospecific hydrogenation of aromatic precursors (Scheme 1).^[5] Metal binding of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) with its four distinct binding sites

(i)–(iv) has already been studied;^[4] however, the coordination chemistry of further examples such as all-*cis*-2,4,6-triaminocyclohexanol (tachol), 1,3-diamino-1,2,3-trideoxy-*cis*-inositol (daci), and 1,4-diamino-1,4-dideoxy-*cis*-inositol (ddci) has not yet been reported; ddc i has been prepared many years ago,^[5b] and we confirmed now its all-*cis* configuration by a crystal structure analysis;^[6] tachol, the hydrogenation product of picric acid, appeared to be completely unknown up to date. Representing a substructure of the taci geometry, metal binding of tachol is restricted to a type (i) or type (ii) mode. We prepared $[\text{Zn}(\text{tachol})_2]\text{Br}_2$ (**C1**) and $[\text{Ni}(\text{tachol})(\text{H}_2\text{O})_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (**C2**) as examples.^[6] For daci and ddc i, however, a variety of new types of coordination modes, such as the mixed triaxial N,N,O or N,O,O modes (v) and (viii) or the ax-eq-ax O,O,N or O,O,O modes (vi) and (vii), are available. Here, we report the structure, magnetic properties and the reversible dehydration/rehydration reaction of $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2](\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (**C3**).

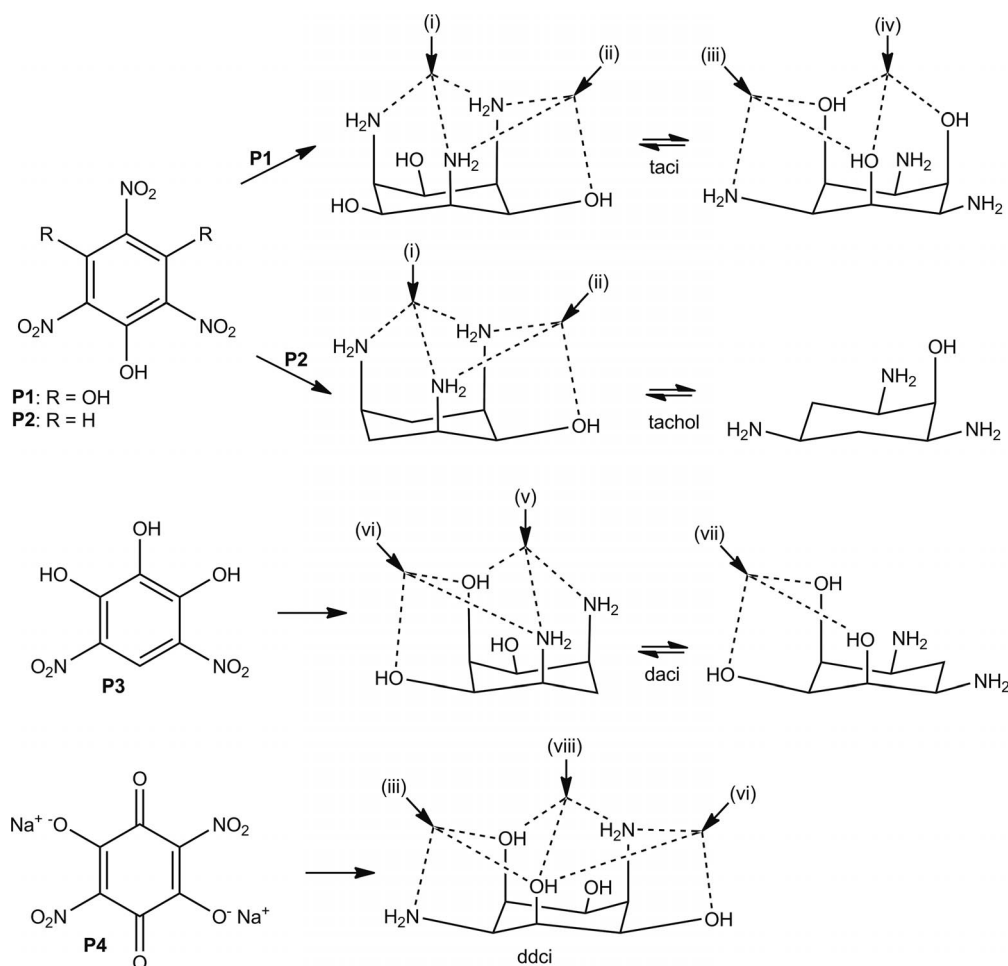
Result and Discussion

The crystal structure of **C3** contains two virtually identical $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}$ complexes. In these pentanuclear units, a central Cu^{II} cation located on a $\bar{1}$ site is bonded to two doubly deprotonated $\text{H}_2\text{daci}^{2-}$ entities,^[7] both exhibiting a type (vii) ax-eq-ax coordination mode (Scheme 2, Figure 1). Although considered to be highly nitrophilic, $\text{Cu}^{\text{II}}_{\text{cent}}$ is exclusively coordinated to oxygen donors. Each of the two $\text{H}_2\text{daci}^{2-}$ ligands binds two additional Cu^{2+} cations through an axial oxygen and an equatorial nitrogen donor in a bidentate fashion, the oxygen donors acting as μ_2 -bridges. The coordination spheres of the four peripheral Cu^{II} ions are completed by the binding of

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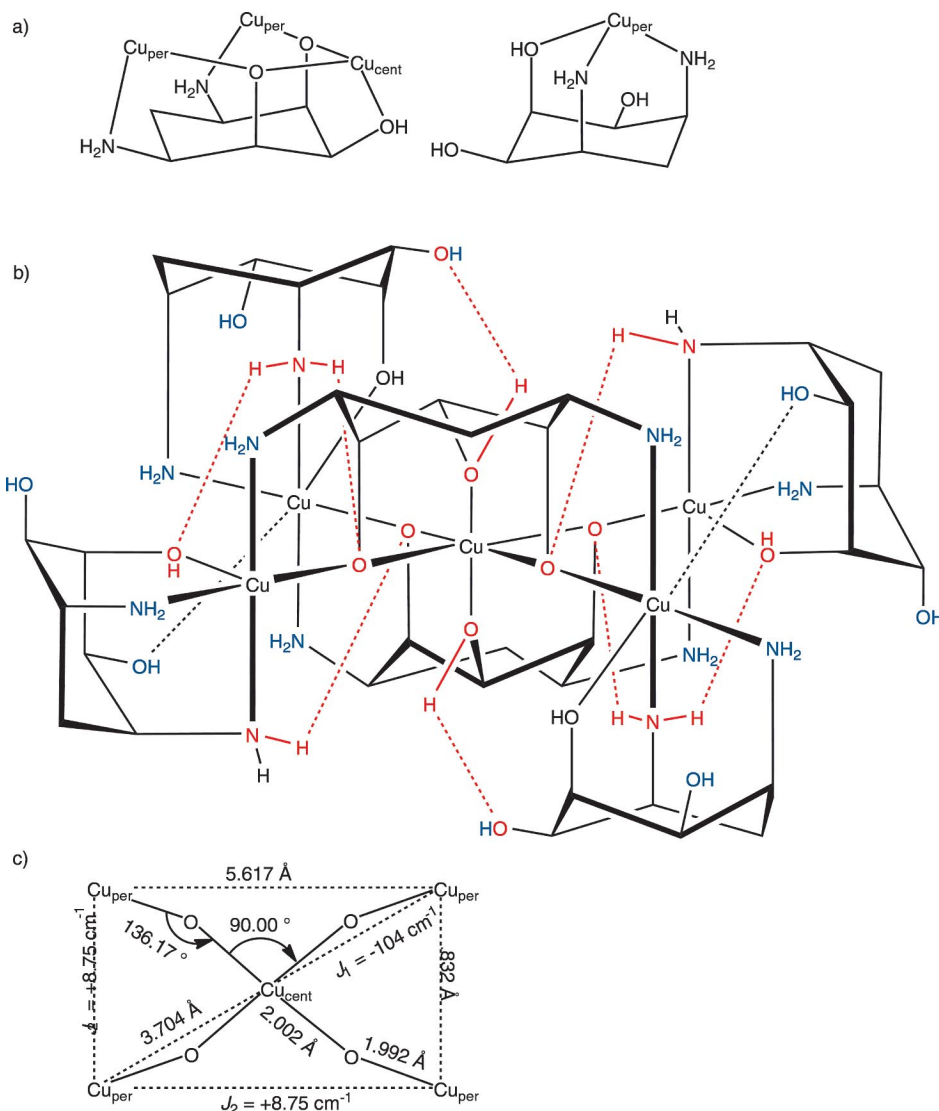
Scheme 1. Preparation of cyclic polyaminopolyalcohols (PAPAs) with an all-*cis* configuration from an aromatic polynitro precursor by catalytic hydrogenation.

a type (v) coordinating daci ligand. Remarkably, both chair conformations shown in Scheme 1 are thus formed in this complex. The coordination sphere of $\text{Cu}^{\text{II}}_{\text{cent}}$ corresponds to the well-known, elongated octahedron with significant displacement of the two remote atoms from the ideal apical position. The four peripheral Cu^{II} ions show a five-coordinate, almost ideal square-pyramidal geometry.^[8] Two of them display an additional weak interaction to one of the equatorial hydroxy groups of an adjacent daci ligand with $\text{Cu}\cdots\text{O}$ distances of 2.71 Å (molecule 1) or 2.90 Å (molecule 2).

Further inspection of the crystal structure established that hydrogen bonding constitutes a basic interaction type not only *between* the individual components but also *within* the $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}$ units. The four peripheral $[\text{Cu}(\text{daci})]^{2+}$ moieties are attached to the central $[\text{Cu}(\text{H}_2\text{daci})_2]^{2+}$ unit in such a way that an optimal arrangement of donor–acceptor interactions is achieved. The four alkoxy oxygen atoms of the central unit all act as proton acceptors, binding the hydrogen atom of a coordinating amino group of the four peripheral ligands, whereas two coordinated hydroxy groups donate their hydrogen atoms to a non-coordinating hydroxy group of a peripheral ligand. An additional

intramolecular hydrogen bond is formed between a coordinated amino group (donor) and a coordinated hydroxy group (acceptor) of two adjacent peripheral daci ligands. The remaining coordinated amino groups and non-coordinating hydroxy groups are all involved in intermolecular interactions by binding either SO_4^{2-} anions or additional water molecules. These $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}\cdots\text{SO}_4^{2-}$ interactions constitute an open, porous network with channels, which are filled with water molecules (Figure 1b).

Magnetic susceptibility measurements of **C3** exhibited antiferromagnetic coupling interactions between $\text{Cu}^{\text{II}}_{\text{per}}$ and $\text{Cu}^{\text{II}}_{\text{cent}}$, as well as moderate ferromagnetic interactions between the four $\text{Cu}^{\text{II}}_{\text{per}}$ ions. The simulation of the data by using the Hamiltonian $\hat{H} = -2J_1(S_1\cdot S_2 + S_1\cdot S_3 + S_1\cdot S_4 + S_1\cdot S_5) - 2J_2(S_2\cdot S_3 + S_2\cdot S_4 + S_3\cdot S_5 + S_4\cdot S_5)$ revealed exchange constants $J_1 = -104\text{ cm}^{-1}$, $J_2 = +8.8\text{ cm}^{-1}$, $g = 1.98$ (Figure S4, Scheme 2c). The fairly strong antiferromagnetic interaction is well in line with the large $\text{Cu}_{\text{cent}}-(\text{R})\text{O}-\text{Cu}_{\text{per}}$ angle of 136.17° in which the alkoxy oxygen atom bridges the magnetic $d_{x^2-y^2}$ orbitals of the copper ions; the ferromagnetic interaction between the $\text{Cu}^{\text{II}}_{\text{per}}$ ions is easily rationalized considering that no direct exchange pathway between the peripheral Cu^{II} ions is given and the O–



Scheme 2. Representation of the pentanuclear $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}$ architecture of **C3**. (a) Different coordination modes for the central and the four peripheral Cu^{II} ions. (b) Hydrogen-bonding interactions; intramolecular hydrogen bonding is shown in red, the H-donors for the SO_4^{2-} binding are shown in blue. (c) Cu_5 skeleton with mean distances and angles and the coupling constants J evaluated from magnetic susceptibility measurements.

$\text{Cu}_{\text{cent}}\text{--O}$ angle is 90° , leading to strictly orthogonality of the orbitals contributing to a magnetic exchange interaction.^[9] To confirm the resulting high-spin state at low temperature, measurements of the magnetization vs. temperature at applied magnetic fields of 1, 4 and 7 T were performed. No splitting of the curves was observed, and the data were satisfactorily simulated with a Brillouin function for an $S = 3/2$ ground state. No zero-field splitting was found, and the high-spin state was confirmed being well separated from higher lying energy levels.

Thermogravimetric analyses exhibited a weight loss of about 17% in the range of 25–150 °C (Figure S5), corresponding to a complete loss of the water of crystallization. Between 150 and 200 °C the sample weight remained constant. Above 200 °C, additional weight loss was observed, and the weight of 38.4% reached at 400 °C, was interpreted in terms of $[\text{Cu}(\text{SO}_4)]_3[\text{Cu}(\text{CO}_3)]_2$ formation. A sample,

which was dehydrated at 150 °C, completely regained the initial weight upon standing in humid air at room temperature in a few days, and therefore the question arises, whether structural changes occur in a dehydration/rehydration cycle. This question is of special interest, since the crystal-structure analysis exhibited disorder for some of the SO_4^{2-} anions and in particular for the H_2O molecules. The dehydration/rehydration process was thus monitored by X-ray powder-diffraction analyses. A sample was heated to 150 °C for 15 h and was then allowed to cool again to room temperature (Figure 2). The immediate collection of a diffractogram exhibited almost complete loss of intensities. Subsequent standing in humid air for 60 h restored, however, the original diffraction pattern. Obviously, removal of the H_2O molecules resulted in a complete breakdown of the lattice architecture. However, the structure appears to have a “memory” for appropriate H_2O locations, and during the

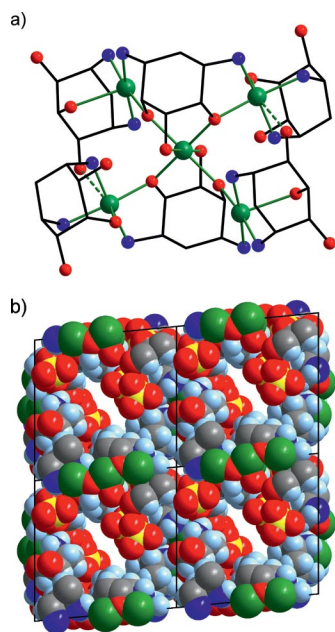


Figure 1. (a) Ball-and-stick model of $[\text{Cu}_5(\text{daci})_4(\text{H}_2\text{daci})_2]^{6+}$. (b) Space-filling model of the cation-anion network of **C3**. View along the crystallographic a axis, showing channels open for the accommodation of H_2O molecules (Cu green, S yellow, O red, N blue, C grey, H light blue).

rehydration process the entering water molecules were guided to appropriate positions whereby the lattice structure is completely restored.

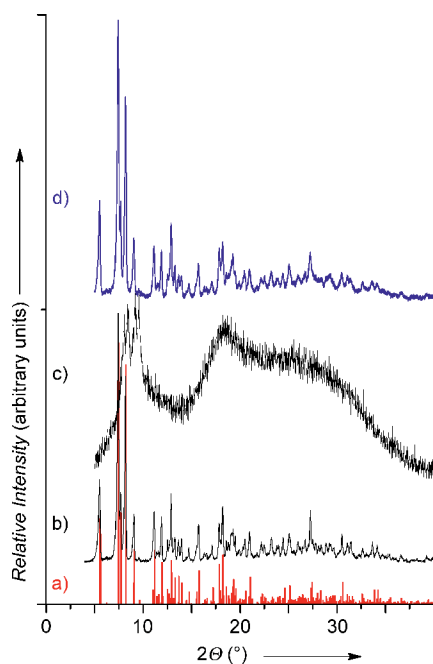


Figure 2. Powder X-ray diffractograms of **C3**. (a) Calculated line pattern. (b) Diffractogram of a freshly prepared, microcrystalline solid at 20 °C. (c) Diffractogram of the dehydrated sample (15 h at 150 °C), measured after cooling to room temperature (the observed peaks originate from the starting rehydration, see Figure S6); (d) Diffractogram of the fully rehydrated sample (60 h at room temperature in humid air).

For looking to this interesting phenomenon in more detail, we used a device allowing direct data collection at elevated temperatures (see Figures S6–S9, Supporting Information). A series of diffractograms was taken in the range of 30–180 °C. Above 50 °C, most of the diffraction pattern was lost, and only two intense peaks at $2\theta = 7.5$ and 9.0° appeared as major observations. A steady decrease of intensity was noted upon further heating for both peaks, and at a temperature of 150 °C, the material became completely amorphous.

The kinetics of this process was analyzed at a constant temperature of 100 °C. A strongly biphasic behavior was noted. In a first, rapid step, the major part of the diffraction pattern vanished, and two peaks, again at $2\theta = 7.5$ and 9.0° , appeared. This part of the reaction was actually too fast to be monitored by the setup used. In a second step, a continuous, monotonic decrease in intensity was observed for the two peaks over a period of about one week. Tracing of the dehydration kinetics on the thermobalance exhibited, however, a complete loss of water within a few minutes (Figure S10). Obviously, the entire multistep process can be separated in a rapid loss of water molecules followed by much slower structural changes. Based on the large number of possible hydrogen donors in **C3**, new anion-cation interactions are probably formed after removal of the H_2O molecules. The formation of such new interactions obviously constitutes the slow part of the dehydration kinetics (Figure S8) and occurred at random. All the more, it is amazing that the entire dehydration process is completely reversible: An amorphous sample, which was exposed to a steady stream of moisturized He at 30 °C, rapidly developed two broad peaks at $2\theta = 8.2$ and 9.3° . Remarkably, the $2\theta = 7.5^\circ$ peak (one of the two remainders in the dehydration experiment) appeared at a later stage. After a period of 3 d, the original diffraction pattern was restored. It appears thus that the entering water molecules trigger a reformation of the primary hydrogen-bonding network, and this process is not limited to local environments but concerns the entire lattice structure. The rehydration is, however, not a simple inversion of the dehydration reaction and corresponds to a complex, multistep process (Figure S9). **C3** represents thus one of the rare examples of a “guest-induced crystal-to-amorphous transformation” with a completely amorphous phase (Figure S6) of the dehydrated stage and full recovery of crystallinity after rehydration.^[10]

Experimental Section

The tachol, $\text{daci}^{[5a]}$ and $\text{ddci}^{[5b]}$ ligands were prepared by hydrogenation of **P2**, **P3**^[11a] and **P4**^[11b] (5 bar H_2 , 20–45 °C, aqueous H_2SO_4) using a Pt/Rh-on-C catalyst (see Supporting Information). **Caution!** Polynitro compounds are potentially explosive. Single crystals of **C1** and **C2** were obtained from aqueous solutions of corresponding metal salts and the free ligands.

Hydrogenation of **P3** yielded a crude mixture (ca. 50% $\text{daci} \cdot \text{H}_2\text{SO}_4$), which was purified by recrystallization. Although the resulting product still contained some 10% of byproducts,^[5a] it could be used for the synthesis of **C3**: 1.17 g of this material was

dissolved in H₂O and deprotonated on an anion exchange resin (Dowex 2-X8, OH-form). CuSO₄·5H₂O (530 mg, 2.1 mmol) was added. The deep-blue solution was concentrated under reduced pressure to a total volume of 50 mL and was then allowed to concentrate slowly at ambient conditions. Deep-blue single crystals of **C3**, which were washed with a small amount of H₂O, appeared after a few days. C₃₆H₁₁₆Cu₅N₁₂O₄₈S₃ (1899.28): calcd. C 22.77, H 6.16, N 8.85, Cu 16.73; found C 22.78, H 6.00, N 8.72, Cu 16.67. TGA measurements of **C3** were performed with an automated Mettler Toledo TGA/DSC1 apparatus (gas flow of 50 mL N₂/min, heating rate of 2 °C min⁻¹). The magnetic susceptibility of powdered **C3** was measured (2–290 K) with a SQUID magnetometer (MPMS-7, Quantum Design, applied field of 1 T). The data (corrected for diamagnetism) were analyzed by least-squares calculations (CLUMAG computer program, irreducible tensor operator formalism).^[12]

X-ray powder diffraction data were recorded with a Stadi P STOE or a D5000 Bruker AXS diffractometer (Cu-K_α radiation). Temperature- and time-dependent experiments (100 mg samples, ZrO₂ crucible) were performed by using a high temperature device (Anton Paar, ±0.5 °C accuracy). Helium was used as carrier gas. In the dehydration experiment, each acquisition time was 1030 s, followed by an intermission of 3600 s. The rehydration was performed at 30 °C under He, which was scrubbed with H₂O (20 mL/min flow rate). The data were recorded in intervals of 520 s per scan (no intermission).

Single-Crystal X-ray Diffraction Data of **C3**: STOE IPDS diffractometer, 200 K, graphite-monochromated Mo-K_α radiation, empirical absorption correction. Direct methods, full-matrix least-squares calculations on F².^[13] Anisotropic displacement parameters for all non-hydrogen atoms, calculated positions (riding model) for H(-C) and H(-N) atoms. H(-O) atoms were not considered. Crystal data: C₃₆H₁₁₆Cu₅N₁₂O₄₈S₃, triclinic, space group *P* $\bar{1}$, *a* = 14.5420(3), *b* = 16.0164(3), *c* = 16.3667(3) Å, *α* = 93.9480(10), *β* = 100.1820(10), *γ* = 97.9830(10)°, *Z* = 2, *ρ*_{calcd.} = 1.705 g cm⁻³, *μ* = 1.610 mm⁻¹, *Θ*_{max} = 27.14°, 61053 measured, 16284 unique, 11444 observed reflections [*I* > 2σ(*I*)]. Some H₂O molecules and two SO₄²⁻ ions proved to be disordered; 9.1 H₂O molecules could be assigned meaningfully in the asymmetric unit; however, analysis of the remaining electron density indicated the presence of further solvent molecules. At this stage, the refinement of 994 parameters resulted in *R* = 0.0635 [*I* > 2σ(*I*)] and *wR*₂ = 0.1968 (all data). The Program SQUEEZE of the PLATON^[14] package was then applied to the data set, accounting for additional 91 electrons (9.1 H₂O molecules) per asymmetric unit, and the agreement factors decreased to *R* = 0.0566 and *wR*₂ = 0.1726.^[6] A total of about 18 H₂O molecules is in agreement with elemental analysis and thermogravimetric measurements.

Supporting Information (see footnote on the first page of this article): Synthetic protocols; structural parameters, thermograms and magnetic data for **C3**; crystallographic data for **C1**, **C2** and ddcu·H₂SO₄·H₂O; powder diffractograms of **C3** for the dehydration/rehydration process.

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A Zinc Phosphate Structure with Unusual Double-Sheet Layers Templated by a Cobalt Hexaammine Complex

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Keywords: Layered compounds / Microporous materials / Template synthesis / Cobalt / Zinc phosphate

A new layered zinc phosphate, $[\text{Co}(\text{NH}_3)_6]_3[\text{Zn}_8(\text{HPO}_4)_8(\text{PO}_4)_2](\text{PO}_4)$ (ZnPO-CJ68), has been successfully prepared by using cobalt hexaammine as a template. Single-crystal structure analysis revealed that the structure of ZnPO-CJ68 contains double-sheet layers constructed by strict alternation of Zn- and P-centered tetrahedra. The host framework of the double-sheet layer features unusual 3D microporosity with 8-

ring apertures along three directions. The guest $\text{Co}(\text{NH}_3)_6^{3+}$ cations are located not only between but also within the host layers. The shape of the guest $\text{Co}(\text{NH}_3)_6^{3+}$ cation perfectly matches that of the void within the layered host framework. ZnPO-CJ68 was further characterized by powder X-ray diffraction, thermogravimetric analysis, and inductively coupled plasma spectroscopy.

Introduction

As a subset of microporous materials, layered inorganic compounds have drawn much attention.^[1] Among layered structures, those possessing 3D microporous host frameworks are of particular interest due to their potential applications in catalysis, adsorption, and ion exchange. Layered host frameworks with 3D microporosity may also be used as precursors to synthesize new zeolites, nanocomposites, and microporous films. Unfortunately, such layers have not been as frequently reported as other layered structures, such as dense nonporous layers and 1D or 2D microporous layers.^[2] To the best of our knowledge, only two layered structures contain 3D microporous host frameworks: silicate AMH-3, which has 8-ring apertures in all three principal crystal directions,^[2] and $\text{K}_4[\text{B}_8\text{Ge}_2\text{O}_{17}(\text{OH})_2]$, which has intersecting 8- and 9-ring channels.^[3]

To synthesize materials with micropores, the introduction of a structure-directing agent (SDA) is necessary. Conventional SDAs include alkali metal cations, alkaline earth metal cations, and protonated organic amines. A series of microporous compounds has been synthesized by using metal amine complex cations as the SDAs.^[4–7] Compared with conventional SDAs, metal complexes are more rigid and can offer more H bonds that can direct the formation

of new open-framework structures. Based on the successful synthesis and theoretical calculations of a series of microporous compounds directed by metal complex cations, Yu and coworkers proposed that a chirality transfer mechanism occurred between the chiral metal complex cations and the inorganic host frameworks through H-bonding interactions.^[8]

Herein we report the synthesis of a new zinc phosphate structure, $[\text{Co}(\text{NH}_3)_6]_3[\text{Zn}_8(\text{HPO}_4)_8(\text{PO}_4)_2](\text{PO}_4)$ (ZnPO-CJ68), which used cobalt hexaammine as the SDA. The structure of ZnPO-CJ68 contains unusual layered host frameworks with interconnecting 8-ring apertures along the thickness of the layers as well as in the planes of the layers. As the structural template, the guest cobalt hexaammine complex perfectly fits the shape of the intralayer micropore.

Results and Discussion

ZnPO-CJ68 crystallizes in the tetragonal space group $I4/m$ (No. 87) with $a = 10.0717(8)$ and $c = 26.442(4)$ Å. Detailed crystallographic data are listed in Table 1. The phase purity of ZnPO-CJ68 was confirmed by its powder XRD pattern, which is in good agreement with that simulated from the single-crystal structure (Figure S1, Supporting Information). The structure of ZnPO-CJ68 consists of macroanionic $[\text{Zn}_8(\text{HPO}_4)_8(\text{PO}_4)_2]^{6-}$ layered host frameworks constructed by strict alternation of Zn- and P-centered tetrahedra. Charge neutrality is achieved by extra-framework $\text{Co}(\text{NH}_3)_6^{3+}$ cations and PO_4^{3-} anions. The layered framework of ZnPO-CJ68 contains one crystallographically distinct Zn and two P atoms (Figure 1). The zinc atom, Zn(1), is tetrahedrally connected to four adjacent P atoms through bridging O atoms. The Zn–O bond lengths are 1.922(3)–1.975(2) Å, and the O–Zn–O angles

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are 100.20(10)–121.71(12)°. The two distinct P atoms are both tetrahedrally coordinated to O atoms. P(1) is connected to four adjacent Zn atoms through bridging O atoms, and P(2) is connected to three Zn atoms, with one remaining O atom forming the terminal hydroxy group. The P–O distances are 1.524(3)–1.555(3) Å. Selected bond lengths for ZnPO-CJ68 are presented in Table S1.

Table 1. Crystal data and structure refinement for ZnPO-CJ68.

Identification code	ZnPO-CJ68
Empirical formula	H _{7.75} Co _{0.375} N _{2.25} O _{5.50} P _{1.375} Zn
Formula weight	257.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	tetragonal, <i>I4/m</i>
Unit cell dimensions	<i>a</i> = 10.0717(8) Å <i>c</i> = 26.442(4) Å
Volume	2682.3(5) Å ³
Z, calculated density	16, 2.549 g cm ^{−3}
Absorption coefficient	4.865 mm ^{−1}
<i>F</i> (000)	2052
Crystal size	0.3 × 0.3 × 0.2 mm ³
Theta range for data collection	2.16–28.35°
Limiting indices	−13 ≤ <i>h</i> ≤ 9 −13 ≤ <i>k</i> ≤ 13 −35 ≤ <i>l</i> ≤ 35
Reflections collected/unique	9787/1726 [<i>R</i> _{int}] = 0.0396]
Completeness to $\theta = 28.35$	99.9%
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1726/0/107
Goodness-of-fit on <i>F</i> ²	1.096
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] [^a]	<i>R</i> ₁ = 0.0295, <i>wR</i> ₂ = 0.0837
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0343, <i>wR</i> ₂ = 0.0863
Largest diff. peak and hole	1.505 and −0.486 e Å ^{−3}

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 14.9244P]$ where $P = (F_o^2 + 2F_c^2)/3$.

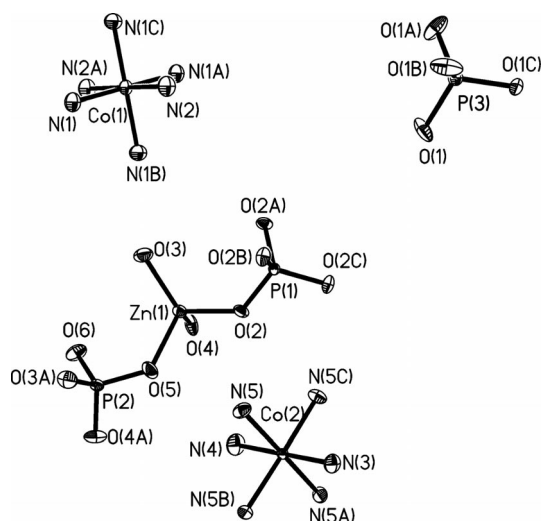


Figure 1. ORTEP view of ZnPO-CJ68 (50% thermal ellipsoids).

The Zn(1)O₄ and P(2)O₃OH tetrahedra are alternately linked through bridging O atoms to form a (4,8)-net sheet perpendicular to the [001] direction (Figure 2a). Each (4,8)-net sheet is connected to its *n*-glide image through P(1)O₄ tetrahedra to construct an unusual double-sheet layer. In

each double-sheet layer, there are 8-ring apertures along the [001], [110], and [1 $\bar{1}$ 0] directions (Figure 2b). The 8-ring apertures along the [001] direction run through the thickness of the layered framework with pore openings of 3.6×3.7 Å (O...O distances). The 8-ring apertures along the [110] and [1 $\bar{1}$ 0] directions are symmetry related, and run through the plane of the layered framework with pore openings of 2.6×5.3 Å. These apertures are perpendicular to each other and interconnected within the layered host framework to form an 8⁶ cavity. To the best of our knowledge, this is only the third structure that contains 3D microporous layered host frameworks. Compared with the two known layered structures, AMH-3 and K₄[B₈Ge₂O₁₇(OH)₂], ZnPO-CJ68 has much larger voids within the host framework due to the existence of the 8⁶ cavities. The double-sheet layers in ZnPO-CJ68 are stacked in an ABAB sequence along the [001] direction, whereas the layers in both AMH-3 and K₄[B₈Ge₂O₁₇(OH)₂] are stacked in an AAAA sequence.

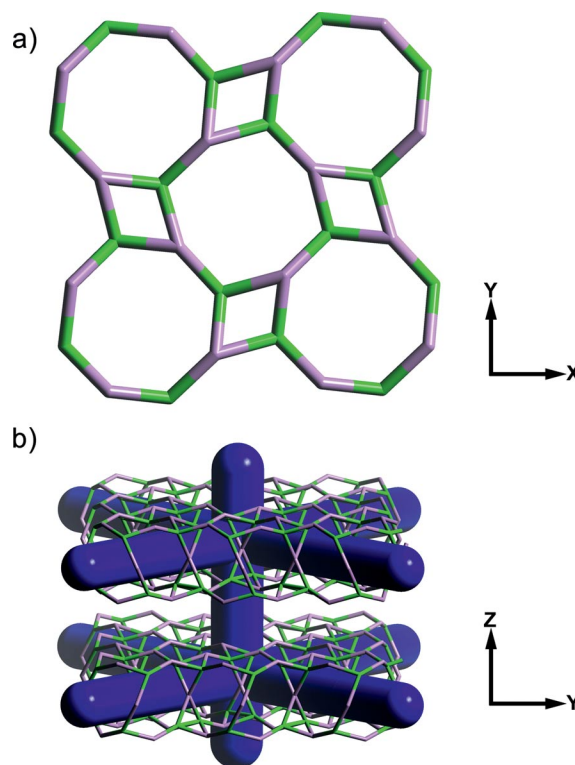


Figure 2. (a) The (4,8)-net sheet viewed along the [001] direction and (b) the 3D micropores within the layered host frameworks are shown as blue cylinders. Framework O atoms are omitted for clarity. (Green: Zn, pink: P)

Co(NH₃)₆³⁺ cations were used as the SDA for the synthesis of ZnPO-CJ68. There are two types of crystallographically distinct Co(NH₃)₆³⁺ cations in this structure (Figure 3a). One type is located in the voids between adjacent layered hosts, and the other type is located at the centers of the 8⁶ cavities within the layered hosts. As shown in Figure 3b, the six NH₃ ligands in each intralayer Co(NH₃)₆³⁺ cation point towards the six 8-ring apertures of the 8⁶ cavity in the layered host framework. The shape of the Co(NH₃)₆³⁺ cation perfectly matches the shape of the 8⁶ cavity.

In this sense, the $\text{Co}(\text{NH}_3)_6^{3+}$ cation can be regarded as the template of the micropore in the host framework. In addition to $\text{Co}(\text{NH}_3)_6^{3+}$ cations, disordered $\text{P}(3)\text{O}_4^{3-}$ groups are also found between adjacent layered hosts. These extraframework species are believed to stabilize the whole layered structure by donating H bonds and balancing the negative charges in the layered hosts. To the best of our knowledge, this is the first example of the shape of a micropore within the layered host that is directly affected by the shape of the SDA. In AMH-3 and $\text{K}_4[\text{B}_8\text{Ge}_2\text{O}_{17}(\text{OH})_2]$, the SDAs were Na^+ , Sr^{2+} , and K^+ cations, respectively, and the extraframework species in these two structures are too small to directly affect the shape of the micropores in the host frameworks.

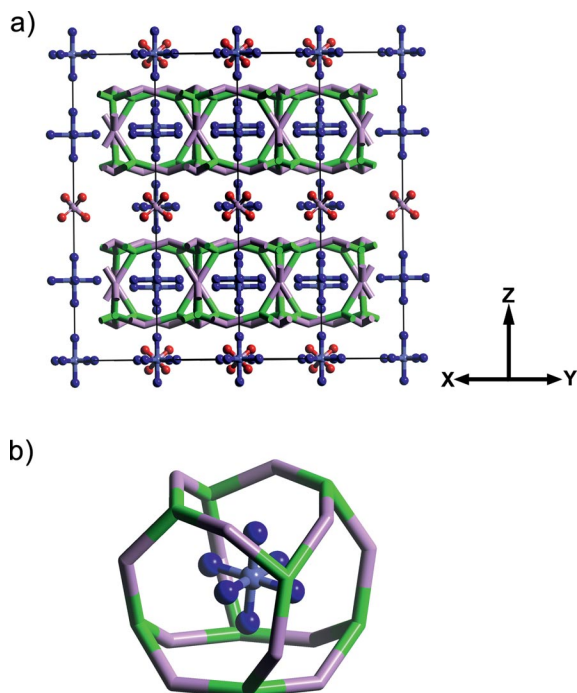


Figure 3. (a) The two types of cobalt hexaammine complex cations and the extraframework PO_4 groups, which are located in the voids between and within the layered hosts. (b) The intralayer cobalt complex cation located in the 8^6 cavity. Framework O atoms are omitted for clarity. (Green: Zn, pink: P, red: O, deep blue: N, light blue: Co)

Thermogravimetric analysis was carried out with a Perkin–Elmer TGA 7 unit instrument in air at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. A major weight loss of 22.29% (calcd. 21.47%) occurred at 300–500 $^\circ\text{C}$ (Figure S2), which is attributed to the decomposition of the metal complexes and the loss of hydroxy groups. The powder XRD pattern of the final residue suggested that ZnPO-CJ68 might turn into dense cobalt and zinc phosphates after calcination.

Conclusions

A new zinc phosphate structure, ZnPO-CJ68, has been prepared by using cobalt hexaammine as the template. Its structure contains unusual 3D microporous layered host

frameworks with 8-ring apertures that run along the thickness of the layers as well as in the planes of the layers. Guest $\text{Co}(\text{NH}_3)_6^{3+}$ cations are located in the voids not only between but also within the layered hosts. The shape of the intralayer guest $\text{Co}(\text{NH}_3)_6^{3+}$ cation perfectly matches the shape of the micropore within the host layer. The successful synthesis of ZnPO-CJ68 opens new possibilities to prepare layered frameworks with desired microporosity by using appropriate structural templates.

Experimental Section

Synthesis and Characterization: Large single crystals of ZnPO-CJ68 were synthesized under hydrothermal conditions from a mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, H_3PO_4 (85%), $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, and H_2O in a molar ratio of 1.00:5.00:0.25:555.56. Typically, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g) was dissolved in H_2O (10 mL) and H_3PO_4 (0.34 mL, 85%) was added with stirring. $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (0.067 g) was then added to the reaction mixture with stirring. The resulting homogeneous mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 110 $^\circ\text{C}$ for 6 d. Orange, cubic, single crystals were separated by filtration, washed with distilled water, and air-dried. Inductively coupled plasma spectroscopy gave the contents of Zn (found 22.7 wt.-%, calcd. 25.41 wt.-%), P (found 14.7 wt.-%, calcd. 16.54 wt.-%), and Co (found 7.52 wt.-%, calcd. 8.58 wt.-%).

X-ray Structure Determination: A suitable single crystal of ZnPO-CJ68 with dimensions of $0.3 \times 0.3 \times 0.2$ mm was selected for single-crystal X-ray diffraction analysis. The intensity data were collected at room temperature with a Siemens SMART CCD diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). 9787 reflections ($-13 \leq h \leq 9$, $-13 \leq k \leq 13$, $-35 \leq l \leq 35$), 1726 independent, were collected in the ω scan mode ($R_{\text{int}} = 0.0396$). Data processing was accomplished with the SAINT program.^[9] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELX-97.^[10] The Zn, P and Co atoms were easily located; N and O atoms were found afterwards in difference Fourier maps. All atoms were refined anisotropically.

CCDC-828757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental and simulated powder XRD patterns, thermogravimetric curve, and selected bond lengths.

Acknowledgments

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An Iron(III) Dithiolene Complex as a Functional Model of Iron Hydrogenase

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Keywords: [Fe] hydrogenase / H₂ evolution / EPR spectroscopy / Cyclic voltammetry / Dithiolenes / Iron

The iron(III) dithiolene complex [PPh₄]₂[Fe(mnt)₂(SPh)] (**1**, mnt = maleonitrile dithiolate) has a highly distorted square-pyramidal geometry and an intermediate spin ferric ion (*S*_{Fe} = 3/2), and catalyzes electrochemical H₂ evolution at the lowest achievable reduction potential known for iron-containing electrocatalytic systems to date: *E*_p = −0.309 V in CH₃CN and

*E*_p = −0.53 V in water vs. Ag/AgCl using a modified glassy carbon working electrode. Control experiments suggest that the electrochemical H₂ evolution at low potential is promoted by metal-assisted protonation at the S donors of the thiophenolato and mnt ligands, which liberate H₂ gas upon electrochemical reduction.

Introduction

Hydrogenases catalyze the biological activation of hydrogen [Equation (1)], which involves the reversible two-electron reduction of two protons to H₂ gas and vice versa.^[1]



The three known classes of hydrogenases, [NiFe], [FeFe] and FeS cluster-free hydrogenases contain iron at their active site, which is coordinated by thiolates, CO, CN[−] or a light sensitive cofactor.^[2] Several model compounds of hydrogenases have been reported that structurally or functionally resemble hydrogenase active sites.^[3] Electrochemical proton reduction or hydrogen activation catalyzed by the model compounds is one of the current methods of estimation of hydrogenase activity, in which the catalytic efficiency is correlated to the shift of the reduction/oxidation potentials positively towards 0 V (−0.41 V at pH 7.0). The design of a complex that can catalyze electrochemical hydrogen activation at lower potentials than the Pt working electrode under ambient conditions is a challenge. Iron-containing electrochemical catalysts that are known to date include the mononuclear iron(II) complexes, [Fe^{II}(S₂C₆H₄)(CO)₂(PMe₃)₂] and [Fe^{II}(S₂C₆H₂Cl₂)(CO)₂(PMe₃)₂], an FeS cluster with Fe_{cubane}(μ-SR)Fe_{subsite} and [Fe₂(CN)(CO)₄H(PMe₃)(S₂C₃H₆)], which function at moderately high reduction potentials, *E*_p ≈ −1.0 V.^[4] However, several electrochemical catalysts that contain other transition metals are known, e.g. carbon nanotube grafted-[Ni(PPh₂N^{Ph})₂](CH₃CN)][BF₄]₂, (CpMoμ-S)₂S₂CH₂, cobalt macrocyclic glyoxime/tetraimine complexes and a nickel(II) dithiolene

complex, which function at considerably lower reduction potentials.^[5] Herein we report an iron(III) dithiolene complex, [PPh₄]₂[Fe(mnt)₂(SPh)] (**1**, mnt = maleonitrile dithiolate), which has unique structural features and electrocatalyzes proton reduction at a very low reduction potential, *E*_p = −0.309 V.

Results and Discussion

Complex **1** was synthesized by the reaction of FeCl₃ with Na₂mnt and PhSH in CH₃CN in the presence of Et₃N under an argon atmosphere. Single crystals suitable for X-ray diffraction were obtained by recrystallization from a CH₃CN/Et₂O mixture. Crystals of **1** contained the [Fe^{III}-(mnt)₂(SPh)]^{2−} anion (**1a**) and [PPh₄]⁺ cations in a 1:2 ratio. The perspective view of **1a** is displayed in Figure 1 and indicates that the iron(III) center is pentacoordinate in a highly distorted square pyramidal fashion. The sulfur atoms of the mnt ligands are each shifted by 0.192–0.196 Å from the

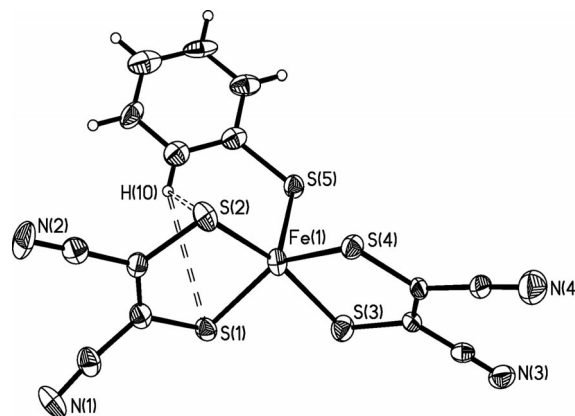


Figure 1. Perspective view of **1a**. Selected bond lengths [Å]: Fe(1)–S(1) 2.2604(16), Fe(1)–S(2) 2.2561(17), Fe(1)–S(3) 2.2706(16), Fe(1)–S(4) 2.2848(15), Fe(1)–S(5) 2.3574(16), S(2)⋯H(10) 2.911, S(1)⋯H(10) 3.144.

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mean basal plane, and the Fe^{III} ion is shifted by 0.540 Å. The basal Fe–S distances are 2.256–2.285 Å, and the axial Fe–S distance is 2.357 Å. The room temperature magnetic susceptibility measurement of **1** suggests that the complex has a quartet ground state with a magnetic moment (μ_{eff}) of ca. 3.80 μ_{B} at 298 K.

The intermediate spin state ($S = 3/2$) of **1** is further supported by its EPR spectral features (Figure 2A–C), which are similar to iron(III) complexes with intermediate spins in the literature.^[6] The solid-state EPR spectra are almost identical at 298 and at 120 K, and fine splitting is observed in the region corresponding to $g = 2.07$ in frozen CH₃CN at 120 K (Figure 2C). In its UV/Vis spectrum, **1** exhibited a low energy band at around $\lambda_{\text{max}} = 984$ nm ($\epsilon = 300$ M^{−1} cm^{−1}) with a shoulder at around $\lambda_{\text{max}} = 702$ nm ($\epsilon = 500$ M^{−1} cm^{−1}) in CH₃CN. Complex **1** underwent a reversible one-electron redox process at $E_{1/2} = -247$ mV (vs. Ag/AgCl), which can be assigned to an mnt-based redox process (Figure 2D) as this reversible wave has been observed in several of our other iron complexes: [PPh₄]₂[Fe^{IV}(mnt)₃],

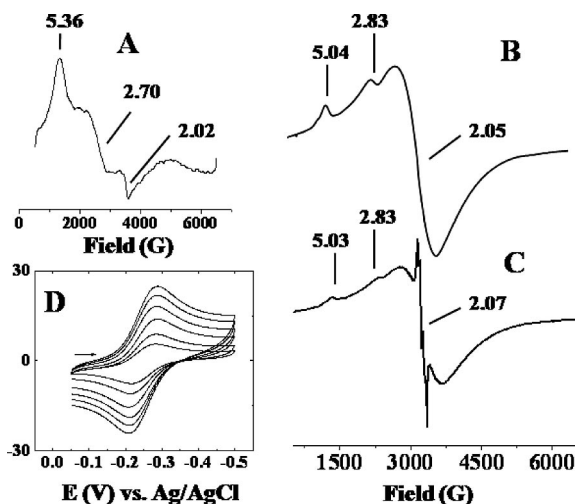


Figure 2. (A–C) X-band EPR spectra of **1** with g values highlighted: (A) Solid at 298 K, (B) solid at 120 K and (C) in CH₃CN at 120 K. (D) Cyclic voltammograms of **1** (1 mM) at different scan rates (50, 100, 200, 300, 400 and 500 mV s^{−1}; bottom–top) in CH₃CN/NBu₄ClO₆ (0.2 M) using GCE working, Pt auxiliary and Ag/AgCl reference electrodes.

[PPh₄]₂[Fe^{III}(mnt)₂]₂, [NBu₄]₄[Fe₄(μ₃-S)₄(mnt)₄], and [PPh₄]₂[Fe^{III}(mnt)Br]. Complex **1** is highly stable in CH₃CN, and the irreversible wave at $E_p = +1.553$ V is assigned to PhS[−] oxidation. In its mass spectrum (ESI, −ve), **1** displayed a peak at $m/z = 468$, which is due to the presence of [Fe^{III}(mnt)₂(SPh)]Na[−] in CH₃CN.

Complex **1** catalyzes electrochemical H₂ evolution at the lowest achievable reduction potential ($E_p = -0.309$ V) from *p*-toluenesulfonic acid (TsOH) in CH₃CN. The cyclic voltammograms of **1** as a function of increasing concentrations of TsOH (10 μM) are displayed in Figure 3A. The CV profile shown as a dashed line is that of **1** before addition of TsOH. Upon addition of 100 μL of TsOH in CH₃CN, the current values due to the reductive process at $E_p = -0.309$ V increase as shown Figure 3A. Controlled potential electrolysis of **1** (2 mmol) was carried out in CH₃CN with excess TsOH (100 mmol) at $E_p = -0.8$ V.

Complex **1** also catalyzes electrochemical proton reduction to H₂ gas in water that contains TsOH. The cyclic voltammetry experiment in water was performed with a modified glassy carbon electrode (GCE), which was prepared as reported previously.^[5f] A single reductive response at $E_p = -0.53$ V vs. Ag/AgCl was observed (Figure 3B), which can be assigned to the reduction of TsOH protons. A blank experiment using a standard GCE and TsOH in water in the absence of **1** displayed a reductive response at $E_p = -1.4$ V vs. Ag/AgCl.^[5f] Electrochemical H₂ evolution at such a low reduction potential is promoted by the protonation of the mnt and thiophenolato ligands, which is assisted by the iron(III) center (Scheme 1). Upon addition of TsOH, the more basic S donor of the mnt ligand and the thiophenolato S donor are protonated. These protons can interact with the iron(III) center, which was inferred from EPR and UV/Vis spectroscopy. The doubly protonated complex is further electrochemically reduced to yield H₂ gas and **1**. The iron(III) center initially assists the protonation by holding the thiophenolato ligand by intramolecular C–H(10)⋯S(2) and C–H(10)⋯S(1) (2.911 and 3.144 Å, respectively) interactions, which was inferred from the X-ray structure determination, and may assist the formation of an H–H bond at the metal center, which leads to H₂ evolution.

Complex **1** is the first compound that can catalyze electrochemical H₂ evolution from TsOH in CH₃CN at such a

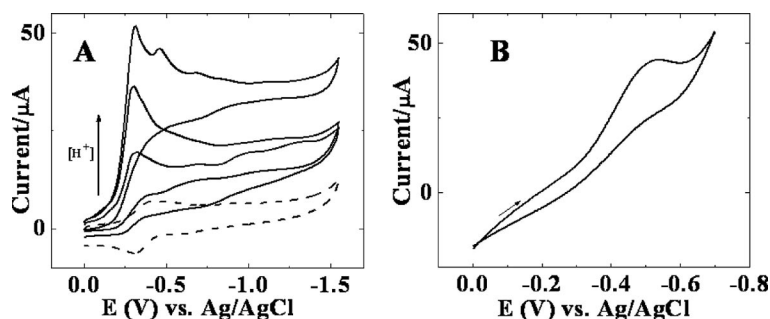
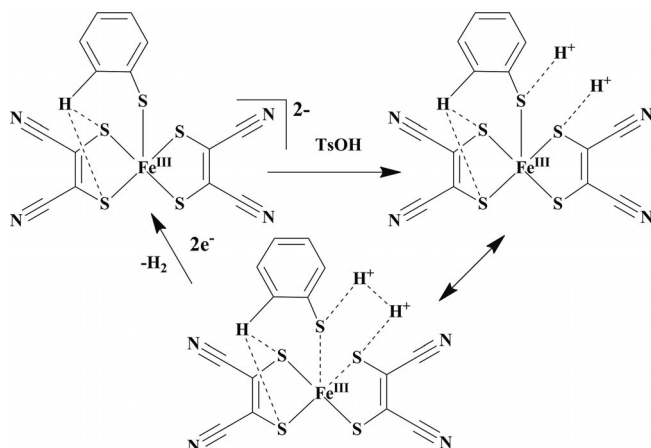


Figure 3. (A) Cyclic voltammograms of **1** (1 mM) in CH₃CN as a function of the increasing concentration of added TsOH (10 μM), supporting electrolyte = NBu₄ClO₆ (0.2 M). (B) Cyclic voltammogram of TsOH in water using a modified GCE coated with **1** (3 mM), supporting electrolyte = NaClO₄ (0.2 M).



Scheme 1. Proposed mechanism for electrochemical H_2 evolution catalyzed by **1**.

low reduction potential. Several iron complexes have been reported that catalyze electrochemical H_2 evolution at higher potentials, $E_p \approx -1.0$ V.^[4] However, a molybdenum–sulfur dimer, $(\text{CpMo}\mu\text{-S})_2\text{S}_2\text{CH}_2$, and its derivatives catalyze electrochemical H_2 evolution at $E_p = -0.26$ V vs. SCE in CH_3CN with *p*-cyanoanilinium as the acid source.^[5e] A square-pyramidal complex,^[6b] $[\text{PPh}_4]_2[\text{Fe}(\text{mnt})_2\text{Br}]$ (**2**), which has a bromide ligand at the axial position, catalyzes proton reduction to H_2 gas at a higher potential of $E_p \approx -1.1$ V (Figure 4A). X-ray structural characterization of **2** (Figure 4B) indicated that it has an axially coordinated bromide ligand in a perfect square-pyramidal fashion where double protonation, which leads to the electrochemical formation of H_2 gas as shown in Scheme 1, is not possible. However, a complex ligated by a *tert*-butylthiolato ligand, $[\text{PPh}_4]_2[\text{Fe}(\text{mnt})_2(\text{S}t\text{Bu})]$ (**3**), which is expected to have a similar structure to **1**, catalyzes electrochemical H_2 evolution at a low reduction potential, $E_p \approx -0.348$ V.

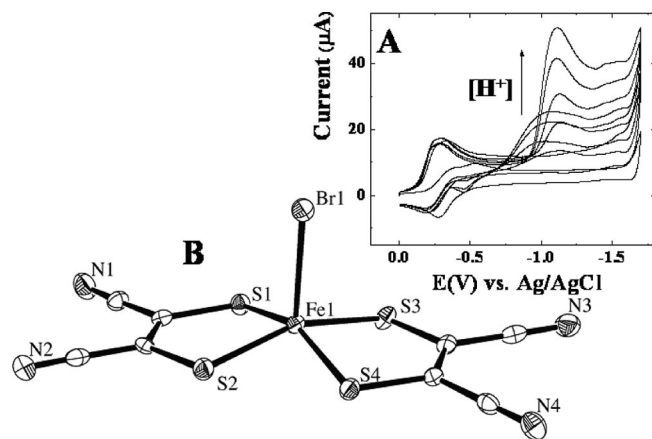


Figure 4. (A) Cyclic voltammograms of **2** (1 mM) in CH_3CN as a function of the increasing concentration of added TsOH (10 μM), supporting electrolyte = NBu_4ClO_4 (0.2 M); (B) Perspective view of the complex anion in **2**. Selected bond lengths [Å]: Fe(1)–S(1) 2.2511(14), Fe(1)–S(2) 2.2460(14), Fe(1)–S(3) 2.2638(14), Fe(1)–S(4) 2.2412(14), Fe(1)–Br(1) 2.4685(9).

Conclusions

Pentacoordinate iron(III) dithiolene **1** catalyzes electrochemical H_2 evolution at the lowest achievable reduction potential known to date for iron-containing electrocatalysts ($E_p = -0.309$ V in CH_3CN and $E_p = -0.53$ V in water). Control experiments suggest that the electrochemical H_2 evolution at low potential is promoted by the iron-assisted protonation of the S donors of the coordinated mnt and thio-phenolato ligands, which liberates H_2 gas upon electrochemical reduction. Our results also indicate that pentacoordinate iron(III) complexes with similar structures, i.e. with an axially substituted S donor ligand, can also catalyze electrochemical H_2 evolution at similarly low potentials.

Experimental Section

CCDC-840514 (for **1**) and -840515 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Materials, methods, synthesis, characterization and crystal data for **1** and **2**, electronic and EPR spectral changes of **1** as a function of TsOH additions.

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Barium Bis(dimethylsilyl)amide – Adduct vs. Oxo Formation

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Keywords: Barium / Amides / Molecular oxides / 1,10-Phenanthroline / Agostic interactions

Silylamide $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ reacts with 1,10-phenanthroline (Phen) in toluene to give the donor adduct $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{Phen})]_2$. X-ray structure analysis revealed a dimeric solid-state structure with two bridging silylamido ligands and $\text{Ba}\cdots\text{SiH}$ β -agostic interactions, which are most pronounced for the terminal silylamido ligands. Treatment of

$[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ with GaMe_3 did not lead to the isolation of putative Lewis acid adduct $[\text{Ba}(\mu\text{-}\{\text{N}(\text{SiHMe}_2)_2\})(\mu\text{-Me})(\text{GaMe}_2)]$ but resulted in the soluble, low aggregated barium oxo complex $[\text{Ba}(\mu_4\text{-O})(\text{GaMe}_3)_2(\text{toluene})]_2$, which is reminiscent of inverse crown ethers.

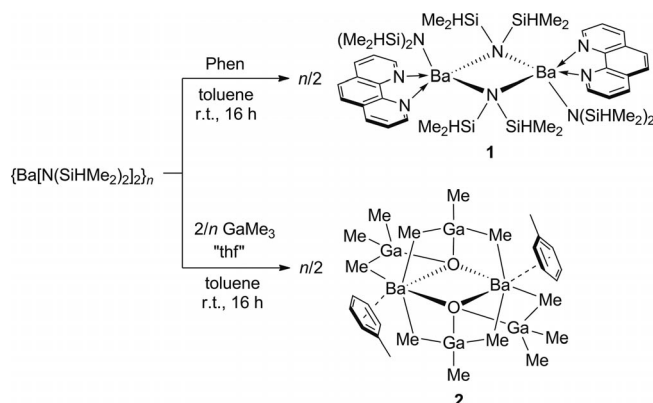
Introduction

Heavy alkaline-earth metal (Ca, Sr, Ba) amides have proved to be valuable synthesis precursors for amine/amido elimination protocols,^[1] which give access to homogeneous and heterogeneous catalysts for, e.g., asymmetric hydroamination or polymerization reactions.^[2,3] In particular, bulky secondary silylamido ligands impart a stabilizing environment for low-coordinate metal complexes, even for the large barium(II) center.^[1,4,5] Caulton et al. have presented the X-ray structures of the homoleptic barium bis(trimethylsilyl)amide complexes $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$, $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$, and $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$, which were obtained by direct metalation of $\text{HN}(\text{SiMe}_3)_2$ with barium in the presence of gaseous ammonia in tetrahydrofuran (thf).^[6] Ruhlandt-Senge et al. have explored secondary arylsilylamido ligands to obtain monobarium complexes $[\text{Ba}\{\text{N}(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})(\text{SiMe}_3)_2(\text{thf})_2\}]$ ^[7] and $[\text{Ba}\{\text{N}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\text{SiMe}_3)_2(\text{Do})_2\}]$ ($\text{Do} = \text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine, $\text{pmdta} = N,N,N',N'',N'''$ -pentamethyldiethylenetriamine).^[8] Recently, we and others have reported the synthesis of donor-free $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$,^[9,10] which was easily transformed into the thf adduct $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{thf})_4]$.^[9] These dimethylsilylamide complexes have emerged as crucial precursors for the peralkylated complexes $[\{\text{Ba}(\text{AlR}_4)_2\}_n]$ ($\text{R} = \text{Me}, \text{Et}$)^[9] and the heteroleptic silylamide/siloxide cluster $[\text{Ba}_3\{\text{OSi}(\text{OrBu})_3\}_3\{\text{N}(\text{SiHMe}_2)_2\}_3]$, which is not subject to the Schlenk-type equilibrium.^[11] Herein we give a preliminary account of two other features of this silylamido li-

gand:^[12] its engagement in pronounced $\text{Ba}\cdots\text{SiH}$ β -agostic interactions and its involvement in the formation of an unusual molecular barium oxide.

Results and Discussion

The treatment of $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ with an equimolar amount of 1,10-phenanthroline (Phen)^[13] in toluene at ambient temperature gave a dark purple solution of $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{Phen})]_2$ (**1**, Scheme 1). Complex **1** was identified by elemental analysis and FTIR and NMR spectroscopy (Figures S1–S3, Supporting Information), and its solid-state structure was unequivocally proven by X-ray structure analysis (Figure 1).^[14] The asymmetrically bridged dibarium complex reveals at first sight two five-coordinate metal centers each with one η^2 -Phen ligand and one terminal and two bridging silylamido ligands. Short $\text{Ba}\cdots\text{Si}$ distances from 3.444(1)–3.674(1) Å, and Ba-N-Si angles from 93.6(1)–116.1(2)° indicate the presence of additional $\text{Ba}\cdots\text{SiH}$ β -agostic interactions.^[9,10,15]



Scheme 1. Reaction pathways for **1** and **2**.

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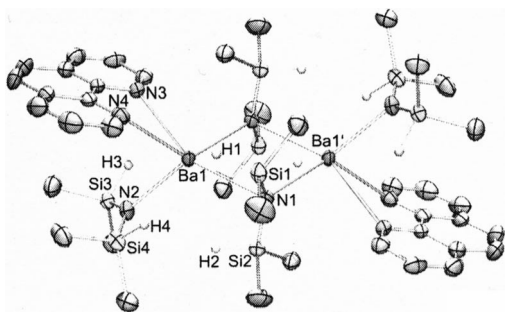


Figure 1. Molecular structure of **1** with 50% probability ellipsoids; except for SiH, hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Ba1–N1 2.798(3), Ba1–N1' 2.984(3), Ba1–N2 2.630(3), Ba1–N3 2.892(3), Ba1–N4 2.902(3), Ba1...Si1 3.517(1), Ba1...Si2 3.534(1), Ba1...Si3 3.674(1), Ba1...Si4 3.444(1); N1–Ba1–N1' 77.5(1), Si1–N1–Ba1 93.6(1), Si2–N1–Ba1 94.4(1), Si3–N2–Ba1 116.1(2), Si4–N2–Ba1 104.5(2), N1–Ba1–N3 85.0(1), N2–Ba1–N4 80.9(1).

This is also supported by the IR spectrum of **1**, which displays two separate strong SiH bands at 2011 and 1920 cm^{-1} . Both the terminal Ba–N(silylamido) bond length of 2.630(3) Å and the bridging ones of 2.798(3) and 2.984(3) Å compare well with those in six-coordinate $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{thf})_4]$ [2.669(2) Å] and $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{AlMe}_3)_2]$ [2.993(4) Å]^[9] and seven-coordinate $[(\text{LO}^3)\text{BaN}(\text{SiHMe}_2)_2]$ ($\text{LO}^3 = 2-[(1,4,7,10\text{-tetraoxa-13-azacyclopentadecan-13-yl)-methyl}]-4,6\text{-di-tert-butylphenolate}]$ [2.6885(17) Å].^[10]

We and others have previously shown that homoleptic alkaline-earth metal silylamide complexes also form adducts with Lewis acids.^[9,16] For example, Westerhausen et al. have isolated $[\text{M}(\mu\text{-}\{\text{N}(\text{SiMe}_3)_2\})(\mu\text{-Et})\text{GaEt}_2]$ ($\text{M} = \text{Ca}, \text{Sr}$) from the addition of GaEt_3 to $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$.^[17] Similarly, treatment of $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]$ with one equivalent of AlMe_3 in toluene gave $[\text{Ba}(\mu\text{-}\{\text{N}(\text{SiHMe}_2)_2\})(\mu\text{-Me})\text{AlMe}_2]$.^[9] We found that under the same reaction conditions, $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]$ and the less Lewis acidic monomeric GaMe_3 did not produce the putative adduct $[\text{Ba}(\mu\text{-}\{\text{N}(\text{SiHMe}_2)_2\})(\mu\text{-Me})\text{GaMe}_2]$ (Scheme 1). Crystallization at -40°C from toluene resulted in single-crystals (> 40%) suitable for X-ray diffraction analysis. In agreement with the NMR spectra, all of the silylamido ligands had been displaced in the new barium compound. Surprisingly, a molecular oxide of composition $[\text{Ba}(\mu_4\text{-O})(\text{GaMe}_3)_2(\text{toluene})_2]$ (**2**) was generated (Figure 2).^[14]

The solid-state structure of **2** revealed the formation of a dibarium complex, which features a planar $[\text{Ba}(\mu\text{-O})_2]$ core with O–Ba–O and Ba–O–Ba angles that average 79.89 and 100.10°, respectively. Two η^6 -coordinating toluene molecules^[18,19] and four GaMe_3 molecules shield this Ba_2O_2 entity. Two GaMe_3 molecules bridge the barium centers by two Ba–CH₃ contacts and one Ga–O bond each, whereas the other two molecules each interact with one barium center by heterobridged moieties of the type $\text{Ba}(\mu\text{-CH}_3)(\mu\text{-O})\text{-GaMe}_2$. Rapid exchange of the bridging and terminal methyl groups at ambient temperature is suggested by the

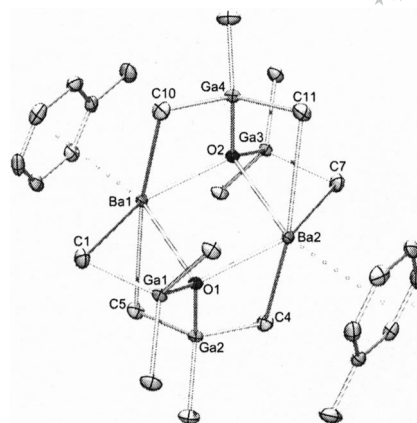


Figure 2. Molecular structure of **2** with 50% probability ellipsoids; H atoms are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Ba1–O1 2.573(1), Ba1–O2 2.515(1), Ba2–O1 2.518(1), Ba2–O2 2.576(1), Ba1–C1 3.140(2), Ba1–C5 3.136(2), Ba1–C10 3.202(2), Ba2–C4 3.229(2), Ba2–C11 3.176(2), Ba1–C_{toluene}(av) 3.010, Ba2–C_{toluene}(av) 3.013, Ga1–O1 1.939(1), Ga2–O1 1.933(1), Ga3–O2 1.941(1), Ga4–O2 1.934(1), Ga1–C1 2.040(2), Ga1–C2 2.017(2), Ga1–C3 1.985(2), Ga2–C4 2.021(2), Ga2–C5 2.040(2), Ga2–C6 1.986(2); O1–Ba1–O2 79.95(4), O1–Ba2–O2 79.82(4), Ba1–O1–Ba2 100.09(4), Ba1–O2–Ba2 100.11(4), Ba1–C1–Ga1 82.83(6), Ba1–C5–Ga2 83.15(6), Ba1–C10–Ga4 83.51(6).

appearance of single signals in the ^1H and ^{13}C NMR spectra (Figures S4 and S5).^[9] The Ba–O(oxo) bond lengths in **2** average 2.546 Å, which is considerably shorter than those found in the few metalorganic barium oxo clusters known to date. Representative examples of these clusters comprise the oxoaryloxide cluster $[\text{Ba}(\mu_4\text{-O})\{\mu_2\text{-OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_3\text{-2,4,6}\}_6\cdot 3(\text{toluene})]$ [Ba–O(oxo) 2.65(2) and 2.675(7) Å]^[20] and the heterobimetallic oxoalkoxide clusters $[\text{Li}_3(\mu_6\text{-O})\text{-Ba}_3(\mu_6\text{-O})\{(\text{thf})_3\cdot\text{Ba}_3\}(\text{O}t\text{Bu})_{11}]$ [Ba–O(oxo) 2.60–2.77 Å]^[21] and $[\text{Ba}_4\text{Ti}_{13}(\mu_3\text{-O})_{12}(\mu_5\text{-O})_6(\mu_5\text{-}\eta^1\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}(\mu_1, \mu_3\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_{12}]$ [Ba–O(oxo) 2.916(9) and 3.080(9) Å].^[22] In all of these barium clusters, the source of the interstitial oxo moiety was water or remained ambiguous. It is well known for other oxophilic metal centers that the appearance of “undesired” oxide anions is difficult to trace, with degradation of ethereal solvents or unintentional partial hydrolysis as the dominant reaction pathways.^[13c,22] The oxygen scavenging properties of alkaline-earth metal-containing organometallic compounds, and those of barium metal in particular, are well-known.^[23–25] Recently, Roesky et al. have reported soluble molecular CaO and SrO complexes that are stabilized by Al-based Lewis acids, $[\{\text{LAl}(\text{Me})(\mu\text{-O})\text{M}(\text{thf})\}_2]$ [$\text{M} = \text{Ca}, \text{Sr}$; $\text{L} = \text{CH}[\text{C}(\text{CH}_3)]\text{-}(\text{CMe})(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N})_2]$, which were designed from $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$ and $[\text{LAlMe}(\text{OH})]$.^[26] However, the synthetic protocol and structural features of **2** are reminiscent of s block-metal inverse crowns,^[27] which display functional molecules with four distinct components (M^+ , M^{2+} , R_2N^- , and anion[−] or dianion^{2−}; Figure 3A), and their formation involves traces of $\text{O}_2/\text{H}_2\text{O}$. Compound **2** is composed of Ba^{2+} , Ga^{3+} , CH_3^- , and dianion(O)^{2−} (Figure 3B).^[28,29]

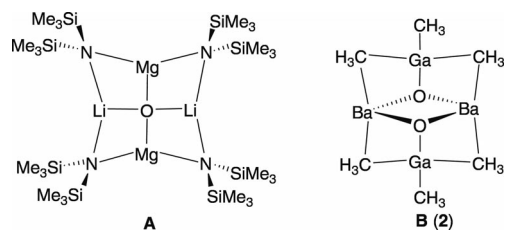


Figure 3. Structural motifs of (A) inverse crown ether $[\text{Li}_2\text{Mg}_2\{\text{N}(\text{SiMe}_3)_2\}_4(\text{O}_2)_x(\text{O})_y]^{27}$ and (B) **2**.

Conclusions

The oligomeric/polymeric structure of $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ can be easily disrupted by the chelating Lewis base 1,10-phenanthroline. The resulting dibarium complex $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2(\text{Phen})]_2$ reveals the propensity of the dimethylsilylamido ligand to engage in $\text{M}\cdots\text{SiH}$ β -agostic interactions. Although serendipitously obtained, elucidation of the molecular barium oxide $[\text{Ba}(\mu_4\text{-O})(\text{GaMe}_3)_2(\text{toluene})_2]_2$ might give entry to unprecedented heterobimetallic mixed alkyl/amido chemistry according to Mulvey's concept of inverse crown ethers.

Experimental Section

[Ba{N(SiHMe₂)₂}₂(Phen)]₂ (1): In a glovebox, $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ (200 mg, 0.50 mmol) was suspended in toluene and Phen (90 mg, 0.50 mmol) was added. Instantaneously, the reaction mixture turned into a clear solution, which was stirred at ambient temperature for 16 h. The dark purple solution was filtered and concentrated. Crystals of **1** suitable for X-ray diffraction were obtained at -40°C (65%, 0.33 mmol). ^1H NMR (C_6D_6 , 25°C): δ = 0.48 [d, $J(\text{H},\text{H})$ = 2.65 Hz, 48 H, SiCH_3], 5.47 (br., 8 H, Si-H), 7.08 (br., 4 H, Phen), 7.10 (s, 4 H, Phen), 7.52–7.54 (m, 4 H, Phen), 9.58 (s, 4 H, Phen) ppm. ^{13}C NMR (C_6D_6 , 25°C): δ = 4.6 (SiCH_3), 123.6 (Phen), 129.5 (Phen), 137.6 (Phen), 146.2 (Phen), 150.6 (Phen) ppm. IR (Nujol): $\tilde{\nu}$ = 2011 (m), 1920 (m), 1622 (vw), 1585 (vw), 1568 (vw), 1236 (m), 1140 (m), 1093 (s), 964 (m), 941 (m), 919 (s), 882 (s), 840 (m), 765 (m), 732 (m), 669 (w), 562 (w) cm^{-1} . $\text{C}_{40}\text{H}_{76}\text{Ba}_2\text{N}_8\text{Si}_8$ (1168.44): calcd. C 41.26, H 6.23, N 9.62; found C 43.03, H 6.03, N 8.99.

[Ba($\mu_4\text{-O}$)(GaMe₃)₂(toluene)]₂ (2): In a glovebox, $[\text{Ba}\{\text{N}(\text{SiHMe}_2)_2\}_2]_n$ (100 mg, 0.25 mmol) was suspended in toluene and GaMe_3 (57 mg, 0.50 mmol) was added. Instantaneously, the reaction mixture gave a clear solution, which was stirred at ambient temperature for 16 h. The solution was filtered and concentrated. Crystals of **2** suitable for X-ray diffraction were harvested at -40°C (40%, 0.10 mmol). ^1H NMR (C_6D_6 , 25°C): δ = -0.02 (s, 36 H, GaCH_3), 2.24 (s, 6 H, tol), 7.05–7.15 (m, 10 H, tol) ppm. ^{13}C NMR (C_6D_6 , 25°C): δ = -0.4 (GaCH_3), 21.4 (tol), 125.7 (tol), 128.5 (tol), 129.3 (tol), 137.3 (tol) ppm. $\text{C}_{26}\text{H}_{52}\text{Ba}_2\text{Ga}_4\text{O}_2$ (950.24): calcd. C 32.86, H 5.52; found C 32.30, H 5.58.

CCDC-844927 (for **1**) and -844928 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): General procedures as well as spectroscopic details for all new compounds.

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- Compound **1** ($\text{C}_{40}\text{H}_{72}\text{Ba}_2\text{N}_8\text{Si}_8$, M_r = 1164.46) crystallized from toluene in the monoclinic space group $P2_1/c$ with a = 12.9566(13), b = 16.0725(10), c = 13.1910(13) Å, β = 93.269(8)°, V = 2742.5(4) Å³, and $\rho_{\text{calcd.}}$ = 1.410 g cm^{-3} for Z = 2. Data were collected with Mo radiation (0.71073 Å) at 173(2) K with a STOE IPDS II system. The structure was solved by direct methods, and least-squares refinement of the model based on 5597 (all data) and 4499 [$I > 2.0\sigma(I)$] converged to a final R = 0.0398 and $wR2$ = 0.0672, respectively. Compound **2** ($\text{C}_{26}\text{H}_{52}\text{Ba}_2\text{Ga}_4\text{O}_2$, M_r = 950.24) crystallized from toluene in the monoclinic space group $P2_1/c$ with a = 20.9580(8), b = 17.3855(7), c = 14.9112(6) Å, β = 105.6900(10)°, V = 5230.7(4) Å³, and $\rho_{\text{calcd.}}$ = 1.810 g cm^{-3} for Z = 6. Data were collected with Mo radiation (0.71073 Å) at 103(2) K with a Bruker Ultra TXS CCD system. The structure was solved by direct methods, and least-squares refinement of the model based on 15984 (all data) and 14446 [$I > 2.0\sigma(I)$] converged to a final R = 0.0217 and $wR2$ = 0.0562, respectively.

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Concentration-Dependent Dehydrogenation of Ammonia–Borane/Triglyme Mixtures

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Keywords: Ammonia borane / Dehydrogenation / Hydrogen storage / Kinetics / Reaction mechanisms / Thermolysis

The dehydrogenation reaction of the hydrogen-storage compound ammonia–borane (AB) dissolved in triglyme (TG) reveals an unexpected but favourable concentration dependence of its dehydrogenation behaviour. Formal reaction-order considerations and ¹¹B NMR spectroscopic analytics point towards a complex AB decomposition and hydrogen-release scheme that in highly concentrated solutions partly begins to resemble that of the solid-state case. The analysis

of the gas-release characteristics identified two hydrogen desorption events that display an increasing peak overlap with increasing initial AB concentration. ¹¹B NMR spectroscopic studies indicate that the concentration-dependent stability of the intermediate diammoniate of diborane, the presence of which appears to influence the rates of several dehydrogenation steps by interacting with various other intermediates, is one of the key factors for the overall hydrogen release.

Introduction

Ammonia–borane (AB) is regarded as a promising candidate to fulfil the requirements for a high-density and easy-to-handle hydrogen source material.^[1] With its high hydrogen content of 19 wt.-% and a release of 13.5 wt.-% at temperatures below 140 °C,^[1,2] it possesses outstanding qualities for this application. In this respect, one important obstacle to using pure AB is given by its poor dehydrogenation kinetics, which would limit its use to applications with a high energy-demand-to-power ratio. To achieve the necessary improvements in dehydrogenation kinetics, a detailed understanding of structure, hydrogenation/dehydrogenation mechanisms and their rate-limiting steps is imperative and have been the subject of a significant number of studies during the past decade.^[1–5]

Consistent with earlier findings that the thermally induced dehydrogenation reaction of solid AB has an induction period, recent investigations show that the dehydrogenation of solid AB may be characterized by a nucleation and growth process.^[3] After the induction period, the release seems to follow a two-step scheme.^[2] The first release step has its onset at about 120 °C, which is just above the

melting point of AB.^[2] These findings suggest a kinetic enhancement for the dehydrogenation due to the presence of mobile phases.

In a recent publication,^[3] thermal decomposition of solid AB was found to be initiated by a species AB*, which is assumed to be mobile. Thereafter, two mobile AB* units may form the intermediate called diammoniate of diborane [BH₂(NH₃)₂]⁺[BH₄][–] (DADB), which is regarded as a nucleus for the dehydrogenation reaction. Once formed, or externally added to pure AB, DADB seems to promote the dehydrogenation kinetics significantly.^[3] The kinetics of this reaction were also substantially enhanced in ionic liquids (e.g., bmimCl, in which bmim = 1-butyl-3-methylimidazolium).^[4] Here, too, DADB was described as an intermediate.^[4] From their recent work on AB in diglyme, Autrey et al.^[6] reported on possible traces of DADB in a 2 M solution at 50 °C. From these results they concluded that DADB in solutions requires stabilization by a polar environment.^[4,6]

Hence, controlling the DADB formation by the means of the reaction environment could enhance the mobility of AB and seems to be a promising approach to improve the dehydrogenation kinetics. For high gravimetric hydrogen densities in the storage medium, however, the weight fraction of the reaction environment (e.g., the solvents or catalysts) and the chemical performance has to be optimized.

In this paper, the findings of significant amounts of DADB in highly concentrated solutions of AB in the weakly polar solvent triglyme (TG) and its positive consequences for the dehydrogenation kinetics of AB and the possible underlying reaction pathways will be discussed. For this purpose, we combined the method of gas volumetric measurements with ex situ ¹¹B NMR spectroscopy.

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Results and Discussion

Dehydrogenation Kinetics

Dehydrogenation characteristics of the thermolysis reaction (at $T = 70\text{ }^{\circ}\text{C}$) were investigated over a wide range of concentrations, from dilute solutions of $[\text{AB}]_0 = 0.1\text{ M}$ up to suspensions of $[\text{AB}]_0 = 23.0\text{ M}$ (Figure 1a). The time needed to release 1 mol of H_2 per mol of AB [$t_{1/2}(\text{H}_2)$] as a function of the initial AB concentration ($[\text{AB}]_0$) decays asymptotically to $(40 \pm 10)\text{ min}$ at the saturation concentration $[\text{AB}]_0 \approx [\text{AB}]_{\text{sat}} = 7.5\text{ M}$ and rises again for concentrations $[\text{AB}]_0 \geq 9.0\text{ M}$ (suspensions). Experiments with concentrations well above $[\text{AB}]_{\text{sat}}$ show nucleation and growth characteristics that are typical of solid AB according to the literature^[3] (see Figure 1). Hence, the best dehydrogenation kinetics are achieved in highly concentrated AB solutions. Therefore, the work presented will only focus on systems with AB in solution.

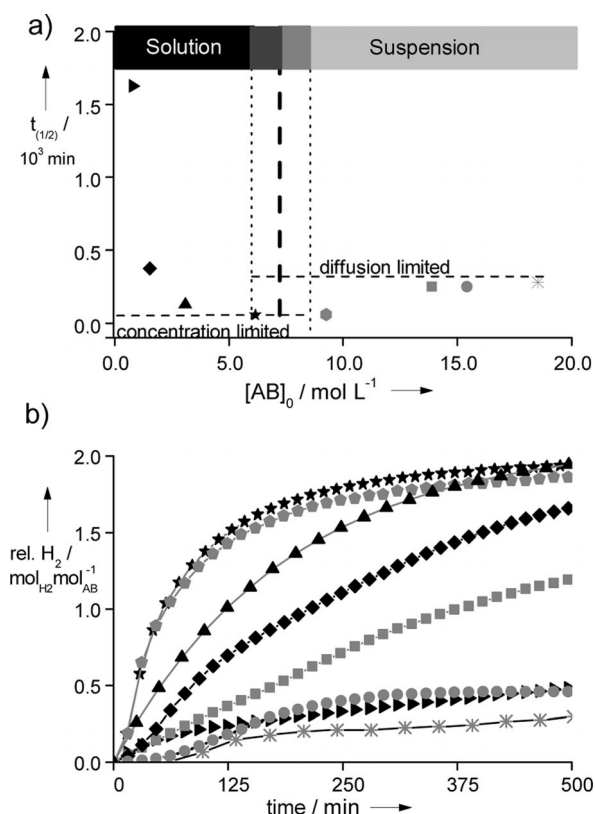


Figure 1. Hydrogen-release characteristics of AB in TG at $T = 70\text{ }^{\circ}\text{C}$ for mixtures with concentrations between 1.5 and 18 M. (a) Plot of the half-time of the total hydrogen release (i.e., the equivalent of 1 mol of H_2 per mol of BH_3NH_3) versus the concentration of the initial AB concentration in TG. (b) Amount of hydrogen released as a function of time given in mol H_2 per mol BH_3NH_3 .

In a first step to determine the kinetics of the dehydrogenation reaction, the emitted gas volume was characterized by a plot of the time required to release 0.5, 1.0 and 1.5 mol H_2 per mol of AB ($t_{1/4}$, $t_{1/2}$ and $t_{3/4}$, respectively) as a function of $[\text{AB}]_0^{-1}$ (Figure 2a) and $[\text{AB}]_0^{-2}$ (Figure 2b). For the early dehydrogenation phase, a linear dependence of

$t_x = 1/4(\text{H}_2)$ on $[\text{AB}]_0^{-1}$ can be estimated, which would correspond to a second-order kinetics (see Figure 2a). In contrast, the kinetics of the later dehydrogenation phase are better characterized by a linear dependence of $t_{1/2}(\text{H}_2)$ and $t_{3/4}(\text{H}_2)$ on $[\text{AB}]_0^{-2}$, which would correspond to a formal third-order rate law for the formation of H_2 as a function of $[\text{AB}]_0$ (see Figure 2b).

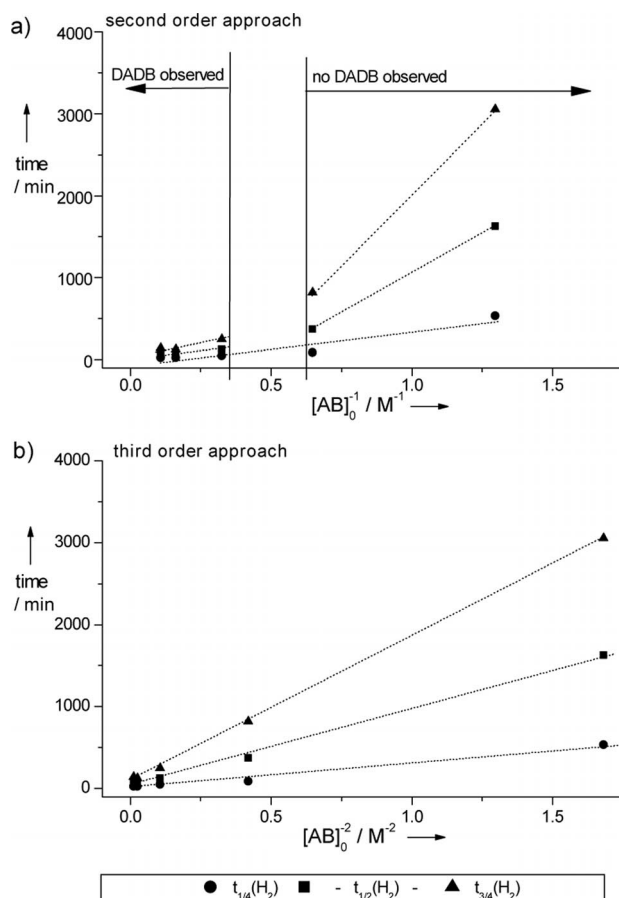


Figure 2. Time elapsed until the release of 0.5, 1.0 and 1.5 mol-equiv. of H_2 [$t_x = 1/4, 1/2, 3/4(\text{H}_2)$] at $T = 70\text{ }^{\circ}\text{C}$ plotted versus (a) $[\text{AB}]_0^{-1}$ (a distinct deviation from a second-order behaviour is observed for $t_x \geq 1/2$) and (b) $[\text{AB}]_0^{-2}$ (as a test for third-order kinetics).

The simple assumption that one third-order reaction is governing the dehydrogenation process appears to be very unlikely if one takes into account that AB decomposes in glymes according to a second-order rate law with respect to the AB concentration.^[6] In addition, calculations of the rate constants according to a third-order law do not result in a single value for all curves in Figure 2b, thus indicating that this rate law also does not apply.

One possible explanation for the aforementioned dehydrogenation behaviour can be extracted from the time derivative of the released hydrogen gas volume (see Figure 3). It can be seen that at least two distinct desorption events more strongly overlap with increasing $[\text{AB}]_0$ concentrations. The simultaneous occurrence of these two desorption events leads to an enhanced hydrogen development at higher concentrations during the early reaction phase (see Figure 2a, left-hand side).

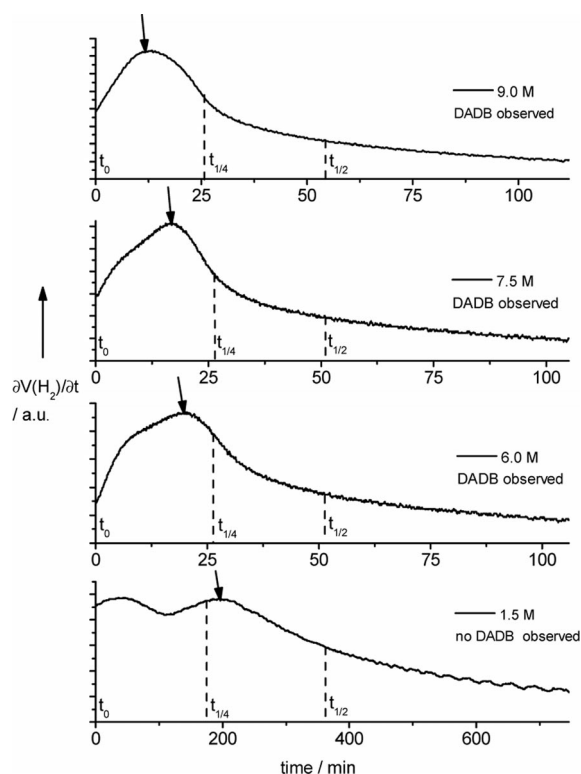


Figure 3. Time derivation of the gas volume of the hydrogen released at 70 °C from AB/TG solutions with different initial AB concentrations.

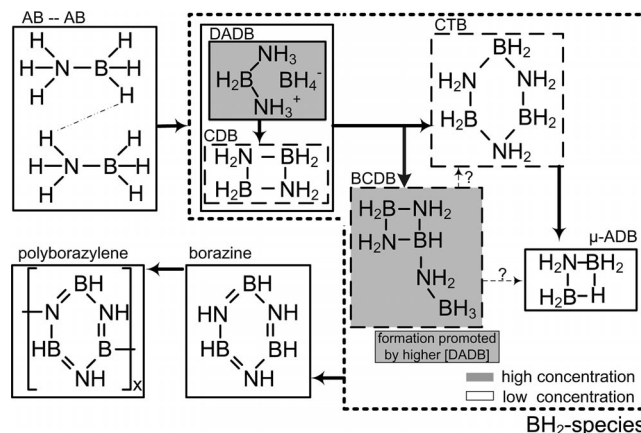
Moreover, the first event displays its maximum hydrogen flow significantly after t_0 . Such behaviour indicates that the hydrogen release is not governed by a single elementary decomposition reaction of any order but needs to proceed through an intermediate compound.

To understand the underlying mechanistic steps responsible for such behaviour, we coupled the dehydrogenation experiments with ex situ ^{11}B NMR spectroscopy.

^{11}B NMR Spectroscopy of the Reaction Phase $t < t_{1/4}$

As stated above, during the early reaction phase, the dehydrogenation kinetics can be fit to a second-order law, which may be satisfactorily explained by the bimolecular

reaction of two AB molecules to DADB with a subsequent cyclization to cyclodiborazane (CDB, $c\text{-B}_2\text{N}_2\text{H}_8$) under the release of 1 mol-equiv. H_2 (see Scheme 1). Such a mechanism was recently proposed for AB/glyme mixtures by Autrey et al. but could not yet be confirmed since the authors found only traces of DADB at low reaction temperatures.



Scheme 1. Proposed dehydrogenation pathways of AB in TG at 70 °C based on NMR spectroscopy. Solid boxes denote unambiguous observed signals; dashed boxes indicate proposed species based on results of Shaw et al.;^[6] dotted boxes frame BH_2 species. DADB was observed only at $[\text{AB}]_0 > 1.5 \text{ M}$ but seems to promote the formation of *B*-(cyclodiborazanyl)aminoborohydride (BCDB).

Our ^{11}B NMR spectra of the early reaction of dilute solutions ($[\text{AB}]_0 < 1.5 \text{ M}$) also show only two significant resonances. Beside the prominent AB-related quintet at $\delta = -21.5 \text{ ppm}$, a signal at $\delta = -10.5 \text{ ppm}$ is observed, which is assigned to CDB according to other publications (see Table 1).^[6,7]

For highly concentrated solutions ($[\text{AB}]_0 > 1.5 \text{ M}$), we observe an additional quintet resonance at $\delta = (-36.5 \pm 0.5) \text{ ppm}$ (see Figure 4a), which can be assigned to DADB.^[3,4] This assignment is also supported by the correlation with the signal of the BH_2 group at $\delta = -10.7 \text{ ppm}$. Because various components {CDB, cyclotriborazane ($c\text{-B}_3\text{N}_3\text{H}_{12}$, CTB), *B*-(cyclodiborazanyl)aminoborohydride

Table 1. Assignment of ^{11}B NMR spectroscopic signals to the relevant species found during AB/TG dehydrogenation experiments.

Species	^{11}B (20 °C) ^[a] [ppm]	$^1J_{\text{B,H}}$ [Hz]	Referenced literature
DADB	$(-36.5 \pm 0.5) (\text{BH}_4)^{[b]}$	79 (quint)	[3,6]
AB	-21.5 (BH_3)	78 (quint)	[6,7]
$\mu\text{-ADB}$	-26.5 (H-N-BH_2)	56 (d), 113 (t)	[7,9]
BCDB	-4.5 (NH_2BH_3)	[c]	[6]
CTB, CDB, BCDB	-10 to -13 (BH_2)	[c]	[3,4,6]
Boroxide (traces)	1.5 (BO)	—	—
Polyborazylene	25.0 ($(\text{BHNH})_x(\text{BH}_2)_x(\text{BH}_3)_x^{[d]}$)	—	[4,6]
Borazine	30.5 (HNBH_3) ^[d]	113 (d)	[3,4,6,7]

[a] ^{11}B chemical shifts are referenced to the IUPAC standard $\text{BF}_3\cdot\text{OEt}_2$ ($\delta = 0 \text{ ppm}$) at 20 °C. [b] Species only found in samples $[\text{AB}] > 1.5 \text{ M}$. [c] No multiplets observable. [d] $[\text{AB}] < 18 \text{ M}$.

(*cyc*[NH₂BH₂NH₂BH]-NH₂BH₃, BCDB)} also contribute to this signal, it is not correlated with the DADB signal at $\delta = -36.5$ ppm and thus does not follow its decrease with the progress of the dehydrogenation reaction. Our findings in highly concentrated solutions strongly support Autrey and co-workers^[6] assumption that the AB decomposition proceeds by means of the formation of DADB and CDB to CTB. Because our resolution of the $\delta = -10.7$ ppm peak is not sufficient, it is not evident whether or not CDB forms after or simultaneously with DADB.

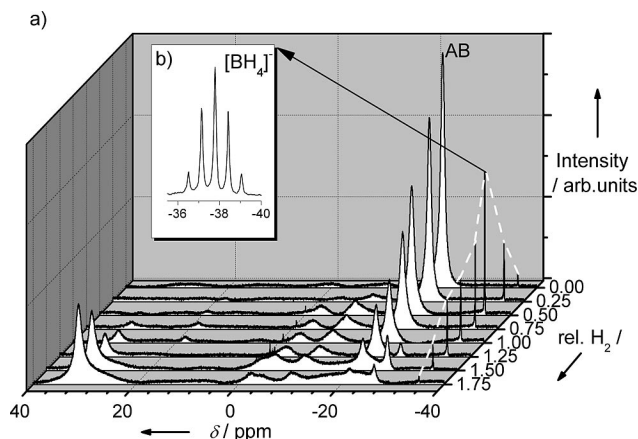


Figure 4. (a) $^{11}\text{B}\{^1\text{H}\}$ NMR spectra depicting the dehydrogenation evolution from an AB/TG solution ($[\text{AB}]_0 = 6.0$ M) at 70 °C. (b) The quintet signal at $\delta \approx (-36.5 \pm 0.5)$ ppm in the coupled spectra is identified as the BH_4 resonance of DADB and can be traced almost along the whole dehydrogenation process.

Although it cannot be stated for diluted solutions ($[\text{AB}]_0 \leq 1.5$ M) whether or not the absence of DADB-related signals is due to DADB concentrations that are below the detection limit, the observation, however, that the hydrogen release rate for $[\text{AB}]_0 = 1.5$ M reaches its maximum shortly after t_0 (see Figure 3) supports the assumption of the presence of an early intermediate, be it DADB or CDB.

During the early reaction phase $t < t_{1/4}$, the BH_2 signal at $\delta \approx -10.7$ ppm grows and slightly shifts to $\delta = -10.0$ ppm (see Figure 5). From DADB-enriched AB/TG solutions compared to pure AB/TG solutions, one has to assign the signal at $\delta = -10.7$ ppm to the BH_2 group of DADB. Based on the experiments with the diluted solutions ($[\text{AB}]_0 \leq 1.5$ M), we assign the $\delta = -10.7$ ppm signal to CDB as well. Together with the observation described in the literature^[6] that the CTB- BH_2 signal is slightly shifted to lower absolute ppm values in respect to the CDB- BH_2 signal, we interpret the evolving peak at $\delta = -10.0$ ppm as a result of the formation of CTB out of DADB and/or CDB.

Since the occurrence of the third-order decomposition law could not be simply derived from the early reaction mechanism, an analysis of the formation of intermediates by ^{11}B NMR spectroscopy was also performed for the reaction phase $t > t_{1/4}(\text{H}_2)$.

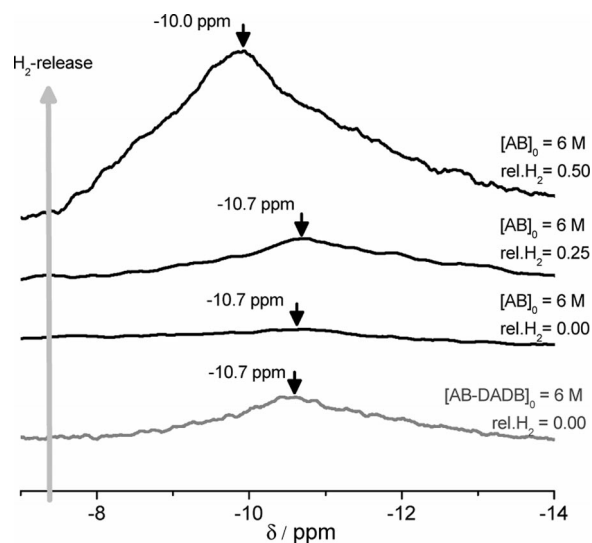


Figure 5. Excerpt of ^{11}B NMR spectra representing only BH_2 signals. All spectra are normalized by their integrals, representing the total boron content of each sample and thus allowing the direct comparison of the intensities. Grey: spectrum of a DADB-enriched AB/TG solution before dehydrogenation. Black: spectra of AB/TG solutions at different stages of dehydrogenation. The very shallow maximum at $\delta = -10.7$ ppm at the beginning of the recording of the hydrogen evolution ($\text{rel. H}_2 = 0$) is most likely due to a minute hydrogen release that was not detected during the sample preparation.

^{11}B NMR Spectroscopy of the Reaction Phase $t > t_{1/2}$

By the determination of the relative peak area of the signal at $\delta \approx 30.5$ ppm, we estimate that about $(15 \pm 2)\%$ of the total boron content is bound in borazine in all samples with $[\text{AB}]_0 > 1.5$ M after the reaction has proceeded to $t_{1/2}(\text{H}_2)$ (see Figure 4).

Samples with lower concentrations in which no DADB was observed show significantly less borazine [about $(5 \pm 1)\%$] at this point of reaction. These findings suggest that the hydrogen release from these mixtures is 15% higher than would be expected from the reaction of AB through DADB to CDB alone.

The DADB-related signal peaks around $t_{1/4}$ with a relative peak area of $(2 \pm 1)\%$ for $[\text{AB}]_0 = 3.0$ M and of $(4 \pm 1)\%$ for $[\text{AB}]_0 = 6.0$ M. The correlation between the high DADB and the high borazine concentrations at $t_{1/2}$ suggests that DADB is linked to an accelerated decomposition to borazine and the accompanied hydrogen release.

Shortly after the rise of the DADB-related signal, a resonance at $\delta = -4.5$ ppm occurs, the relative area of which also increases with increasing $[\text{AB}]_0$ concentrations (see Figure 6). We attribute this signal to the BNH_3 fragment of the recently identified BCDB.^[6] The relative peak area of this signal at $\delta = -4.5$ ppm follows a two-step pattern. Here, each step is followed by a short plateau (see Figure 6). The levels of these plateaus rise with increasing $[\text{AB}]_0$ concentrations. Prior to the onset of the second plateau, a sharp de-

cline of the signal's relative area at $\delta \approx -10.5$ ppm is observable, which we attribute to BH_2 resonances and interpret as a transition from $\text{CDB}^{[6,7]}$ to BCDB .

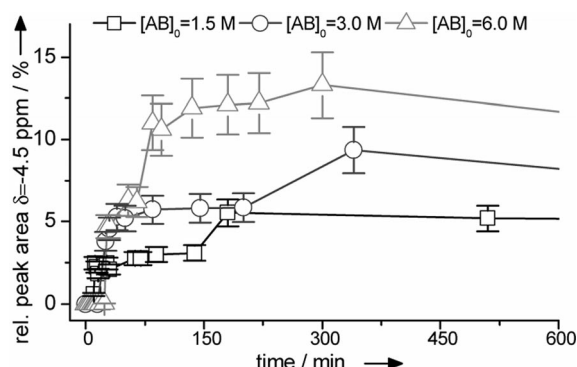


Figure 6. Analysis of the relative area of the BCDB-related peak at $\delta = -4.5$ ppm for different $[\text{AB}]_0$ values. The BCDB formation characteristics display two plateaus during the reaction. The relative peak areas rise with increasing $[\text{AB}]_0$.

Thus, in our measurements, higher $[\text{AB}]_0$ values seem to correlate with both higher $[\text{BCDB}]$ and higher $[\text{DADB}]$ ones. An apparent correlation between increased $[\text{DADB}]$ and increased $[\text{BCDB}]$ levels is supported by experiments we conducted with separately prepared mixtures of AB and DADB, which were prepared according to the procedure described by Shore et al.^[8] During the significantly enhanced dehydrogenation process, a rise of the relative peak area at $\delta = -4.5$ ppm (BCDB) was observed (see Figure 7).

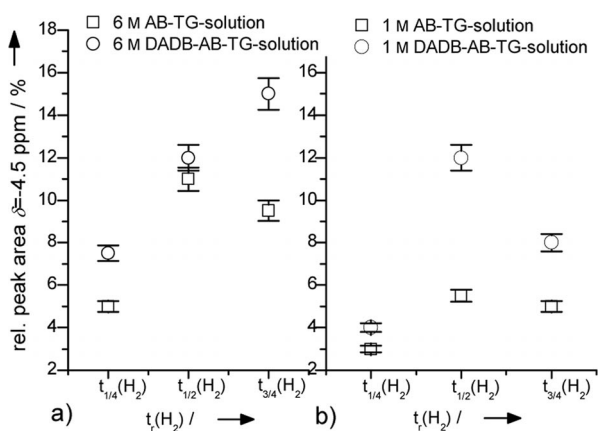


Figure 7. Evolution analysis of the relative areas of the BCDB-related ^{11}B NMR spectroscopic peak at $\delta = -4.5$ ppm for different $[\text{AB}]_0$ values during the dehydrogenation reaction of (a) 6.0 M and (b) 1.0 M solutions of AB/TG and AB/DADB/TG mixtures. The addition of DADB significantly promotes the formation of BCDB.

On the basis of experiments with separately prepared and heated CTB/TG samples, we ruled out the formation of BCDB from CTB, since we could not detect the $\delta = -4.5$ ppm signal, even at elevated temperatures (see Figure 8).

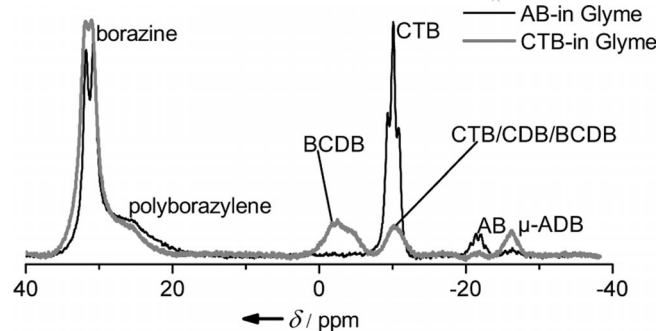


Figure 8. Coupled $^{11}\text{B}\{^1\text{H}\}$ NMR spectra^[8] of samples of AB (black line) and CTB (grey line) in glyme, which were dehydrogenated at 90 and 130 °C for 4 h, respectively. The spectrum of CTB does not show any signal of BCDB or CDB, whereas highly concentrated AB/TG solutions react to form CDB, BCDB and significant amounts of $\mu\text{-ADB}$.

Hence, we interpret the noticed acceleration of the formation of borazine from CDB through BCDB as being induced or promoted by the increased presence of DADB.

^{11}B NMR Spectroscopy of the Reaction Phase $t > t_{1/2}$

For the reaction phase $t > t_{1/2}$, the building of $\mu\text{-amino-diborane}$ ($\mu\text{-ADB}$, $\mu\text{-}[\text{NH}_2\text{BH}_2]$) seems to be another vital intermediate step to form borazine. The sextet signal at $\delta = -26.5$ ppm, which we assign to $\mu\text{-ADB}$, shows up shortly after $t_{1/2}(\text{H}_2)$ and remains present until all hydrogen is released (see Figure 4). In the separately prepared CTB samples, $\mu\text{-ADB}$ is the only compound found beside borazine (see Figure 8).

The detected dehydrogenation of pure CTB/TG samples is significantly slower than in CDB- or BCDB-rich AB/TG samples with $[\text{AB}]_0 > 1.5$ M. Thus, we assume two alternative pathways to borazine: an early, fast one that occurs through BCDB and a late, slow one through $\mu\text{-ADB}$. For diluted solutions, however, with $[\text{AB}]_0 < 1.0$ M both of these pathways seem, at least partially, to be blocked at 70 °C since neither DADB nor $\mu\text{-ADB}$ were detected.

In accordance with this interpretation, the measured hydrogen yield strongly deviates from the theoretical expected value of 2 mol H_2 per mol of AB. For example, for the initial concentrations of $[\text{AB}]_0 = 0.8, 0.5$ and 0.15 M, only 1.8, 1.5 and 0.3 mol H_2 per mol of AB were released, respectively.

Conclusion

We have found a concentration-dependent overlap of at least two distinct dehydrogenation events by gas kinetic analysis in AB/TG solutions. ^{11}B NMR spectroscopy demonstrates that the relative amounts both of DADB as well as of BCDB formed during thermal decomposition are increased in highly concentrated solutions. Moving from decomposition experiments with highly concentrated AB/TG solutions to the ones enriched with DADB, even higher rel-

ative amounts of BCDB are found. In addition, the presence of the latter compound appears to accelerate the formation of borazine (i.e., its formation is observed earlier and in higher amounts with respect to the relative amount of hydrogen released). If we recall that the borazine formation is accompanied by hydrogen emission, we can conclude that through the formation of BCDB, DADB is indirectly responsible for the observed accelerated hydrogen release by the earlier occurrence of the second desorption event. In this context, the observed experimental third-order law of the decomposition kinetics appears to be a consequence of a shift in the downstream reaction pathways.

As a consequence of above deduced relationship between the DADB and BCDB concentrations, the absence of detectable DADB in samples with $[AB]_0$ concentrations below 1.5 M indicates that the BCDB pathway for the conversion of CDB to borazine becomes less important. This could also explain the incomplete dehydrogenation in such samples at 70 °C.

The presence of DADB in highly concentrated solutions in a weakly polar organic solvent gives reason to reconsider the hypothesis that such an environment destabilizes the ion pair $[NH_3BH_2NH_3]^+[BH_4]^-$.^[4,6] Either this hypothesis is untenable or strongly concentrated solutions of AB in glymes lead to an increasingly polar environment that stabilizes DADB.

From these investigations it can be stated that the decomposition behaviour in highly concentrated solution, and naturally also in suspensions, resembles the decomposition mechanism in solid AB with respect to the importance of DADB.

These results have important implications for the development of possible high-capacity hydrogen-generation devices based on AB in organic solvents, since the dehydrogenation kinetics is one critical factor in the reactor design and layout in all conceivable applications.

Experimental Section

Materials: All experiments and measurements were performed under argon 5.0. AB was purchased from SAFC and purified by means of Soxhlet extraction with dry diethyl ether. Triglyme (2,5,8,11-tetraoxadodecane) was obtained from Aldrich (purity 98%) and distilled from sodium at 90 °C and 0.2 bar. DADB was synthesized according to literature methods^[8] and characterized by XRD, and ^{11}B and ^1H NMR spectroscopy. The obtained product was >75% pure with AB as the only byproduct. CTB was synthesized as described in the literature^[10] and was further purified by vacuum sublimation to result in a purity of 98% as demonstrated by ^{11}B and ^1H NMR spectra.

NMR Spectroscopy Sample Preparation: In a typical NMR-spectroscopy-monitored dehydrogenation experiment, triglyme (12–16 g) and an amount of AB, which varied from 0.07 g (0.1 M) to

2.75 g (6.0 M), were mixed in a two-necked Schlenk flask. For suspensions ($[AB]_0$ from 16 to 23 M) the amount of AB was fixed at 2.0 g. The flask was connected to a reflux condenser and a silicon oil trap. The hydrogen release of the samples was measured volumetrically. About 15–20 samples were dynamically taken during each dehydrogenation experiment. Samples were taken by using a metal-free syringe with a polytetrafluoroethylene (PTFE) needle to prevent catalytic effects. The samples were filled into NMR spectroscopy tubes and diluted with TG from the 1:2 to the 1:5 ratio (according to their original concentration) to reduce signal broadening.

Pressure Measurements: The above-described AB/TG mixtures (1–23 M, 0.3–3.0 g) were isothermally decomposed in a Schlenk flask at temperatures that ranged from 70 to 110 °C. The vessel was connected to a reflux condenser and a 2 L gas tank equipped with pressure and temperature sensors. The pressure and temperature of the gas tank were constantly monitored during the experiments.

^{11}B NMR Spectroscopic Measurements: All samples were measured with a Bruker DPX 400 spectrometer (7.06 T) operating at 400 MHz for ^1H and 128 MHz for ^{11}B . ^{11}B shifts were referenced externally to $BF_3 \cdot Et_2O$ ($\delta = 0$ ppm).

Computation of Relative Peak Areas: Relative ^{11}B NMR spectroscopic peak areas were determined by fitting the corresponding peaks with the software PeakFit, which determined the value of their integrals and divided them by the ones of the complete spectrum (the latter representing the total boron content). The given error bars (when stated) reflect the influence of the integration borders of the signals in the case of overlapping peaks.

Acknowledgments

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Synthesis and Characterization of Nanocrystalline FeSb₂ for Thermoelectric Applications

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Keywords: Antimony / Iron / Nanostructures / Crystal growth / Thermoelectricity / Thermal conductivity

We report an ethanol-mediated surfactant-free solvothermal synthesis of phase-pure *Pnmm* FeSb₂ nanocrystals with an average size of 40 nm. The capping free growth of the nanocrystals resulted in the formation of inherent orthorhombic shapes. The nanocrystals were densified by spark plasma sintering to prepare a polycrystalline bulk material that consisted of 40–200 nm FeSb₂ nanocrystal domains (nanocomposite). Low-temperature Seebeck coefficient, resistivity, and thermal conductivity were measured on parallelepipeds cut from the densified specimen and compared to bulk

FeSb₂ prepared by a solid-state synthesis process. The FeSb₂ nanocomposite showed a large reduction in lattice thermal conductivity relative to the bulk due to significant grain-boundary phonon scattering. If one notes that the solution-phase synthesis of *Pnmm* FeSb₂ nanocrystals is accounted here for the first time and the low-temperature thermoelectric properties indicates a significant reduction in lattice thermal conductivity for this material, this work represents an important step towards optimizing thermoelectric properties for cooling applications.

Introduction

As research on thermoelectric (TE) materials with improved properties continues, interest in correlated electron semiconductors for TE applications has recently accelerated following the discovery of a colossal Seebeck coefficient (*S*) in FeSb₂ below room temperature.^[1–3] The electrical and magnetic properties revealed in FeSb₂ may have technological implications for TE refrigeration^[1–6] and spintronics.^[7–11] Since this discovery,^[1,2] research on single-crystal and bulk polycrystalline FeSb₂ has intensified.^[3–7,9] Although FeSb₂ single crystals possess huge *S* values at cryogenic temperatures, the thermoelectric performance is restricted due to a large lattice thermal conductivity (κ_L).^[1–3] Nanostructuring has been the most direct way of reducing thermal conductivity (κ) due to increased interface scattering of phonons at the grain boundaries, as demonstrated for many TE materials systems.^[12–14] Most recently, bulk FeSb₂ with spatially distributed Sb/InSb nanoinclusions have been synthesized by combining a solid-state reaction of the elements with spark plasma sintering (SPS).^[15] However, when nanoscale grains are of interest, solid-state approaches do not always allow for simple control of the size of the grains or inclusions. Chemical syntheses allow for processing the nanocrystals in a size-controlled and scalable manner, most useful in investigations of size-dependent TE properties.^[12,13,16–19] Herein we report on a simple, low-temperature solvothermal approach for the synthesis of FeSb₂ nanocrystals with space group *Pnmm* (no. 58), the

structure type of interest for TE applications, and the resulting TE properties after consolidation of the nanocrystals by employing SPS.

An investigation into nanostructured FeSb₂ has been mainly limited by the lack of a suitable preparative process. Nevertheless, there are a few reports on the synthesis of FeSb₂ nanocrystals by solution-based processes.^[20,21] Recently, the synthesis of FeSb₂ nanorods with *Pnn2* crystal structure by using surfactant molecules has been reported.^[21] However, to the best of our knowledge, the synthesis of *Pnmm* FeSb₂ nanocrystals has yet to be reported. We describe a bottom-up approach for obtaining bulk polycrystalline *Pnmm* FeSb₂ with nanoscale grains by means of a two-step process that involves the controlled synthesis of *Pnmm* FeSb₂ nanocrystals followed by consolidation into the polycrystalline form by SPS. Since the nanocrystals were synthesized without using any surfactant, we were able to omit the postsynthesis annealing step routinely undertaken in solution-based syntheses for removing surfactant ligands in nanocrystalline TE materials.^[12,22] The polycrystalline FeSb₂ with nanoscale domains exhibited substantially lower lattice thermal conductivity (κ_L) than the bulk. Low-temperature resistivity (ρ) and *S* were also investigated and compared to that of bulk FeSb₂.

Results and Discussion

Figure 1 (a) shows the indexed XRD pattern of the as-prepared FeSb₂ nanocrystals in comparison to the calculated XRD pattern for *Pnmm* FeSb₂. XRD analysis of polycrystalline FeSb₂ after consolidation of the nanocrystals by means of SPS suggests that the crystal structure is retained

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after densification. No other XRD-detectable impurity phases were present in the nanocrystals and in the densified specimen. Energy-dispersive X-ray spectroscopy (EDS) confirmed the formation of stoichiometric FeSb_2 . Figure 1 (b) shows a low-resolution TEM image of agglomerated FeSb_2 nanocrystals. The nanocrystals were nearly homogeneous in size (at 40 nm), polygonal in shape, and resembled bipyramidal forms. Orthorhombic crystal forms were preferred for the FeSb_2 nanocrystals presumably because no surfactant or template molecules were used in the reaction process to control the shape of the nanocrystals. Selected-area electron diffraction (SAED) patterns showed linear dot patterns (Figure 1, c), thus indicating that the FeSb_2 nanocrystals are single crystals. The SAED pattern also confirmed the d spacings of the major diffraction planes of $Pnmm$ FeSb_2 (not shown in the figure). The presence of twin diffraction spots in the SAED pattern (shown by arrows in Figure 1, c) are from lattice planes with the same diffraction angle, also indicated in Figure 1 (a). Figure 1d illustrates the lattice fringes of a FeSb_2 nanocrystal. The lattice fringe spacings correspond to the (111) planes of $Pnmm$ FeSb_2 . Hence from both XRD and HRTEM studies, we concluded that the FeSb_2 nanocrystals have crystallized in the $Pnmm$ space group. The absence of any planar defects and the distinct presence of uninterrupted lattice planes suggest that the FeSb_2 nanocrystals are highly crystalline. In addition, the shape of the FeSb_2 nanocrystals may be closely related to the crystallographic surfaces that enclose the nanocrystals.^[23] Surface energies are typically

higher for higher-symmetry planes, such as (110) and (100), and decrease for lower-symmetry planes such as (111).^[23] For a spherical nanocrystal, the surface always has the high-symmetry crystallographic planes, whereas the nanocrystal shape evolves more towards tetrahedrons when growth is along the (111) planes.^[23] Steplike edges (as observed in the inset of Figure 1, d) suggest that growth proceeded from these edges and ultimately evolved into bipyramidal structural forms. Figure 1 (e) shows a schematic diagram that depicts the reaction and growth mechanism for the formation of these FeSb_2 nanocrystals.

SPS densification (Thermal Technology LLC, 25-10) of the FeSb_2 nanocrystals was carried out at 100 MPa and 210 °C for 5 min. A density of 88% of the theoretical density was achieved after densification. After SPS, the grain size was in the range of 40–200 nm. To compare the TE properties of the polycrystalline FeSb_2 with nanoscale grains, henceforth referred to as a dimensional nanocomposite, a polycrystalline $Pnmm$ FeSb_2 bulk specimen of comparable density was prepared by reacting the elements to form FeSb_2 ^[24] followed by hot pressing at 320 °C and 150 MPa for 2 h.

Four-probe ρ , steady-state S (gradient sweep method), and κ measurements between 12 and 300 K were conducted on $2 \times 2 \times 5 \text{ mm}^3$ parallelepipeds in a custom radiation-shielded vacuum probe with uncertainties of 4, 6, and 8%, respectively, at 300 K.^[25] Room-temperature four-probe Hall measurements were conducted on $0.5 \times 2 \times 5 \text{ mm}^3$ parallelepipeds at multiple positive and negative magnetic

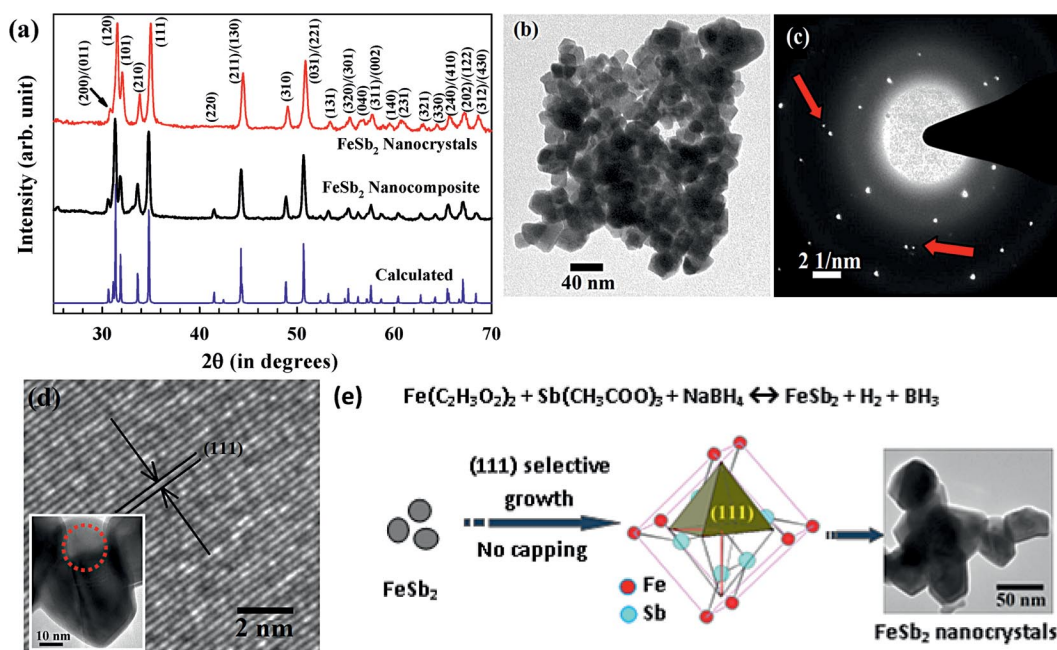


Figure 1. (a) Indexed powder XRD patterns of $Pnmm$ FeSb_2 nanocrystals synthesized by a low-temperature solvothermal process, polycrystalline FeSb_2 with nanoscale grains (nanocomposite) prepared by densifying the FeSb_2 nanocrystal by means of SPS, and the calculated powder pattern for $Pnmm$ FeSb_2 . (b) Low-resolution TEM image of an agglomeration of 40 nm orthorhombic $Pnmm$ FeSb_2 nanocrystals. (c) SAED pattern obtained from an individual $Pnmm$ FeSb_2 nanocrystal that shows the single-crystalline nature of the nanocrystals. Arrows indicate the presence of diffraction spots from concurring lattice planes. (d) Lattice fringe pattern obtained from a $Pnmm$ FeSb_2 nanocrystal (inset) with the (111) plane indexed. (e) Illustration of the reaction process: reduction of Fe and Sb precursors to form FeSb_2 followed by (111) growth of FeSb_2 nanocrystals.

fields up to 1 T to eliminate voltage probe misalignment effects by using a custom-built Hall measurement system with an uncertainty of 4%. In FeSb₂, the thermoelectric figure of merit (ZT) is degraded due to a large κ that is dominated by κ_L .^[1–7,15,26] We estimated κ_L by calculating the electronic contribution to the thermal conductivity (κ_e) using the Wiedemann–Franz relation $\kappa_e = L_0 T / \rho$, for which $L_0 = 2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ and ρ was measured as described above, and subtracting it from the measured κ ($\kappa_L = \kappa - \kappa_e$). Figure 2 shows the temperature dependence of κ_L for the two FeSb₂ specimens. The κ_L values for our bulk polycrystalline FeSb₂ are lower than that for single-crystal FeSb₂^[1] due to the relatively small grain size (with a grain-size distribution of <1 μm to 10 μm) as well as the porosity of the specimen; however, it exhibits a $1/T$ temperature dependence (Figure 2) typical of crystalline semiconductors dominated by phonon–phonon scattering. The FeSb₂ nanocomposite has smaller κ_L values than the bulk polycrystalline specimen with a very weak temperature dependence above 30 K. The nanoscale grains in the FeSb₂ nanocomposite (Figure 2, inset) results in this reduction in κ_L , with nearly an order-of-magnitude reduction in κ_L at low temperatures. From $\kappa_L = 1/3 C(v_s)l_p$, for which v_s is the sound velocity (3116 ms^{-1})^[1] and C is the specific heat,^[2] we estimate the room-temperature phonon mean-free path, l_p , in our bulk polycrystalline FeSb₂ (shown in open circles in Figure 3) to be 0.5 μm . This estimated l_p value is much larger than the average grain size of the FeSb₂ nanocomposite and is an indication of the effect of grain-boundary scattering. This effect is significant at lower temperatures.

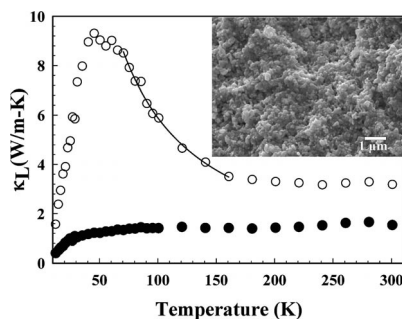


Figure 2. κ_L of the FeSb₂ nanocomposite (solid circle) and bulk FeSb₂ (open circle). The line of $1/T$ dependence (solid line) is indicative of phonon–phonon scattering. The inset shows an SEM image of a fractured surface of the FeSb₂ nanocomposite.

Figure 3 shows the temperature-dependent S for the two specimens. Both have positive S values at room temperature, 26.1 and 20.6 $\mu\text{V K}^{-1}$ for the nanocomposite and bulk FeSb₂, respectively. These values are in general agreement with those previously reported on polycrystalline FeSb₂ specimens.^[2,15] The temperature dependence of S for both specimens is similar, with a maximum (S_{max}) of $-64 \mu\text{V K}^{-1}$ at 35 K for the nanocomposite and $S_{\text{max}} = -181 \mu\text{V K}^{-1}$ at 25 K for our bulk specimen. The shift to higher temperature as well as the smaller absolute S_{max} value for the nanocomposite may be attributed to the large carrier concentra-

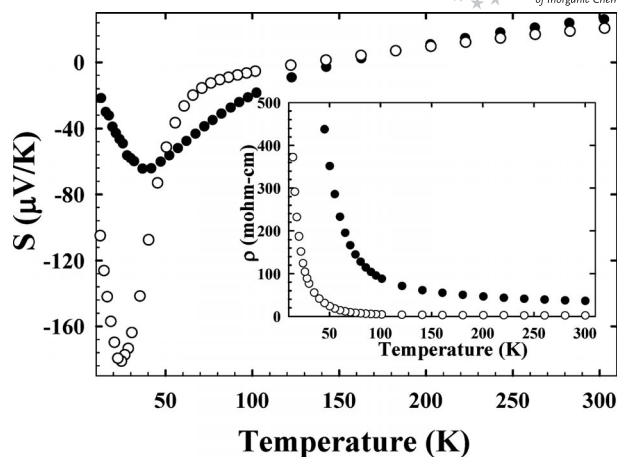


Figure 3. Temperature dependence of S and ρ (inset) for the FeSb₂ nanocomposite (solid circle) and bulk FeSb₂ (open circle).

tion ($3.2 \times 10^{20} \text{ cm}^{-3}$ at 300 K) and very low mobility ($0.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K) in the nanocomposite compared to the FeSb₂ single crystals for which a mobility as high as around $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed.^[27] Studies on oriented FeSb₂ thin films revealed similar suppression of S_{max} due to low mobility of charge carriers.^[28–30] It was also observed previously that the position and magnitude of S_{max} is very sensitive to doping and charge-carrier concentration for FeSb₂ single crystals^[2] as well as for FeSi.^[31] In addition, charge-carrier scattering due to an increased number of grain boundaries in the FeSb₂ nanocomposite may play a role in reducing the potential across the grains, thereby reducing the absolute value of S_{max} .^[27–30] The temperature dependence of ρ is shown in the inset of Figure 3. In both specimens, ρ increases as temperature decreases, a temperature dependence that is similar to that observed previously.^[1–3,10,11,15] Although porosity will greatly affect ρ , the difference in ρ for the two specimens is also ascribed to the large difference in average grain size between the two specimens.

Conclusion

In conclusion, phase-pure *Pnnm* FeSb₂ nanocrystals with an average size of 40 nm have been prepared by an ethanol-mediated, low-temperature solvothermal process. No template or capping chemical was used in processing these nanocrystals, thereby allowing the crystals to grow in their inherent orthorhombic symmetry. SPS densification of only FeSb₂ nanocrystals resulted in the preparation of polycrystalline bulk FeSb₂ with nanoscale grains. The FeSb₂ nanocomposite showed a significant reduction in κ_L relative to that of a micron-grain-sized bulk specimen of similar density. The magnitude and temperature dependence of κ_L of the FeSb₂ nanocomposite suggests significant grain-boundary scattering. In spite of this low κ_L , the high ρ values results in a low thermoelectric figure of merit ZT ($= S^2 / \rho \kappa T$) for the FeSb₂ nanocomposite. However, these results represent a potential approach towards reducing κ_L signifi-

cantly at low temperatures. If we note that doping of TE materials can readily be accomplished by chemical synthetic approaches,^[17,18] and the fact that SPS densification can provide dense polycrystalline TE materials with nanoscale grains or inclusions,^[14–18] this work represents a new direction towards enhanced TE properties of FeSb₂. Further study into doping of the FeSb₂ nanocrystals before densification is warranted. We expect this method to be generally applicable to other materials systems of this type, such as FeSi, and that it can be employed for the optimization of both thermal and electrical properties for TE applications.

Experimental Section

General: *Pnnm* FeSb₂ nanocrystals were synthesized by using a surfactant and template-free, ethanol-mediated solvothermal process. Analytical grades of iron(II) acetate [Fe(CH₃COO)₂] and antimony(III) acetate [Sb(CH₃COO)₃] were used as the Fe and Sb sources, respectively. An excess molar quantity of Fe(CH₃COO)₂ was always maintained in the solution because of the large difference in the reduction potential between Fe⁺² (Fe⁺² + 2e[−] ↔ Fe, −0.409 V) and Sb⁺³ (Sb⁺³ + 3e[−] ↔ Sb, 0.15 V). In a typical synthesis, Fe(CH₃COO)₂ (2 mmol) and Sb(CH₃COO)₃ (2 mmol) were dissolved in anhydrous ethanol (40 mL, 80% volume of the custom-made Teflon[®] reactor). NaBH₄ (3 mmol) was added to the solution as a reducing agent. The entire solution was poured inside a custom-made Teflon reactor and tightly sealed. The Teflon reactor was then inserted into a custom-made stainless-steel chamber and maintained at 220 °C for 16 h. At the end of the reaction, the chamber was gradually cooled to room temperature. The deep black precipitation (FeSb₂) at the bottom of the Teflon chamber was collected after washing first with HCl solution (0.1 M), then several times with distilled water and ACS-grade alcohol. Finally, the washed precipitate was dried in vacuo for 6 h and collected for characterization. This process yielded approximately half a gram of FeSb₂ nanocrystals. The synthesized FeSb₂ nanocrystals were characterized by X-ray diffraction (XRD, Bruker AXS D8 with Lynx Eye position-sensitive detector), energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments INCAX sight), and transmission electron microscopy (TEM, FEI Tecnai F20 S-Twin TEM). For TEM analysis, a very dilute dispersion of FeSb₂ nanocrystals in ethanol was drop cast onto carbon-coated 400 mesh copper grids.

Acknowledgments

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Photocatalytic H₂ Production with a Rhenium/Cobalt System in Water under Acidic Conditions

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Keywords: Hydrogen / Photochemistry / Green chemistry / Cobalt / Homogeneous catalysis

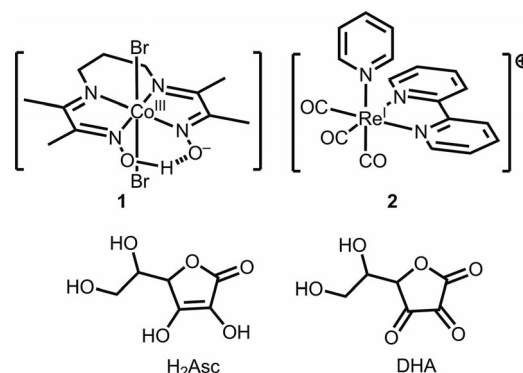
In photocatalytic H₂ formation, tertiary amines are commonly used as sacrificial electron donors, thereby limiting the pH range for studies in water and the concentration of free protons. We found that ascorbate rapidly reductively quenches the excited state of [Re(CO)₃(bipy)(py)]⁺ (bpy = 2,2'-bipyridyl; py = pyridine). In combination with the water reduction catalyst (WRC) [Co{(DO)(DOH)pn}Br₂] [(DO)(DOH)pn =

N²,N²'-propanediylbis(2,3-butanedione 2-imine 3-oxime)], this system produces H₂ upon irradiation with light under acidic conditions (pH range 2–6) and with significantly enhanced turnover numbers. Furthermore, we observed that, in contrast to similar systems with tertiary amines, oxidized ascorbate (dehydroascorbic acid) is slowly re-reduced during the course of photocatalysis.

Introduction

Hydrogen is an important basic fuel or fuel intermediate for securing the energy supply of the future.^[1,2] Whereas H₂ technology is very well developed, the world's consumption of H₂ widely relies on H₂ generated from fossil fuels. Photocatalytically generated H₂ from H₂O would be a clean and inexhaustible source of H₂. Full water-splitting systems based on homogeneous catalysis, which would offer the advantage of tunability of the single catalysts, have not been demonstrated yet. It is therefore feasible to study water oxidation and reduction as separate half-reactions. Extensive studies for reducing water by light have been published, most of them in organic solvents or in mixtures with H₂O, and which employ cobalt-based water reduction catalysts (WRCs) and platinum element photosensitizers or organic dyes.^[3–21] Since water reduction must ultimately be coupled with water oxidation, the solvent of choice for a practicable process is water. We recently reported a system that consisted of the WRC [Co^{III}Br₂{(DO)(DOH)pn}] (1), which has been introduced in the literature,^[22] and the photosensitizer (PS) [Re(CO)₃(py)(bipy)]⁺ (2; bpy = 2,2'-bipyridyl; py = pyridine) (Scheme 1), which produced H₂ upon irradiation with visible light by using triethanolamine (TEOA) as sacrificial electron donor in pure water. Even though this is the highest turnover number (TON) (17 H₂/Co) reported so far for H₂O, it is still very low compared to similar systems in organic solvents. Furthermore, TEOA limited the pH range to alkaline conditions (≥ 7.5).^[23] Under acidic condi-

tions, Co^{III}–H can be protonated more rapidly. This, in turn, stabilizes the cobalt cycle and increases rate and TONs.^[11,24] Therefore, we chose the ascorbate buffer system Hasc[–]/H₂asc to be able to work under acidic conditions (pH range 2–5). Recently, an elegant study showed photocatalytic H₂ formation at low pH with a ruthenium/rhodium or ruthenium/iridium system and with ascorbate (Hasc[–]) as e[–] donor.^[25] Hasc[–] has previously been used as reductive quencher of excited [Ru(bipy)₃]^{2+*}-type complexes but not yet with Re-based photosensitizers.^[26–33]



Scheme 1. Schematic drawing of WRC 1, PS 2, ascorbic acid (H₂Asc), and dehydroascorbic acid (DHA) in its unhydrated form.

Results and Discussion

Upon addition of [Co^{III}Br₂{(DO)(DOH)pn}] to a solution of Hasc[–]/H₂asc in water, the color changed immediately from essentially colorless to red, thus indicating a chemical reduction of Co^{III} → Co^{II} and exchange of the axial bromido ligands with water. The complex [Co^{II}(OH)₂–

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$\{(\text{DO})(\text{DOH})\text{pn}\}^+$ exhibits a characteristic absorption band at 507 nm.^[34] Spectro-electrochemical measurements (Figure 1, left) are in agreement with this assignment. The UV/Vis spectrum after electrochemical reduction was identical to the one found after reduction with Hasc^- . Stopped-flow experiments showed rapid reduction of $[\text{Co}^{\text{III}}(\text{OH}_2)_2\{(\text{DO})(\text{DOH})\text{pn}\}]^{2+}$ at pH = 4.02 (Figure 1, right). By applying a pre-equilibrium model, and assuming the rapid and reversible formation of an encounter complex and subsequent electron transfer from Hasc^- to $[\text{Co}^{\text{III}}(\text{OH}_2)_2\{(\text{DO})(\text{DOH})\text{pn}\}]^{2+}$, the rate constant for the reduction was determined to be $k_2 = 0.15 \text{ s}^{-1}$.

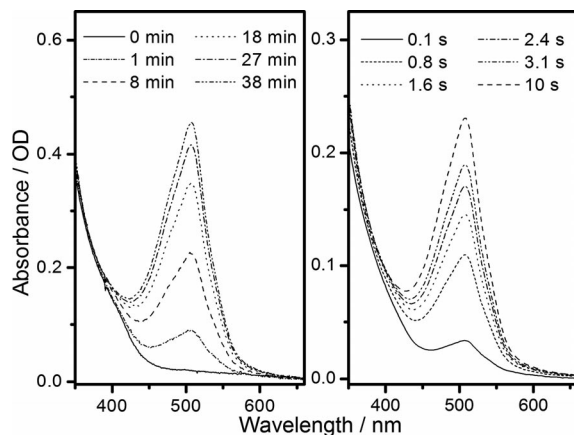


Figure 1. Left: UV/Vis spectra during bulk electrolysis of a solution containing 0.1 mM $[\text{Co}^{\text{III}}(\text{OH}_2)_2\{(\text{DO})(\text{DOH})\text{pn}\}](\text{Tf}_3\text{SO})_2$ (Tf_3SO^- = trifluoromethanesulfonate anion) and 0.1 M KNO_3 at -200 mV relative to Ag/AgCl (1 cm path length). Right: Stopped-flow UV/Vis spectra of a solution containing 0.2 mM $[\text{Co}^{\text{III}}(\text{OH}_2)_2\{(\text{DO})(\text{DOH})\text{pn}\}](\text{Tf}_3\text{SO})_2$ mixed with an equal volume of a solution containing 0.5 M NaHasc/0.5 M H_2asc (0.5 cm path length).

Irradiation of an aqueous solution that contained 0.5 mM of WRC **1**, 0.03 mM of PS **2**, and 0.5/0.5 M $\text{Hasc}^-/\text{H}_2\text{asc}$ (pH = 4.1) with a 380 nm LED light source under argon led to a total production of about 10.9 mL (0.44 mmol) H_2 , which corresponded to turnover numbers of 90 H_2/Co and 3000 H/Re after 30 h. The quantum yield was determined to be 20% at a photon flux of $4.8 \times 10^{-9} \text{ mol s}^{-1}$ (2 mL sample, 0.5 mM **1**, 0.5 mM **2**, and 0.5/0.5 M $\text{Hasc}^-/\text{H}_2\text{asc}$). In the absence of one of the components or without irradiation, no hydrogen was detected. A series of experiments at the same concentrations but at different pH values is shown in Figure 2. Turnover numbers peaked close to the pK_a of H_2asc (4.10).^[35] The decreasing concentration of the reductive quencher $[\text{Hasc}^-]$ at low pH values is likely to be responsible for the reduced rates at $\text{pH} < \text{pK}_a$. The sudden rate decrease at $\text{pH} > \text{pK}_a$ is not understood, since the reaction cycle of the photosensitizer is not impeded by a higher pH (Figure 3, blue trace), and the WRC can in principle operate even in alkaline solutions.^[23] A similar pH-dependence profile was observed for TEOA in the alkaline branch of the pH scale. TONs peaked at about the pK_a of HTEOA^+ and decreased at lower and higher pH values.^[23] In comparison, TONs with Hasc^- are about one order of magnitude higher than in the TEOA system. We attribute this

increase in TONs to efficient protonation of a $\{\text{Co}^{\text{III}}\text{-H}\}$ intermediate and release of H_2 .^[11,24] This reaction favorably competes with the decomposition of the WRC, probably caused by metal-to-ligand hydride transfer.^[36]

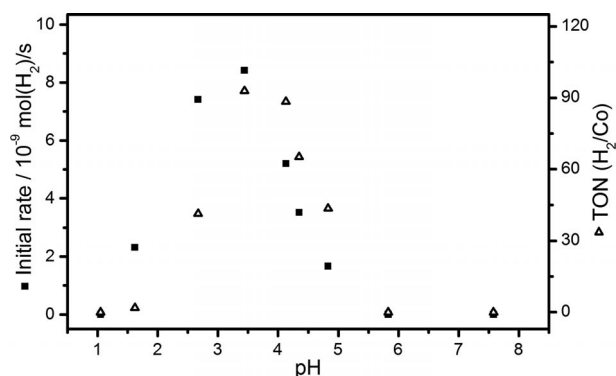


Figure 2. Initial rates and TONs for irradiated solutions (380 nm, 10 mL) containing 0.5 mM **1** and 0.03 mM **2** with 1 M total concentration of ascorbic acid at different pH values.

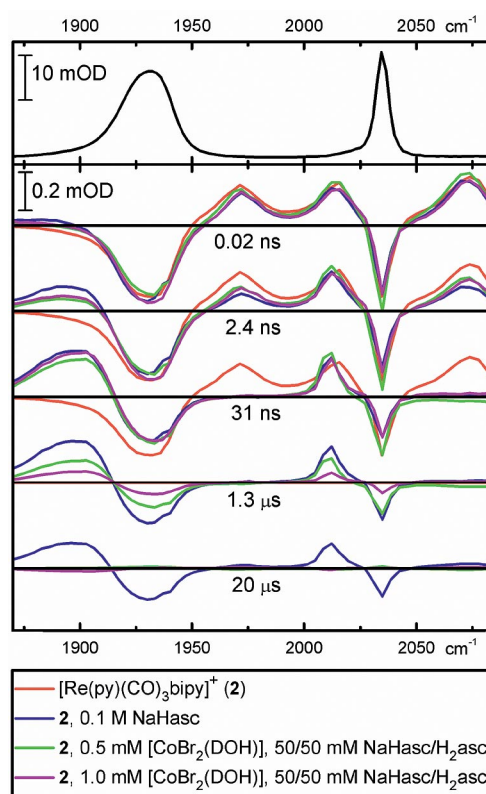


Figure 3. Top: FTIR spectrum of the ground state of **2** in D_2O showing the characteristic $\nu_{\text{CO, sym}}$ at 2034 cm^{-1} and overlapping $2 \times \nu_{\text{CO, asym}}$ at 1932 cm^{-1} . Bottom: Difference spectra in D_2O after 400 nm excitation pulse at given delays. Negative bands are due to depopulation of the ground state of **2**, positive bands are due to the population of new transient species: $^3\text{MLCT } 2^*$ ($\nu_{\text{CO, sym}}$ at 2070 cm^{-1} and $2 \times \nu_{\text{CO, asym}}$ at 1932 and 1971 cm^{-1}) and 2^- ($\nu_{\text{CO, sym}}$ at 1932 cm^{-1} and overlapping $2 \times \nu_{\text{CO, asym}}$ at 1895 cm^{-1}). Note that the blue spectra were taken with pure sodium ascorbate as quencher, thus causing the pD to be 9.2. In case of the green and pink spectra, an equimolar mixture of ascorbic acid and sodium ascorbate was used to buffer the pD at 4.6.

Time-resolved UV-pump/IR-probe spectroscopy was used to monitor the catalytic cycle of the PS, which is initiated by excitation of **2** to the ³MLCT state **2*** with a lifetime of 0.20 μs (Figure 3, orange spectra). Compound **2*** is reductively quenched by Hasc[−] within the first tens of nanoseconds to yield the reduced PS **2[−]** and monooxidized, deprotonated asc[−] (Figure 3, blue, green, and red spectra). The latter disproportionates rapidly, dependent on the pH, to H₂asc and DHA.^[37,38] A bimolecular quenching rate of $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined from concentration-dependent measurements. Figure 4 shows an exemplary set of kinetic traces obtained from one single measurement. They can be modeled by a global, biexponential fit (black lines), which accounts for quenching and subsequent electron transfer. The positive signals directly after excitation (1971, 2016, and 2070 cm^{−1}) show the formation of **2***. At 1932 and 2034 cm^{−1} the bleach of the ground-state bands of **2** is observed. The first process after excitation, which is fit with a time constant of 7.6 ns, corresponds to quenching of **2*** by Hasc[−]. As a result, the signals of **2[−]** at 1895 and 2012 cm^{−1} increase. At the same time, the bleach intensities of the ground state of **2** decrease since only a fraction of the quenching events result in electron transfer rather than undesired energy transfer, which simply regenerates **2**. This cage-escape yield of reductive quenching, Φ_{red} , was about 0.6, as estimated from a comparison of the bleach of the ground state directly after excitation and when quenching was complete. The lifetime of **2*** was taken into account to correct for deactivation of **2*** → **2** not caused by quenching with Hasc[−]. Experiments with [Co^{III}(dmg)(dmgH)(py)₂] (dmgH₂ = dimethylglyoxime) and no electron donor showed fast energy-transfer quenching exclusively, which takes place with **1** as well.^[23] Since the concentration of **1** was much lower than [Hasc[−]], and experiments in the presence and absence of **1** gave identical rates for the quenching of **2***, a potential influence on the quenching process by **1** could be excluded within the accuracy of the measurement.

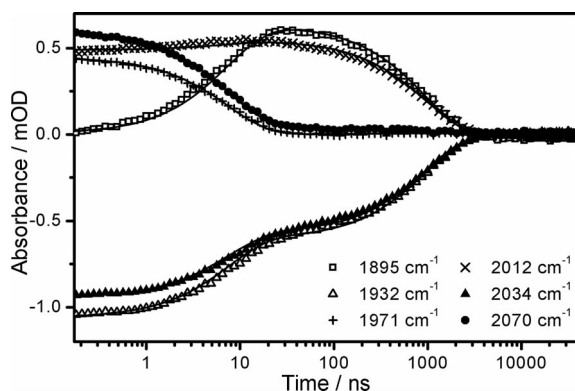


Figure 4. Kinetic traces at selected wavenumbers after 400 nm excitation (sample: 0.5 mM **2**, 1 mM **1**, 0.05 M NaHasc/0.05 M H₂asc in D₂O). The traces were fit with a global, biexponential fit (black lines), thus giving the time constants for quenching (7.6 ns) and electron transfer (0.96 μs).

After reductive quenching of **2*** → **2[−]**, electron transfer from **2[−]** to [Co^{II}(H₂O)₂{(DO)(DOH)pn}] occurred with a rate of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3, green and red spectra; Figure 4; and Figure 5), which corresponds to transfer times of a few microseconds for the millimolar concentrations of the cobalt catalyst. In the example shown in Figure 4, the transfer can be fit by an exponential with the time constant of 0.96 μs. With this process, all signals including the bleaches of the ground-state bands of **2** decay completely, which indicates full regeneration of **2**. It should be noted here that the electron transfer in the TEOA system occurred from Co^{III} → Co^{II} ($1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^[23] In the Hasc[−] system, the transfer is from Co^{II} → Co^I since the WRC **1** is quantitatively reduced in the presence of Hasc[−]. However, the rates in both cases are diffusion-limited and therefore identical.

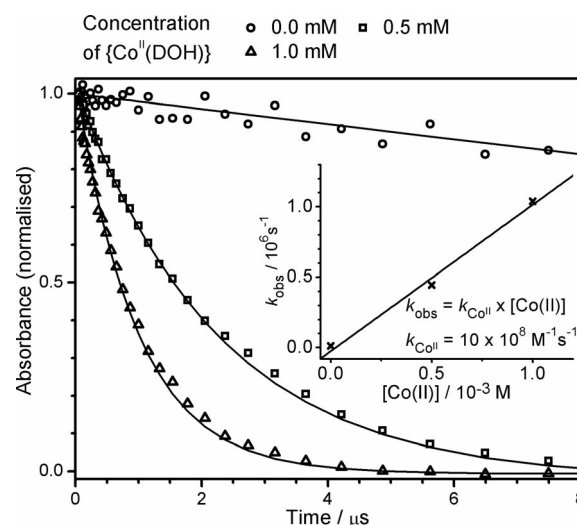


Figure 5. Relative concentration of **2[−]** upon 400 nm excitation at 0.0 mM (circles), 0.5 mM (squares), and 1.0 mM (triangles) {Co^{II}(DOH)} (0.5 mM **2**, 0.05 M NaHasc/0.05 M H₂asc in D₂O). Inset: plot of k_{obs} versus {Co^{II}(DOH)} according to a pseudo-first-order rate law, thus yielding a bimolecular electron-transfer rate of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For 0.0 mM {Co^{II}(DOH)}, the beginning of the electron back-transfer from **2[−]** to DHA is visible.

A striking difference to TEOA as quencher is the behavior of the photosensitizer **2** upon irradiation in the presence of Hasc[−] but in the absence of an electron-accepting WRC. In case of TEOA, **2[−]** has a lifetime beyond the microsecond timescale (Figure 6, circles), but eventually degrades to [Re(OH)(bipy)(CO)₃], an essentially inactive species for photocatalysis in water.^[23] In the Hasc[−]/H₂asc system, even prolonged irradiation did not lead to significant formation of this species or to other decomposition products. The above-mentioned pump/probe experiments already revealed that the signal of **2[−]** is not constant but rather slowly decreasing on the timescale of 20 μs (Figure 3, blue spectra; Figure 5, circles). Therefore, step-scan FTIR spectroscopy was used to cover longer measurement times. In a solution of 0.25/0.25 M Hasc[−]/H₂asc as reductive quencher, the bleach of the ground state of **2** recovered with a time constant of approximately 90 μs (Figure 6, squares). In contrast to oxidized

TEOA, the ascorbate radical and DHA (the disproportionation product of $\text{asc}^{\cdot-}$) are potential electron acceptors that can reoxidize $2^- \rightarrow 2$. To support the electron back-transfer hypothesis from $2^- \rightarrow \text{DHA}$, additional DHA was added to a solution that contained **2** and $\text{Hasc}^-/\text{H}_2\text{asc}$. Upon irradiation, the decay of 2^- was accelerated by a factor of around 10 (Figure 6, triangles), thereby implying that Hasc^-/DHA acts as a reversible electron-donor/-acceptor couple in our system.

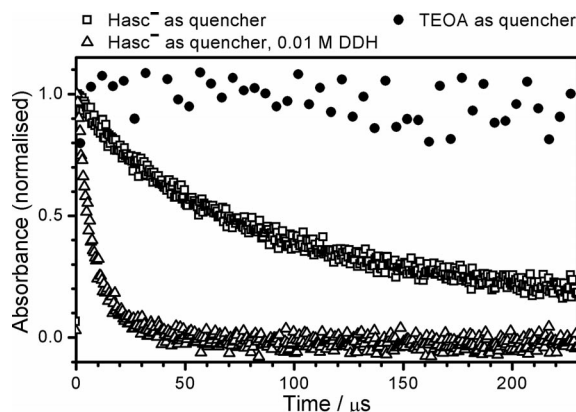
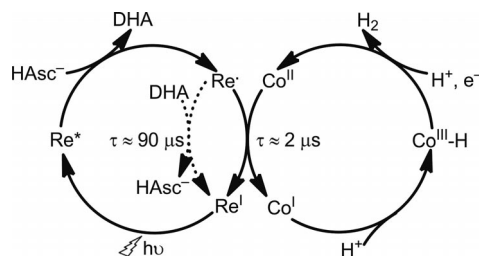


Figure 6. Decay of 2^- after 355 nm excitation/reductive quenching in aqueous (D_2O) solution of 0.25/0.25 M $\text{NaHasc}/\text{H}_2\text{Asc}$ without (squares) and with (triangles) addition of 0.01 M DHA, as measured by the integrated intensity of the absorption bands of 2^- in step-scan time-resolved FTIR experiments. The black dots show the stability of 2^- on the timescale of 150 μs in a solution of 0.1/0.9 M $(\text{HTEOA})^+\text{BF}_4^-/\text{TEOA}$ in D_2O . Data quality is limited due to the decomposition products of 2^- , which precipitate in the flow cell, thus preventing longer averaging.

Thus, as the H_2 formation reaction proceeds and more DHA is produced, electron transfer to DHA and WRC **1** (and thus H_2 formation) start to compete with each other (Scheme 2). This finally leads to a “short cut,” which terminates the H_2 -formation process. To corroborate this hypothesis, H_2 production in the presence of added DHA was investigated. Under our standard experimental conditions, H_2 formation ceased after the generation of about 0.44 mmol of H_2 from 10 mL of the reaction solution and, accordingly, the formation of the same amount of DHA (44 mM). As shown in Figure 7, addition of DHA led to a linear decrease of TON_{Co} (H_2/Co). With no additional DHA, the maximum TON_{Co} was achieved, whereas the addition of 10% DHA (relative to $[\text{Hasc}^-]$) reduced TON_{Co} to around 40, thereby supporting the hypothesis of an electron back-transfer from 2^- to DHA being performance-limiting.

It should be noted here that a fresh standard reaction solution (0.5 mM **1**, 30 μM **2**, 0.5/0.5 M $\text{NaHasc}/\text{H}_2\text{Asc}$) with 50 mM DHA still produced small amounts of H_2 , thus indicating that reduction of DHA is not the only process that limits long-term performance. Decomposition of WRC **1** during photocatalysis still needs to be considered (although **1** itself is photostable in aqueous solution). This assumption is in agreement with experiments at different concentrations of **1** (Figure 8). Apart from higher initial rates at lower WRC concentrations, which are attributed to the absorp-



Scheme 2. Solid lines: schematic representation of the catalytic cycle leading to H_2 formation. Dashed lines: electron back-transfer to form $\text{asc}^{\cdot-}$, followed by disproportionation of the radical. Decay times of 2^- (representing the electron transfer) are given as measured in absence (ca. 90 μs) and presence (ca. 2 μs) of 0.5 mM **1** at the beginning of catalysis.

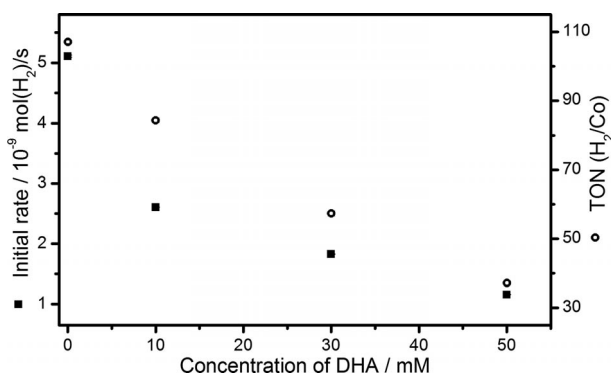


Figure 7. Initial rates and TONs in **1** after irradiation of a solution (380 nm, 10 mL) containing 0.5 mM **1**, 30 μM **2** and 0.5/0.5 M $\text{NaHasc}/\text{H}_2\text{Asc}$ with different amounts of DHA.

tion of light by **1**, the total amount of H_2 increased linearly with increasing cobalt catalyst concentration. TON_{Co} (H_2/Co), however, did not improve. Increased WRC loadings therefore allow production of larger quantities of H_2 , since the ratio between total amounts of produced DHA and the catalyst concentrations is constant. At higher catalyst con-

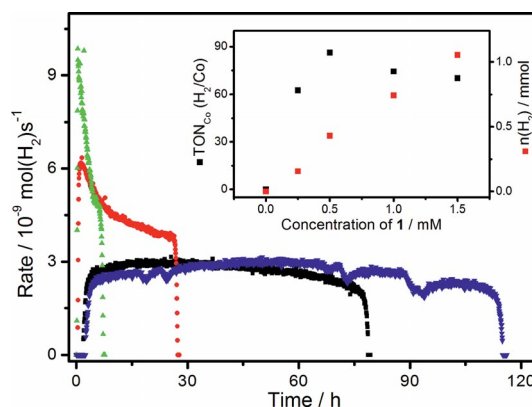


Figure 8. Rate profiles of H_2 -evolution measurement for irradiated aqueous solutions (380 nm, 10 mL) containing 30 μM **2**, 0.5/0.5 M $\text{NaHasc}/\text{H}_2\text{asc}$, and different concentrations of **1** (0.25 mM, green; 0.5 mM, red; 1 mM, black; 1.5 mM, blue). Inset: corresponding TON_{Co} (black squares) and total amount of produced H_2 (red squares) for the same series of experiments.

centrations, the reaction can tolerate higher concentrations of DHA yet still produce hydrogen. Compound **1**, however, is only capable of a limited number of TONs before deactivation.

Conclusion

We present in this study the first rhenium/cobalt-based photocatalytic H₂-formation system in pure water under acidic conditions. Compared to the same system in water under alkaline conditions, TONs_{Co} increased by one order of magnitude. The performance of this Re/Co system in water is still lower than for similar systems in organic solvents. However, this study shows that efficient hydrogen evolution from aqueous media is in principle possible. An important finding in this system is the reversibility of the Hasc[−]/DHA electron-donor/-acceptor couple. Oxidized ascorbate can be reduced, thus giving rise to a slow reoxidation of **2**[−], which prevents decomposition of the photosensitizer in the absence of a WRC and terminates the production of H₂ upon accumulation of DHA. The experimental results of this study also indicate that the stability of the WRC is still a major issue with regards to the long-term stability of homogeneous H₂ formation.

Experimental Section

Materials: Complexes **1** and **2** were synthesized according to literature procedures.^[23,39] Sodium ascorbate, dehydroascorbate, and D₂O were purchased from Sigma Aldrich, ascorbic acid from Acros Organics. All commercial chemicals were used without further purification. Water was doubly distilled before use.

H₂-Evolution Measurements: Gas chromatograms were recorded with a Varian CP-3800 gas chromatograph by using argon as carrier gas with a 3 m × 2 mm packed molecular sieves 13X 80–100 column. Automated measurements were performed as described previously.^[40]

Sample Preparation (Standard Experiment): Compounds **2** (150 μL 2 mM) and **1** (2.290 mg) were added from a stock solution to a freshly prepared aqueous solution (7 mL) of Hasc[−] (0.5 M) and H₂asc (0.5 M). The solution was filled up to 10 mL and degassed directly at the GC before beginning the irradiation. Depending on the type of experiment, DHA was added, or the ratio between Hasc[−] and H₂asc and the amount of **1** were varied.

Stopped-Flow Measurements: Kinetic studies were performed with an Applied Photophysics SX20 UV/Vis stopped-flow spectrometer. Equal volumes of degassed solutions of 1:1 mixtures of Hasc[−]/H₂asc at different concentrations (100 mM to 500 mM in total) and [Co^{III}(OH₂)₂(DO)(DOH)pn](Tf₃SO[−])₂ (0.2 M; Tf₃SO[−] = trifluoromethanesulfonate anion) were injected simultaneously into the UV chamber of the machine, and time-dependent UV/Vis spectra were recorded. Signal evolution at 507 nm was used to determine the initial rates (*v*) for the different concentrations of the reducing agent. Linear fit through the points of a plot of 1/*v* against 1/Hasc[−], following the standard pre-equilibrium methods, gave the resulting *k*₂.

UV-Pump/IR-Probe Spectroscopy: The setup consisted of two synchronized Ti:sapphire-oscillator/regenerative amplifier femtose-

cond laser systems and a two-stage BBO optical parametric amplifier (OPA). The overall system and its key components have been described in detail previously.^[23,41,42] This setup provided a 400 nm pump pulse (ca. 1.3 μJ) and a broadband mid-infrared probe pulse with a variable time delay from 15 ps to 20 μs. Pump and probe pulses were focused into a 100 μm sample cell with a spot size of around 200 μm in diameter, whereas the polarizations were set to a relative angle of 54.7° to allow for direct measurement of the anisotropy free magic angle signal. To ensure efficient exchange of the excited volume, the sample was pumped rapidly by a peristaltic pump to a small sealed reservoir (*V* ≈ 3 mL). The pressurized flow of the reservoir transferred the sample through the flow cell and finally back to the sample tank, which was protected from light. To exclude any oxygen, the sample solution was purged with argon for at least 60 min before and during measurements. During the course of a measurement, sample degradation remained negligibly small (< 5%), which was checked by means of HPLC analysis before and afterwards.

Step-Scan FTIR Spectroscopy: For time-resolved step-scan infrared spectroscopy, a setup that consisted of an FTIR spectrometer (Bruker Vertex 80V) equipped with a photovoltaic MCT detector and a frequency-tripled Nd:YAG laser was used. The latter generates pulses of around 150 μJ/< 10 ns at 355 nm with a repetition rate of 10 Hz used for sample excitation (spot size 1.7 mm diameter, 50 μm sample thickness). The nominal time resolution that can be reached with this setup is about 100 ns. All samples were handled as described in the section on UV-pump/IR-probe spectroscopy.

Acknowledgments

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Multistate Redox-Active Metalated Triarylamines

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trans-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(C $\equiv$ C-4-C₆H₄NPh₂)-(dppe)₂] (**4**; dppe = 1,2-bis(diphenylphosphanyl)ethane) and *trans,trans,trans*-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(dppe)₂-(C $\equiv$ C-4-C₆H₄)₃N] (**7**) have been synthesized from *trans*-[Ru(C $\equiv$ C-4-C₆H₄NPh₂)Cl(dppe)₂] (**3**) and *trans,trans,trans*-[(dppe)₂ClRu(C $\equiv$ C-4-C₆H₄)₃N] (**6**), respectively, and the identities of *trans*-[Ru(C $\equiv$ CH-4-C₆H₄NPh₂)Cl(dppe)₂][PF₆] (**2**, precursor to **3**), **3**, and **4** have been confirmed crystallographically. Chemical oxidation of **4** and **7** afforded the isolable mixed-valence species **4**[PF₆] and **7**[PF₆]₃. The CV of **4** reveals sequential loss of three electrons in fully reversible oxidation steps, whereas the CV of **7** shows five reversible redox waves; in contrast, oxidation of the precursor amines

HC $\equiv$ C-4-C₆H₄NPh₂ and (HC $\equiv$ C-4-C₆H₄)₃N are irreversible processes. All oxidation processes afford reversible changes in the linear optical properties. Complementary time-dependent density functional theory (TD-DFT) studies suggest that the initial oxidation process for **4** and **7** is iron-centered and is followed by one (for **4**) or three (for **7**) ruthenium-centered oxidations. The final reversible oxidation is assigned by TD-DFT as delocalized along the metalla-ethynylarylamine moiety. The intense optical changes consequent on reversible oxidation, together with their charge-transfer character, suggest that **4** and **7** have potential as nonlinear as well as linear optical multistate switches.

Introduction

Unsaturated organometallics can possess greater non-linear optical (NLO) activity than purely organic compounds of similar size.^[1–3] In addition, redox-active carbon-rich organometallic architectures hold great promise as switchable NLO-active compounds, particularly when the oxidized states are low-lying in energy.^[4] One reason is because oxidation of such compounds can “switch on” absorptions at low energy, thus significantly affecting the third-order NLO behavior.^[5–9] We have reported carbon-rich organometallics with three accessible redox states as possible multistate linear optical and NLO switches; in particular, we described the introduction of [(η^5 -C₅Me₅)(dppe)-Fe(C $\equiv$ C-4-C₆H₄C $\equiv$ C)Ru(dppe)₂] [dppe = 1,2-bis(diphenylphosphanyl)ethane] fragments into both linear and three-fold symmetric branched arylenethynylene architectures; the heterodinuclear fragment permits switching between three states.^[10,11] As a continuation of these studies, we now report (i) replacement of the organoiron [Fe(dppe)(η^5 -C₅Me₅)] fragment by the [Fe(η^5 -C₅H₅)(η^5 -C₅H₄-)] moiety,

the ferrocene and ferrocenium units being considerably more air-stable than the aforementioned [Fe^{II}] and [Fe^{III}] fragments, and (ii) the use of a triphenylamine group as a central core in a threefold symmetric star. By using these fragments, new carbon-rich di- and hexanuclear compounds can be isolated that can be reversibly switched between three and five redox states, respectively.

Results and Discussion

Synthesis of the desired complexes was accomplished by using terminal alkyne activation by ruthenium complexes,^[12,13] thereby providing selective formation of vinylidene complexes that are the key intermediates for the formation of mono-alkynyl (by deprotonation with base) and unsymmetric bis-alkynyl complexes (by introduction of a second alkynyl moiety at the ruthenium center of the mono-alkynyl complex). The 16-electron species [RuCl(dppe)₂][PF₆]^[14] was generated from *cis*-[RuCl₂(dppe)₂]^[15] (**1**) by chloride abstraction using NaPF₆ and subsequently treated with 4-ethynyl-*N,N*-diphenylaniline to form the vinylidene complex *trans*-[Ru(C $\equiv$ CH-4-C₆H₄NPh₂)Cl(dppe)₂][PF₆] (**2**, Scheme 1). Deprotonation of **2** by using triethylamine then affords the mono-alkynyl complex *trans*-[Ru(C $\equiv$ C-4-C₆H₄NPh₂)Cl(dppe)₂] (**3**), previously prepared in similar yield by direct treatment of 4-ethynyl-*N,N*-diphenylaniline with **1**, without isolation of the intermediate vinylidene complex.^[16] Substitution of the remaining chlorido ligand in **3** with ethynylferrocene in the presence of NaPF₆/NEt₃

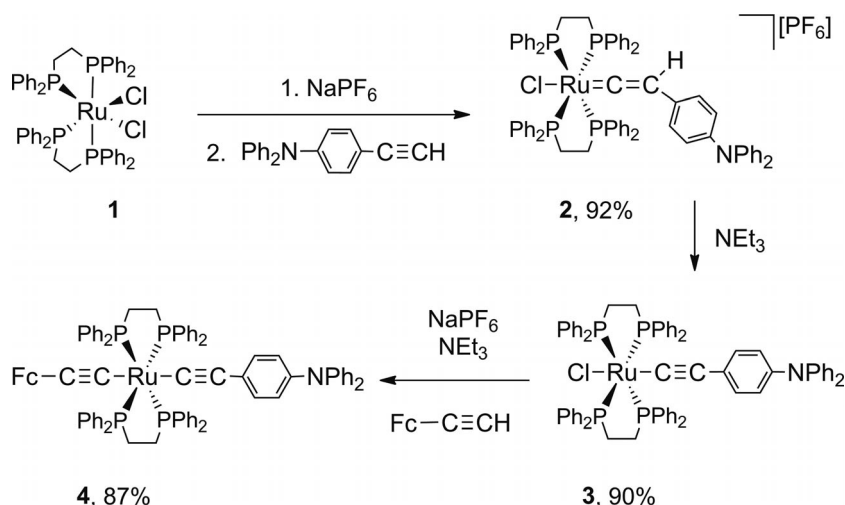
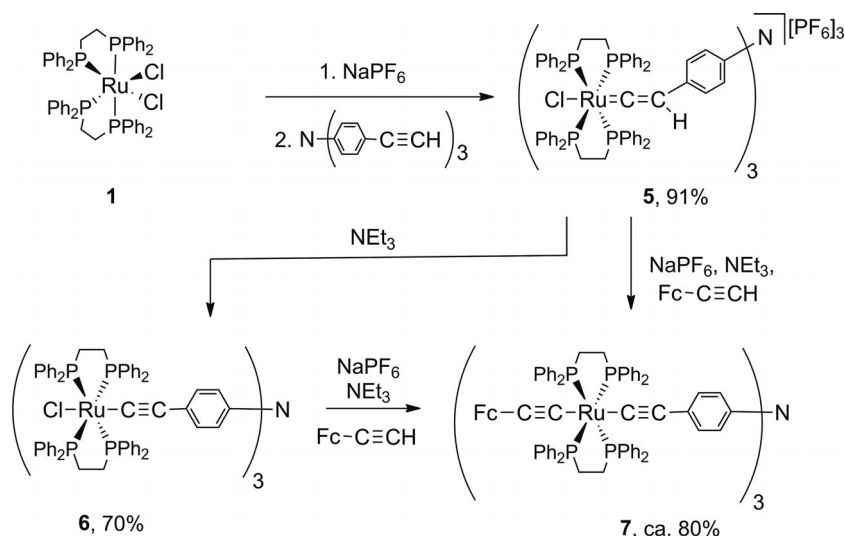
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Scheme 1. Formation of **4** (Fc = ferrocenyl).Scheme 2. Formation of **7**.

resulted in the formation of the unsymmetric bis-alkynyl complex *trans*-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(C $\equiv$ C-4-C₆H₄NPh₂)(dppe)₂] (**4**), which incorporates a ferrocenyl-ethynyl unit. The tris-vinylidene complex *trans,trans,trans*-[(dppe)₂ClRu(C=CH-4-C₆H₄)₃N][PF₆]₃ (**5**) was synthesized by treating [RuCl(dppe)₂][PF₆] with tris(4-ethynylphenyl)amine (Scheme 2). The vinylidene salt **5** was then deprotonated to yield the tris-alkynyl complex *trans,trans,trans*-[(dppe)₂ClRu(C $\equiv$ C-4-C₆H₄)₃N] (**6**); complex **6** had previously been prepared from tris(4-ethynylphenyl)amine and **1** without isolation of the trivinylidene complex.^[16] There was no difference in the reactivity of **5** or **6** towards ethynylferrocene, both of which afforded *trans,trans,trans*-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(dppe)₂(C $\equiv$ C-4-C₆H₄)₃N] (**7**) in similar yields. In contrast, the related tris-vinylidene complex [(dppe)₂ClRu(C=CH-4-C₆H₄- η^1 -C $\equiv$ C)₃C₆H₃]³⁺ was found to react readily with ethynylferrocene to give *trans,trans,trans*-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(dppe)₂(C $\equiv$ C-4-C₆H₄C $\equiv$ C)₃C₆H₃],

whereas the tris-alkynyl derivative *trans,trans,trans*-[(dppe)₂-ClRu(C $\equiv$ C-4-C₆H₄C $\equiv$ C)₃C₆H₃] is reported to be unreactive.^[17]

All complexes were characterized by IR and ¹H and ³¹P NMR spectroscopy, high-resolution mass spectrometry, and satisfactory microanalyses; the structures of complexes **2** (Figure 1), **3** (Figure 2), and **4** (Figure 3) were confirmed by single-crystal X-ray diffraction studies. The IR spectra of the alkynyl complexes contain a $\nu_{\text{C}=\text{C}}$ band at around 2060 cm⁻¹ due to the metal-bonded alkynyl group, whereas the spectra of the vinylidene complexes show a $\nu_{\text{C}=\text{C}}$ band at around 1630 cm⁻¹ together with a strong band at 839 cm⁻¹ that corresponds to the PF₆⁻ counterion. Although most of the proton NMR spectroscopic signals are essentially invariant across this series of complexes, the spectra of the vinylidene complexes contain characteristic multiplets at δ = 3.86 ppm for the protons attached to the β -carbon atom of the metal-bound vinylidene unit. The ferrocenyl substituent in complexes **4** and **7** gives rise to

resonances at $\delta \approx 4.0$ ppm that correspond to the cyclopentadienyl rings. The ^{31}P NMR spectra of all complexes show a single sharp singlet, which is consistent with the *trans* arrangement of the diphosphane ligands around the ruthenium; the phosphorus signals for the vinylidene complexes are $\delta = 10\text{--}15$ ppm upfield of resonances in the alkynyl complexes, which appear at $\delta \approx 50$ ppm for the mono-alkynyl and $\delta = 55$ ppm for the bis-alkynyl complexes. Septuplets are observed at $\delta = -143$ ppm for **2** and **5** due to the PF_6^- counteranion. Mass spectra show a molecular ion for the complex or an ion that corresponds to the loss of H^+ and/or replacement of the chloride by acetonitrile.

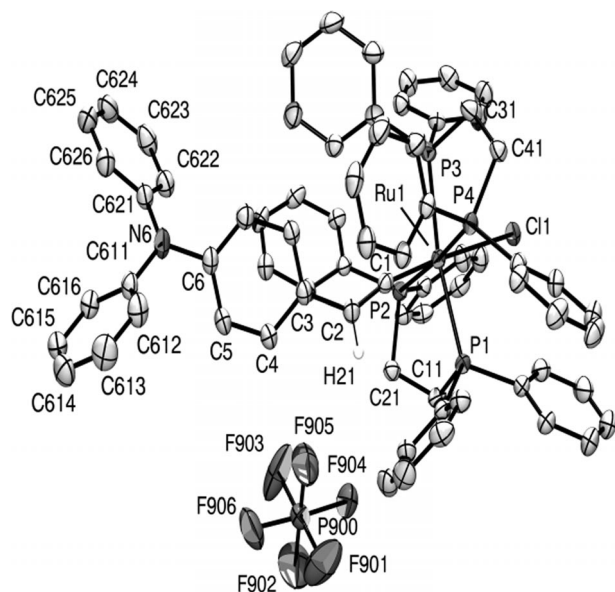


Figure 1. Molecular geometry and atomic labeling scheme for *trans*-[Ru(C=CH-4-C₆H₄NPh₂)Cl(dppe)₂][PF₆] (**2**). Thermal ellipsoids at the 40% probability level are shown for non-hydrogen atoms. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru1–Cl1 2.4831(5), Ru1–C1 1.844(2), C1–C2 1.313(3), C2–C3 1.481(3), C6–N6 1.430(3), N6–C611 1.427(3), N6–C621 1.414(3); Cl1–Ru1–C1 172.87(6), Ru1–C1–C2 168.51(18), C1–C2–C3 133.2(2), C6–N6–C611 118.7(2), C6–N6–C621 118.77(19).

Chemical oxidation of **4** and **7** with [Fe($\eta^5\text{-C}_5\text{H}_5$)₂][PF₆] in THF afforded the mixed-valence species **4**[PF₆] and **7**[PF₆]₃, which were isolated as dark purple powders (Scheme 3). The purity of the complexes was confirmed by cyclic voltammetry (the oxidation products showed identical traces to the corresponding neutral parent), and satisfactory microanalyses. Both **4**[PF₆] and **7**[PF₆]₃ exhibit a strong absorption band in the IR spectra at around 1990 cm^{−1}, which is a lower frequency than the purely Ru–C≡C band (2059 and 2058 cm^{−1} for **4** and **7**, respectively), but higher in energy than a Ru=C=C=C band (≈ 1940 cm^{−1}).^[18,19] This is consistent with electron delocalization from the ruthenium center and a pronounced allenylidene character for the compounds following oxidation of the ferrocenyl group (Scheme 4).^[20,21]

Cyclic voltammetric (CV) data for 4-ethynyl-*N,N*-diphenylaniline, tris(4-ethynylphenyl)amine, and the alkynyl

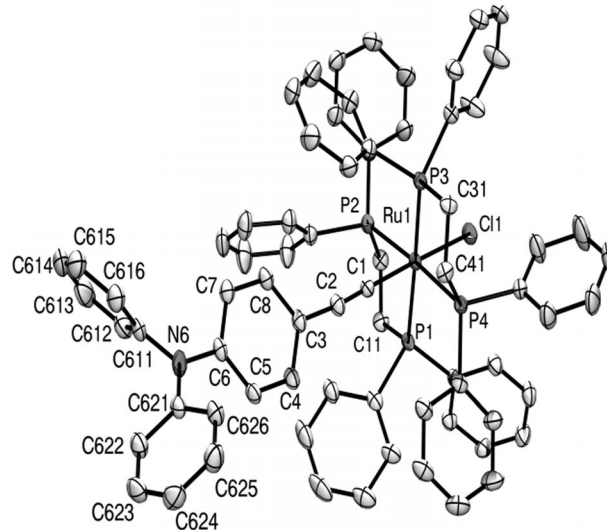


Figure 2. Molecular geometry and atomic labeling scheme for *trans*-[Ru(C≡C-4-C₆H₄NPh₂)Cl(dppe)₂] $\cdot$ CH₂Cl₂ (**3**·CH₂Cl₂). Thermal ellipsoids at the 40% probability level are shown for non-hydrogen atoms. Hydrogen atoms have been omitted for clarity. The solvate CH₂Cl₂ moiety is not displayed. Selected bond lengths [Å] and bond angles [°]: Ru1–Cl1 2.5349(7), Ru1–C1 1.997(3), C1–C2 1.215(4), C2–C3 1.438(4), C6–N6 1.422(4), N6–C611 1.428(4), N6–C621 1.413(4); Cl1–Ru1–C1 174.04(9), Ru1–C1–C2 179.5(3), C1–C2–C3 174.2(4), C6–N6–C611 119.1(3), C6–N6–C621 122.0(3).

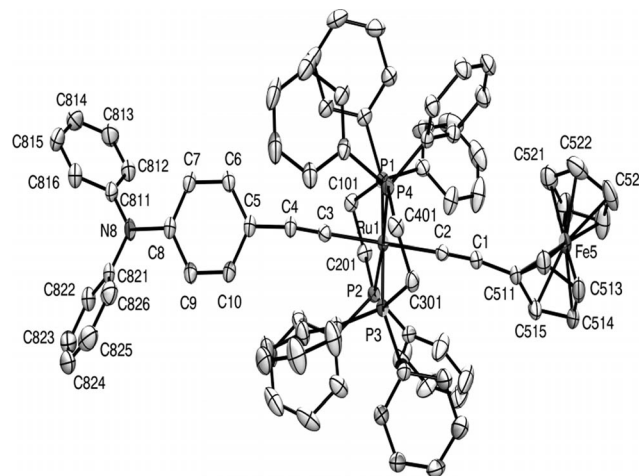
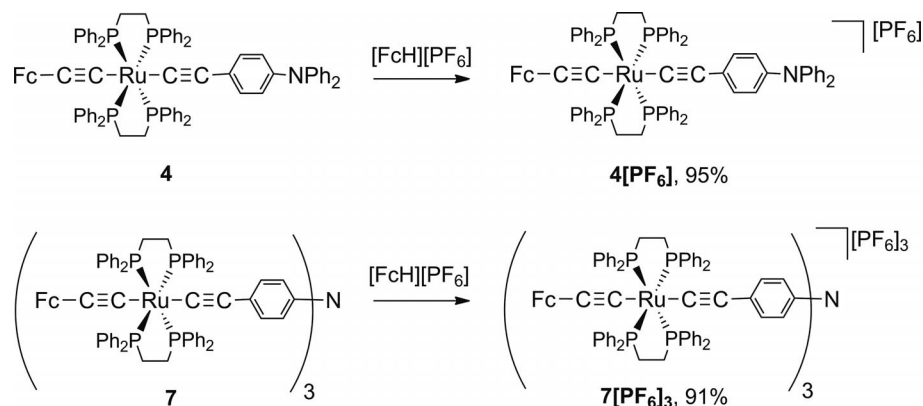
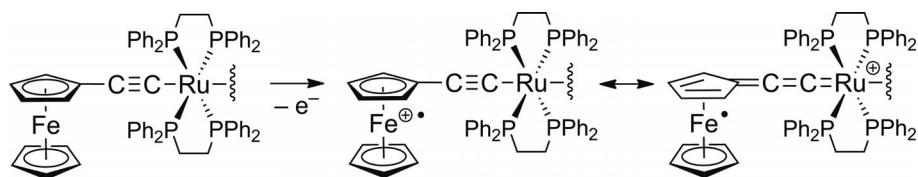


Figure 3. Molecular geometry and atomic labeling scheme for *trans*-[($\eta^5\text{-C}_5\text{H}_5$)Fe($\eta^5\text{-C}_5\text{H}_4\text{-}\eta^1\text{-C}\equiv\text{C}$)Ru(C≡C-4-C₆H₄NPh₂)(dppe)₂] (**4**). Thermal ellipsoids at the 40% probability level are shown for non-hydrogen atoms. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: C511–C1 1.433(4), C1–C2 1.213(4), C2–Ru1 2.082(3), Ru1–C3 2.061(3), C3–C4 1.213(4), C4–C5 1.438(4), C8–N8 1.420(4), N8–C811 1.416(4), N8–C821 1.422(4); C511–C1–C2, 172.5(3) C2–Ru1–C3 177.57(12).

complexes **3**, **4**, **6**, and **7** are collected in Table 1. The organic alkynes each show a single irreversible oxidation process at around 1.4 V, which is assigned to the triphenylamine center. Coordination of 4-ethynyl-*N,N*-diphenylaniline to the electron-donating ruthenium metal center to afford **3** results in a decrease in the potential required for oxidation of the triphenylamine unit to 0.90 V,

Scheme 3. Oxidation of **4** and **7**. $[\text{FcH}]^+ = [\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$.

Scheme 4. Structural change after oxidation of the ferrocenyl substituent.

with a ruthenium-localized oxidation that occurs at 0.37 V, significantly lower than that of the related *trans*- $[\text{Ru}(\text{C}\equiv\text{CR})\text{Cl}(\text{dppe})_2]$ ($\text{R} = \text{H}, \text{Ph}$) complexes, for which $\text{Ru}^{\text{II/III}}$ processes are typically observed at around 0.55 V.^[22] Both the NPh_2 and ruthenium oxidation processes in **3** are fully reversible. The CV of the linear Fe–Ru alkynyl complex **4** is consistent with the sequential loss of three electrons in distinct, fully reversible oxidation steps with E° centered at 0.19, 0.56, and 0.93 V (Figure 4a). By analogy with oxidation processes at the constituent “building blocks,” the wave at the lowest potential can be assigned to oxidation of the electron-rich ferrocenyl unit,^[20,21] whereas that at 0.56 V corresponds to the $\text{Ru}^{\text{II/III}}$ process; the shift to significantly higher potential than **3** reflects the decreased electron density around the ruthenium atom following the preceding oxidation at the iron center. Compared to ethynylferrocene (+0.76 V), there is a cathodic shift in the potential associated with the oxidation of the iron center due to the electron-donating properties of the $[\text{Ru}(\text{dppe})_2]$ center [a Hammett σ_p electronic substituent parameter (ESP) of -0.34 ± 0.04 was previously obtained from analysis of the ^{19}F NMR spectra].^[23] The oxidation of the triphenylamine unit occurs at 0.93 V.

Coordination of the $[\text{RuCl}(\text{dppe})_2]$ center to tris(4-ethynylphenyl)amine affords three distinct oxidation waves in the CV of the resulting trimetallic complex **6** (0.45, 0.69, and 0.90 V); the similar peak heights of each wave suggest three independent one-electron processes, which are assigned to oxidation processes localized at the three ruthenium centers. The hexanuclear bimetallic complex **7** shows five redox waves in the CV (Figure 4b); that at the lowest potential (0.20 V) is around three times the peak height of the subsequent waves and is assigned to the oxidation of the three iron centers (the broad nature of this wave suggests unre-

Table 1. Cyclic voltammetric data.

Compound	$E_{1/2}, (\Delta E_p, i_{pa}/i_{pc})$ [V]	Reference
4-HC $\equiv$ CC ₆ H ₄ NPh ₂	1.36 ^[b]	this work ^[a]
(4-HC $\equiv$ CC ₆ H ₄) ₃ N	1.37 ^[b]	this work ^[a]
3	0.37 (0.09, 1) 0.90 (0.08, 1)	this work ^[a]
4	0.19 (0.10, 1) 0.56 (0.09, 1) 0.93 (0.09, 1)	this work ^[a]
<i>trans</i> - $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}\eta^1\text{-C}\equiv\text{C})\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2]$	0.23 0.80	ref. ^[20]
<i>trans</i> - $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}\eta^1\text{-C}\equiv\text{C})\text{Ru}(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{NO}_2)(\text{dppe})_2]$	0.27 0.93	ref. ^[20]
6	0.24 (0.10, 1) 0.48 (0.10, 1) 0.67 (0.10, 1) 1.0 (0.10, 1)	this work ^[a]
7	0.20 (0.15, 0.8) 0.45 (0.07, 1) 0.69 (0.09, 1) 0.90 (0.08, 1) 1.08 (0.08, 1)	this work ^[a]
<i>trans,trans,trans</i> - $[\{(\text{dppe})_2\text{ClRu}(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{C})\}_3\text{C}_6\text{H}_3]$	0.58 (0.01)	ref. ^[17]
<i>trans,trans,trans</i> - $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}\eta^1\text{-C}\equiv\text{C})\text{-Ru}(\text{dppe})_2(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{C})\}_3\text{C}_6\text{H}_3]$	0.28 (0.08) 0.86 (0.08)	ref. ^[17]

[a] CH_2Cl_2 , Ag/AgCl reference electrode (ferrocene/ferrocenium couple located at 0.56 V, $\Delta E_p = 0.09$ V). [b] Irreversible process.

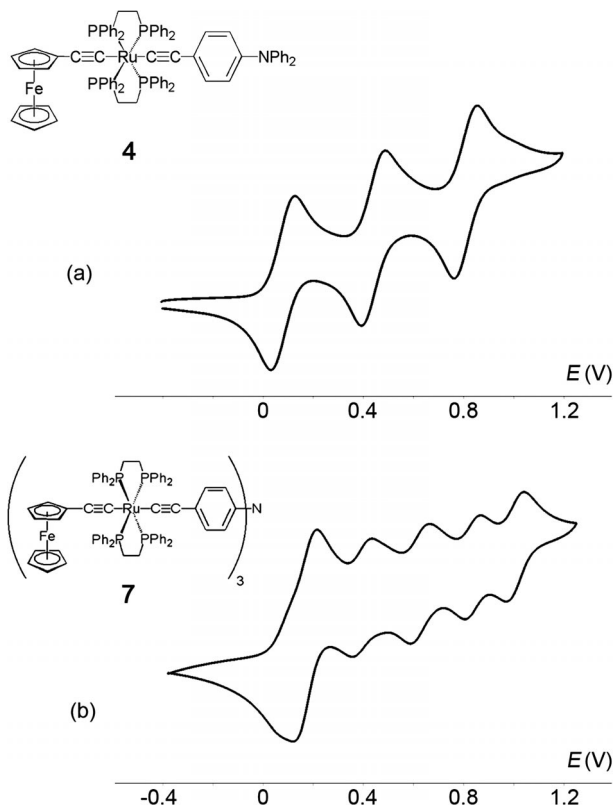


Figure 4. Cyclic voltammograms of (a) **4** and (b) **7**. CH_2Cl_2 solvent, with 0.1 M $[\text{NnBu}_4][\text{PF}_6]$, Ag/AgCl reference, Pt working and auxiliary electrodes; ferrocene/ferrocenium couple located at 0.56 V.

solved stepwise oxidation). The remaining four waves are equal in height and attributed to stepwise oxidation of the three ruthenium centers (0.45, 0.69, 0.90 V) followed by oxidation of the amine unit (1.08 V). The sequential oxidation of each ruthenium metal center in **6** and **7** is in direct contrast to the related complexes *trans,trans,trans*- $[\{(\text{dppe})_2\text{ClRu}(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{C})\}_3\text{C}_6\text{H}_3]$ and *trans,trans,trans*- $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}\eta^1\text{-C}\equiv\text{C})\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{C}-1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{C})\}_3\text{C}_6\text{H}_3]$,^[17] for which only a single redox process is seen for the three ruthenium atoms, which suggests that the tris(4-ethynylphenyl)amine core permits a stronger intermetallic electronic interaction.

Complex **4** shows an absorption band at 28010 cm^{-1} (357 nm, $\epsilon = 4.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which corresponds to a metal-to-ligand charge-transfer (MLCT) transition characteristic of metal alkynyl complexes.^[24,25] The corresponding band in **7** is bathochromically shifted to 26380 cm^{-1} (379 nm) along with a hyperchromic shift ($\epsilon = 11.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). For both **4** and **7**, the absorptivity is slightly greater than in the corresponding chloro analogues **3** (348 nm, $3.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and **6** (373 nm, $7.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

To record the changes in the absorption spectra of **4** and **7** across the possible redox states, both complexes were electrolyzed in situ by using an optically transparent thin-layer electrochemical (OTTLE) cell at -30°C ; results are collected in Table 2. Sequential application of the appropriate potentials (0.2, 0.7, and 1.0 V) to a solution of **4** in CH_2Cl_2

that contained 0.3 M $[\text{NnBu}_4][\text{PF}_6]$ as the supporting electrolyte cleanly afforded oxidation products that resulted from the loss of up to three electrons (**4**⁺, **4**²⁺, and **4**³⁺, respectively; Figure 5). The spectrum of the first oxidation product, **4**⁺, shows only minor changes, with the original MLCT band in **4** undergoing a 50 cm^{-1} redshift and two low-intensity absorption bands that appear at 6080 and 18050 cm^{-1} . In contrast, the spectra of **4**²⁺ and **4**³⁺ show more dramatic changes. The band at 29990 cm^{-1} in the neutral complex is replaced by two strong bands at 22150 and 8970 cm^{-1} in the spectrum of **4**²⁺, and further oxidation to **4**³⁺ results in the replacement of these bands with a strong absorption centered at 15060 cm^{-1} , and with a shoulder at around 16000 cm^{-1} . The low-energy band at 8970 cm^{-1} in **4**²⁺ can be assigned to a ligand-to-metal charge-transfer (LMCT) process by analogy with previous experimental and theoretical studies.^[6,26]

Table 2. UV/Vis/NIR spectral data obtained on electrolysis of complexes **4** and **7** at -30°C in an OTTLE cell.

	λ_{max} [cm^{-1}] [ϵ ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)]		λ_{max} [cm^{-1}] [ϵ ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)]
4	28010 [4.3]	7	26390 [11.5]
4 ⁺	6080 [0.22], 18050 [0.37]	7 ³⁺	6100 [2.5], 17300 [2.8] 27230 [9.5]
4 ²⁺	8970 [2.1], 22150 [2.2]	7 ⁶⁺	6150 [14.9]
4 ³⁺	15060 [4.3]	7 ⁷⁺	6840 sh [5.8], 9120 [9.4]

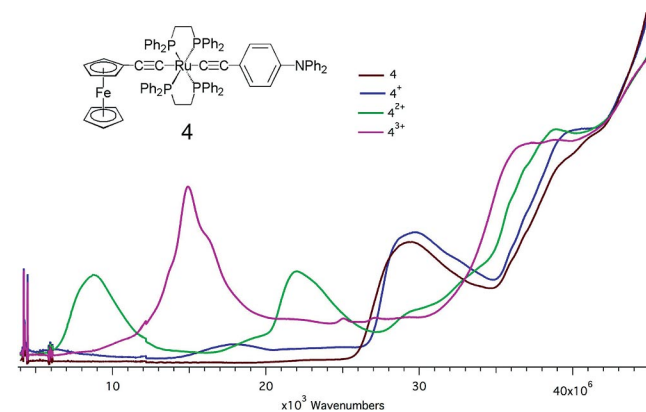


Figure 5. UV/Vis/NIR spectra of **4** (brown), **4**⁺ (blue), **4**²⁺ (green), and **4**³⁺ (pink), obtained by in situ electrolysis of **4** in an OTTLE cell at -30°C .

The spectroelectrochemical changes in the hexametallic complex **7** are shown in Figure 6; initial application of 0.25 V affords the $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$ system **7**³⁺ with two new low-intensity bands at 17300 and 6100 cm^{-1} along with a redshift and slight decrease in the intensity of the MLCT band to 27230 cm^{-1} . Oxidation to the $\text{Fe}^{\text{III}}\text{-Ru}^{\text{III}}$ system (from **7**³⁺ to **7**⁶⁺) was achieved by sequential application of 0.45, 0.70, and 0.90 V (to generate **7**⁴⁺, **7**⁵⁺, and **7**⁶⁺, respectively), and results in the loss of the band at 27230 cm^{-1} and the gradual appearance of a low-energy band at 6150 cm^{-1} , which most likely arises from LMCT. Oxidation of the amine center occurs on application of 1.10 V to give the **7**⁷⁺ state; the spectrum now features a strong band at 9120 cm^{-1}

with a shoulder at 6840 cm^{-1} . In both cases, reduction of the electrogenerated 4^{3+} and 7^{7+} return spectra identical to **4** and **7**, respectively, and isosbestic points were observed for all processes. Note that, in each case, the change observed in proceeding from the neutral complexes to 4^{+} or 7^{3+} was identical to those seen in the spectra of **4** (or **7**) and the chemically synthesized complexes $4[\text{PF}_6]$ (or $7[\text{PF}_6]_3$) (Figure 5 and Figure 6). Theoretical studies were carried out on a model complex similar to **4** to assign the transitions that correspond to the respective bands.

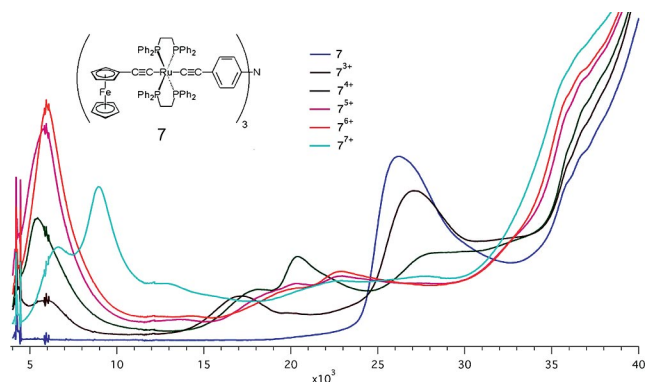


Figure 6. UV/Vis/NIR spectra of **7** (dark blue), 7^{3+} (brown), 7^{4+} (green), 7^{5+} (pink), 7^{6+} (orange), and 7^{7+} (light blue) obtained by in situ electrolysis of **7** in an OTTLE cell at $-30\text{ }^{\circ}\text{C}$.

Calculations on C_s -symmetric **4-Me** (which differs from **4** in replacement of the dppe phenyl groups by methyl groups) identify the three highest-lying occupied orbitals as $^{132}a'$, $^{95}a''$, and $^{133}a'$ (HOMO). It is by electron ejection from these orbitals (Figure 7) that oxidation occurs. Each of these frontier orbitals is substantially delocalized along the carbon backbone, with $^{133}a'$ almost equally divided between Ru (22%) and Fe (20%) character, but with negligible N content (4%). Oxidation to **4-Me⁺** involves loss of an electron from $^{133}a'$, but it is notable that the singly occupied $^{133}a'$ orbital in the cation contains much less Fe character (5%) but retains about the same degree of Ru character (18%) as is evident in the corresponding orbital of the par-

ent neutral. Thus, the assignment of the first oxidation step as Fe-localized is broadly appropriate.

Further oxidation to **4-Me²⁺** can yield a singlet electronic configuration (if both electrons are removed from $^{133}a'$) or a triplet, and our calculations suggest these two possibilities are almost equivalent in energetic cost: the difference in computed energy between closed-shell **4-Me²⁺** and its triplet dication counterpart is only 3 kJ mol^{-1} in our solvent-corrected PBE/TZP calculations, with the singlet state fractionally preferred. For singlet **4-Me²⁺**, it is clearly appropriate to view the second oxidation step as Ru-localized, since this is consistent with the singly occupied molecular orbital (SOMO) character of **4-Me⁺**. For triplet **4-Me²⁺**, the singly occupied $^{132}a'$ and $^{133}a'$ orbitals have a reduced degree of Ru and Fe character, but a modest increase in N character relative to their values in neutral **4-Me**, and thus the description of the second oxidation as Ru-localized is also essentially appropriate in the case that the triplet dication is generated.

Oxidation to **4-Me³⁺** can, in principle, generate a doublet or quartet electronic configuration, but all efforts to obtain convergence for a quartet state were unsuccessful. The doublet electronic configuration found for **4-Me³⁺** is $[(\dots)^{95}a'']^2(^{132}a')^1(^{133}a')^0]$. Frontier orbital analysis for doublet **4-Me³⁺** is not entirely consistent with the description of the third oxidation as N-localized; a substantial fraction of the character for $^{132}a'$ (in singlet **4-Me²⁺**, the HOMO) is spread along the Ru–N corridor, and this character is absent in SOMO $^{132}a'$ for **4-Me³⁺**.

Conclusion

Coupling bis(bidentate diphosphane)ruthenium, ferrocenyl, and triarylamine modules by ethynyl linkages has afforded in high yield redox-active species that can exist in up to six reversibly interconvertible oxidation states with distinct linear optical properties. The various redox states of these multistate molecular switches should possess distinct nonlinear optical properties; studies addressing this possibility are currently underway.

Experimental Section

General Considerations: All reactions and workup procedures of air-sensitive compounds were carried out under dry, high-purity nitrogen using standard Schlenk techniques.^[27] All glassware was oven-dried overnight at $120\text{ }^{\circ}\text{C}$ prior to use. Solvents/reagents were dried and distilled as follows: Et_2O , hexane, and reagent-grade THF (sodium/benzophenone), CH_2Cl_2 (CaH_2), diisopropylamine and triethylamine (KOH), and DMF (activated molecular sieves, $3\text{ \AA}$). Hexane used for column chromatography refers to petroleum spirit (boiling range $60\text{--}80\text{ }^{\circ}\text{C}$). *cis*- $[\text{RuCl}_2(\text{dppe})_2]$ (**1**),^[15] $[\text{PdCl}_2(\text{PPh}_3)_2]$,^[28] $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$,^[29] $(p\text{-BrC}_6\text{H}_4)_3\text{N}$,^[30,31] $(p\text{-OHCC}_6\text{H}_4)\text{NPh}_2$,^[32] $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{C}\equiv\text{CH})]$,^[33] and $\text{LiN-}i\text{Pr}_2$ (LDA) solutions in THF^[34] were prepared as described in the literature. NaPF_6 was recrystallized from MeCN and stored/opened under nitrogen. Other chemicals were purchased from a commercial source (Sigma–Aldrich) and used as received. Flash

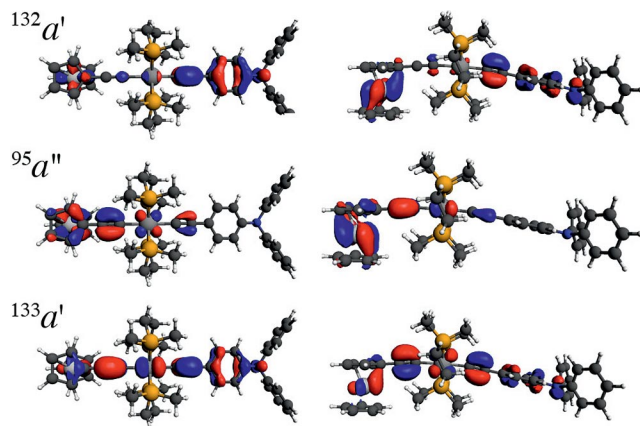


Figure 7. Frontier (occupied) orbitals for **4-Me**, obtained in solvent-corrected SAOP/TZP//PBE/TZP calculations.

column chromatography was performed using silica (Scharlau 60, 230–400 mesh) or basic alumina (Aldrich, Brockman activity I, ca. 150 mesh); 2% NEt_3 was added to the eluent for the column chromatography of ruthenium complexes.

Instrumentation: Infrared spectra were obtained as KBr disks with a Perkin–Elmer System 2000 FTIR spectrometer. NMR spectra were acquired at 298 K with a Varian Gemini-300 FT NMR (^1H , ^{13}C and ^{31}P at 300, 75, and 121 MHz, respectively) as solutions in CDCl_3 . Chemical shifts are referenced to the residual solvent signal for ^1H and ^{13}C ($\delta = 7.26$ and 77.0 ppm, respectively) and external H_3PO_4 ($\delta = 0.0$ ppm) for ^{31}P NMR spectra. Cyclic voltammograms were recorded in dry CH_2Cl_2 solutions (which contained 0.1 M $[\text{NnBu}_4][\text{PF}_6]$, purged with nitrogen and maintained under an inert atmosphere) with an e-corder 401 potentiostat system from eDAQ Pty, Ltd. by using a Pt disk as working electrode, a Pt wire as counter electrode, and an Ag/AgCl reference electrode; the $\text{FeCp}_2^{0/+}$ couple ($E_{1/2} = 0.56\text{ V}$, $\Delta E_p = 0.09\text{ V}$; $i_{pa}/i_{pc} = 1$) was used as an internal calibrant. UV/Vis/NIR spectra were recorded as CH_2Cl_2 solutions by using a 1 cm quartz cell with a Cary 5 spectrometer and are reported as λ_{max} [nm] [ϵ ($10^4\text{ M}^{-1}\text{ cm}^{-1}$)]. Solution spectra of the oxidized species were obtained at 248 K by electrogeneration in an optically transparent thin-layer electrochemical (OTTLE) cell;^[35] solutions were made up with 0.3 M $[\text{NnBu}_4][\text{PF}_6]$ in dry and deoxygenated CH_2Cl_2 under a nitrogen atmosphere. Elemental analysis and unit- and high-resolution mass spectra (EI and ESI) were obtained at the Research School of Chemistry, Australian National University.

4-(2,2-Dibromoethenyl)-*N,N*-diphenylaniline: Carbon tetrabromide (3.32 g, 10.0 mmol) was added portionwise to a mixture of triphenylphosphane (2.62 g, 10.0 mmol) and zinc dust (0.65 g, 10.0 mmol) in CH_2Cl_2 (50 mL) at 0°C . The resulting suspension was stirred for 12 h at room temperature, cooled to 0°C , and 4-(diphenylamino)benzaldehyde (1.37 g, 5.0 mmol) was added portionwise. The reaction mixture was stirred for an additional 2 h at room temperature and then filtered through a short pad of silica ($2.5 \times 4\text{ cm}$). The pad was washed with CH_2Cl_2 (50 mL three times), and the solvent evaporated under reduced pressure. The residue was adsorbed onto silica and loaded on the top of a chromatography column (silica gel, $4 \times 15\text{ cm}$). Elution with hexane/ CH_2Cl_2 (9:1) afforded 4-(2,2-dibromoethenyl)-*N,N*-diphenylaniline (1.75 g, 82%) as a pale yellow powder after removal of the solvent. R_f (hexane/ CH_2Cl_2 , 9:1): 0.45. $\text{C}_{20}\text{H}_{15}\text{Br}_2\text{N}$ (429.15): calcd. C 55.97, H 3.52, N 3.26; found C 56.07, H 3.24, N 3.17. HRMS (EI): calcd. 428.9551 $[\text{M}]^+$; found 428.9549. IR: $\tilde{\nu} = 1585$ (s, $\nu_{\text{C}=\text{C}}$), 1274 (s, $\nu_{\text{C}-\text{N}}$), 823 (m, $\delta_{\text{C}=\text{H}}$), 601 (s, $\text{C}-\text{Br}$) cm^{-1} . ^1H NMR: $\delta = 7.47$ – 7.39 (m, 3 H, aromatic H + $-\text{CH}=\text{}$), 7.31– 7.25 (m, 4 H, aromatic H), 7.13– 6.99 (m, 8 H, aromatic H) ppm. ^{13}C NMR: $\delta = 148.1$ (s), 147.1 (s), 136.2 (s), 129.4 (s), 129.2 (s), 128.3 (s), 125.1 (s), 124.2 (s), 123.6 (s), 121.8 (s), 86.9 (s) ppm.

4-Ethynyl-*N,N*-diphenylaniline: 4-(2,2-Dibromoethenyl)-*N,N*-diphenylaniline (1.72 g, 4.0 mmol) was dissolved in THF (20 mL) and the solution was cooled to -78°C . Lithium diisopropylamide (4.0 mmol) in THF (5 mL) was added dropwise; the reaction mixture was stirred for 30 min at -78°C and then warmed to -40°C . Lithium diisopropylamide (8.0 mmol) in THF (10 mL) was added dropwise and stirring was maintained for 2 h at -40°C before a saturated aqueous NH_4Cl solution (10 mL) was added. The reaction mixture was warmed to room temperature and the two layers were separated. The aqueous layer was extracted with Et_2O (25 mL three times), and the organic layers were washed with water (25 mL three times) and saturated aqueous NaCl solution (25 mL). The aqueous layer was then extracted again with Et_2O (25 mL) and

the second organic extract washed with saturated aqueous NaCl solution (25 mL). The combined organic layers were dried (MgSO_4) and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel, $3.5 \times 15\text{ cm}$) and eluting with hexane/ CH_2Cl_2 (9:1) to afford a yellow powder identified as 4-ethynyl-*N,N*-diphenylaniline (1.03 g, 95%) by comparison with the reported data.^[36] R_f (hexane/ CH_2Cl_2 , 9:1): 0.48. HRMS (EI): calcd. 269.1204 $[\text{M}]^+$; found 269.1213. IR: $\tilde{\nu} = 3265$ (s, $\nu_{\text{Csp}-\text{H}}$), 2102 (m, $\nu_{\text{C}\equiv\text{C}}$), 1284 (s, $\nu_{\text{C}-\text{N}}$), 648 (s, $\delta_{\text{Csp}-\text{H}}$) cm^{-1} . ^1H NMR: $\delta = 7.35$ – 6.96 (m, 14 H, aromatic H), 3.02 (s, 1 H, $\equiv\text{C}-\text{H}$) ppm. ^{13}C NMR: $\delta = 148.4$ (s), 147.1 (s), 133.1 (s), 129.4 (s), 125.1 (s), 123.7 (s), 122.1 (s), 114.8 (s), 83.9 (s), 76.2 (s) ppm.

***trans*-[Ru(C $\equiv$ CH-4-C $_6$ H $_4$ NPh $_2$)Cl(dppe) $_2$][PF $_6$] (2):** *cis*-[RuCl $_2$ -(dppe) $_2$] (1, 0.484 g, 0.5 mmol) and NaPF $_6$ (0.092 g, 0.55 mmol) were dissolved in CH_2Cl_2 (20 mL) and the solution was stirred for 12 h at room temperature with exclusion of light. 4-Ethynyl-*N,N*-diphenylaniline (0.148 g, 0.55 mmol) was added, and the solution heated at 40°C for 2 h. After cooling to room temperature, the reaction mixture was filtered, the inorganic salts were washed with CH_2Cl_2 (5 mL three times), and the CH_2Cl_2 extracts were concentrated under vacuum to 5 mL. Et_2O was added to the CH_2Cl_2 extract to precipitate the vinylidene salt as a pale brown powder, which was collected by filtration, washed with Et_2O (5 mL three times), and hexane (5 mL three times), and finally dried in vacuo (0.620 g, 92%). Crystals suitable for an X-ray study were grown by slow diffusion of diethyl ether into a solution of **2** in CH_2Cl_2 . $\text{C}_{72}\text{H}_{63}\text{ClF}_6\text{NP}_5\text{Ru}\cdot\text{CH}_2\text{Cl}_2$: calcd. C 61.20, H 4.57, N 0.98; found C 61.59, H 4.67, N 1.06. MS (ESI): calcd. 1207 $[\text{M} - \text{H} - \text{Cl} + \text{MeCN}]^+$; found 1207. IR: $\tilde{\nu} = 1637$ (m, $\text{Ru}=\text{C}=\text{C}$), 1273 (m, $\nu_{\text{C}-\text{N}}$), 839 (s, $\text{P}-\text{F}$) cm^{-1} . UV/Vis [ϵ ($10^4\text{ M}^{-1}\text{ cm}^{-1}$)]: $\lambda = 345$ [2.8] nm. ^1H NMR: $\delta = 7.35$ – 6.91 (m, 50 H, aromatic H), 6.36 (d, $^3J_{\text{H,H}} = 9\text{ Hz}$, 2 H, C_6H_4), 5.60 (d, $^3J_{\text{H,H}} = 9\text{ Hz}$, 2 H, C_6H_4), 3.86 (br. s, 1 H, $=\text{C}=\text{CH}$), 2.95 (m, 4 H, CH_2 dppe), 2.77 (m, 4 H, CH_2 dppe) ppm. ^{31}P NMR: $\delta = 38.1$ (s, dppe), -143.1 (sept, PF $_6$) ppm.

***trans*-[Ru(C $\equiv$ C-4-C $_6$ H $_4$ NPh $_2$)Cl(dppe) $_2$] (3):** *trans*-[Ru(C $\equiv$ CH-4-C $_6$ H $_4$ NPh $_2$)Cl(dppe) $_2$][PF $_6$] (2, 0.620 g, 0.45 mmol) was dissolved in CH_2Cl_2 (20 mL) under nitrogen. NEt_3 (0.62 mL, 4.5 mmol) was added, and stirring was maintained for 5 min. The solution was filtered, washed with CH_2Cl_2 (5 mL three times), and the solvents were removed under reduced pressure. The residue was taken up in CH_2Cl_2 and purified by column chromatography (basic alumina, $3.5 \times 10\text{ cm}$). Elution with CH_2Cl_2 gave a yellow band that was collected and concentrated to 5 mL under reduced pressure. MeOH was added to give a pale yellow powder that was collected, washed with MeOH (5 mL three times) and hexane (5 mL three times), and finally dried in vacuo to give **3** (0.485 g, 90%), identified by comparison to the reported spectroscopic data.^[12] Crystals suitable for an X-ray study were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution. $\text{C}_{72}\text{H}_{62}\text{ClNP}_4\text{Ru}$ (1201.71): calcd. C 71.96, H 5.14, N 1.17; found C 71.91, H 5.14, N 1.15. HRMS (ESI): calcd. 1207.316 $[\text{M} - \text{Cl} + \text{MeCN}]^+$; found 1207.303. IR: $\tilde{\nu} = 2070$ (s, $\text{Ru}-\text{C}\equiv\text{C}$), 1273 (s, $\nu_{\text{C}-\text{N}}$) cm^{-1} . UV/Vis [ϵ ($10^4\text{ M}^{-1}\text{ cm}^{-1}$)]: $\lambda = 348$ [3.8] nm. ^1H NMR: $\delta = 7.61$ (m, 8 H, aromatic H), 7.24– 6.94 (m, 42 H, aromatic H), 6.83 (d, $^3J_{\text{H,H}} = 9\text{ Hz}$, 2 H, C_6H_4), 6.59 (d, $^3J_{\text{H,H}} = 9\text{ Hz}$, 2 H, C_6H_4), 2.65 (m, 8 H, CH_2 dppe) ppm. ^{13}C NMR: $\delta = 148.1$ (s, $\text{C}_{\text{ArNPh}_2}$), 142.6 (s, $\text{C}_{\text{ArNPh}_2}$), 136.7 and 135.5 ($2 \times$ m, C_{ipso} dppe), 134.4– 121.9 (m, $\text{C}_{\text{Ar/dppe}}$), 125.6 (br. s, $\text{Ru}-\text{C}\equiv\text{C}$), 113.5 (s, $\text{Ru}-\text{C}\equiv\text{C}$), 30.7 (m, CH_2 dppe) ppm. ^{31}P NMR: $\delta = 50.4$ (s, PPh $_2$) ppm.

***trans*-[(η^5 -C $_5$ H $_5$)Fe(η^5 -C $_5$ H $_4$ - η^1 -C $\equiv$ C)Ru(C $\equiv$ C-4-C $_6$ H $_4$ NPh $_2$)-(dppe) $_2$] (4):** *trans*-[Ru(C $\equiv$ C-4-C $_6$ H $_4$ NPh $_2$)Cl(dppe) $_2$] (6, 0.30 g,

0.25 mmol), NaPF₆ (0.168 g, 1.0 mmol), and ethynylferrocene (0.079 g, 0.375 mmol) were dissolved in CH₂Cl₂ (20 mL). NEt₃ (0.3 mL, 2.0 mmol) was added, and the resulting suspension was stirred for 24 h at room temperature with exclusion of light. The reaction mixture was filtered, washed with CH₂Cl₂ (5 mL three times), and the solvent was removed under reduced pressure. The residue was taken up in a minimal amount of CH₂Cl₂ and adsorbed on top of a chromatography column (basic alumina, 3.5 × 10 cm). An orange band was eluted with CH₂Cl₂ and the volume of the collected eluate was reduced to 5 mL. MeOH was added to precipitate **4** as an orange powder, which was collected by filtration, washed with MeOH (5 mL three times) and hexane (5 mL three times), and dried in vacuo (0.30 g, 87%). Crystals suitable for an X-ray study were grown by slow diffusion of hexane into a CH₂Cl₂ solution. C₈₄H₇₁FeNP₄Ru (1375.30): calcd. C 73.36, H 5.20, N 1.02; found C 73.54, H 5.33, N 0.96. HRMS (ESI): calcd. 1375.293 [M]⁺; found 1375.293. IR: $\tilde{\nu}$ = 2059 (s, C≡C), 1273 (m, ν_{C-N}) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 357 [4.3] nm. ¹H NMR: δ = 7.57 (m, 6 H, aromatic H), 7.52 (m, 6 H, aromatic H), 7.23–6.96 (m, 38 H, aromatic H), 6.86 (d, ³J_{H,H} = 8 Hz, 2 H, C₆H₄), 6.59 (d, ³J_{H,H} = 8 Hz, 2 H, C₆H₄), 4.22 (m, 4 H, Fc), 4.10 (s, 5 H, Fc), 2.64 (m, 8 H, CH₂ dppe) ppm. ¹³C{¹H} NMR: δ = 148.2 (s, C_{ArNPh2}), 142.6 (s, C_{ArNPh2}), 137.3 (m, C_{ipso} dppe), 134.5–121.9 (m, C_{Ar/dppe}), 126.1 (br. s, RuC≡CFc), 122.9 (s, RuC≡CC₆H₄), 115.9 (s, RuC≡CC₆H₄), 110.7 (s, RuC≡CFc), 68.6, 68.3, 65.8 (3 × s, Fc), 31.6 (m, CH₂ dppe) ppm. ³¹P{¹H} NMR: δ = 54.2 (s, PPh₂) ppm.

trans-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C≡C)Ru(C≡C-4-C₆H₄NPh₂)-(dppe)₂][PF₆]₄ (4**PF₆):** *trans*-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C≡C)Ru(C≡C-4-C₆H₄NPh₂)(dppe)₂] (**7**, 0.21 g, 0.15 mmol) and [Fe(η^5 -C₅H₅)₂][PF₆]₄ (0.047 g, 0.14 mmol) were dissolved in THF (25 mL) and the solution was stirred for 1 h. The reaction mixture was evaporated to dryness and the solid was successively re-precipitated three times from CH₂Cl₂/Et₂O. The precipitated **4**PF₆ was collected by cannula filtration, washed with Et₂O (5 mL three times) and hexane (5 mL three times), and finally dried in vacuo to give a purple solid (0.21 g, 95%). C₈₄H₇₁F₆FeNP₅Ru (1520.27): calcd. C 66.36, H 4.71, N 0.92; found C 66.48, H 4.63, N 0.96. IR: $\tilde{\nu}$ = 2062 (w, RuC≡C), 1992 (s, Ru=C=C=Fc), 1276 (m, ν_{C-N}), 835 (s, P–F) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 606 [0.8], 1134 [0.4] nm.

(4-HOMe₂CC≡CC₆H₄)₃N: 2-Methylbut-3-yn-2-ol (4.85 mL, 50.0 mmol) was added to a mixture of tris(*p*-bromophenyl)amine (2.41 g, 5.0 mmol), [PdCl₂(PPh₃)₂] (0.14 g, 0.2 mmol), and CuI (0.076 g, 0.4 mmol) in DMF (20 mL) and diisopropylamine (20 mL). The reaction mixture was heated at 80 °C for 48 h, cooled to room temperature, and solvents were removed by bulb-to-bulb distillation into a liquid-nitrogen-cooled trap. The residue was extracted with ethyl acetate (50 mL three times) and filtered. The filtrate was washed with water (50 mL three times) and saturated aqueous NaCl solution (50 mL). The aqueous layer was extracted with ethyl acetate (25 mL three times) and the extracts were washed with saturated aqueous NaCl solution (25 mL three times). The organic layers were combined, dried (MgSO₄), and the solvent was removed under reduced pressure to give a black oil. The black oil was adsorbed onto silica gel and loaded on the top of a chromatography column (silica gel, 4 × 15 cm). Elution with hexane/ethyl acetate (1:1) afforded the alkyne (4-HOMe₂CC≡CC₆H₄)₃N (1.72 g, 70%) as yellow crystals after recrystallization from ethyl acetate/hexane, identified by comparison with the published spectroscopic data.^[37] R_f (hexane/ethyl acetate, 1:1): 0.40. C₃₃H₃₃NO₃ (491.63): calcd. C 80.62, H 6.77, N 2.85; found C 80.50, H 7.01, N 2.69. HRMS (EI): calcd. 514.2358 [M + Na]⁺; found 514.2358. IR: $\tilde{\nu}$ = 3360 (vs, ν_{OH}), 2931 and 2866 (m, ν_{CH3}), 2225 (w, $\nu_{C\equiv C}$), 1395 and 1159 (s, δ_{OH} and ν_{C-O}), 1377 and 1362 (m, δ_{CH3}), 1285 (m, ν_{C-N})

cm⁻¹. ¹H NMR: δ = 7.30 (d, ³J_{H,H} = 8 Hz, 6 H, aromatic H), 6.91 (d, ³J_{H,H} = 8 Hz, 6 H, aromatic H), 2.59 (br. s, 3 H, OH), 1.63 (s, 18 H, Me) ppm. ¹³C NMR: δ = 147.0 (s), 133.2 (s), 124.2 (s), 117.8 (s), 94.2 (s), 82.2 (s), 66.0 (s), 31.9 (s) ppm.

Tris(4-ethynylphenyl)amine: (4-HOMe₂CC≡CC₆H₄)₃N (0.983 g, 2.0 mmol) and powdered KOH (1.683 g, 30.0 mmol) were suspended in toluene (100 mL) and heated to 80 °C for 1 h. The reaction mixture was cooled to room temperature and filtered through a short pad of Celite (5 × 2 cm). The Celite pad was washed with toluene (25 mL three times) and the combined eluate was evaporated to dryness under reduced pressure. The resulting oil was adsorbed onto silica and subjected to column chromatography (silica gel, 4 × 10 cm). Elution with hexane/CH₂Cl₂ (4:1) gave tris(4-ethynylphenyl)amine as a yellow solid (0.580 g, 91%) after evaporation of the solvent. This compound has been prepared previously by a different method, but spectroscopic data were not reported.^[38] R_f (hexane/CH₂Cl₂, 4:1): 0.39. HRMS (EI): calcd. 317.120 [M]⁺; found 317.121. IR: $\tilde{\nu}$ = 3277 (s, ν_{Csp-H}), 2099 (m, $\nu_{C\equiv C}$), 1283 (s, ν_{N-C}), 672 (m, δ_{Csp-H}) cm⁻¹. ¹H NMR: δ = 7.44 (d, ³J_{H,H} = 8 Hz, 6 H, aromatic H), 7.09 (d, ³J_{H,H} = 8 Hz, 6 H, aromatic H), 3.12 (s, 3 H, C_{sp-H}) ppm. ¹³C NMR: δ = 147.5 (s), 133.9 (s), 124.4 (s), 117.4 (s), 83.9 (s), 77.9 (s) ppm.

trans,trans,trans-[(dppe)₂ClRu(C≡CH-4-C₆H₄)₃N][PF₆]₃ (5**):** Compound **1** (0.508 g, 0.525 mmol) and NaPF₆ (0.098 g, 0.578 mmol) were dissolved in CH₂Cl₂ (20 mL), and the solution was stirred for 12 h at room temperature with exclusion of light. Tris(4-ethynylphenyl)amine (0.0476 g, 0.15 mmol) was added, and the reaction mixture heated to 40 °C for 6 h. After cooling to room temperature, the suspension was filtered, washed with CH₂Cl₂ (5 mL three times), and the washings were concentrated to 10 mL under reduced pressure. Complex **5** was obtained as a green powder by addition of Et₂O to the CH₂Cl₂ extract, the process being repeated twice. The solid was collected by filtration, washed with Et₂O (5 mL three times) and hexane (5 mL three times), and dried in vacuo (0.482 g, 91%). C₁₈₀H₁₅₉Cl₃F₁₈NP₁₅Ru₃ (3552.38): calcd. C 60.86, H 4.51, N 0.39; found C 60.79, H 4.53, N 0.35. MS (ESI): calcd. 1003 [M – 3Cl – 3H]³⁺; found 1003. IR: $\tilde{\nu}$ = 1627 (m, RuC=C), 1275 (m, ν_{C-N}), 839 (s, P–F) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 371 [7.4] nm. ¹H NMR: δ = 7.75–7.12 (m, 120 H, aromatic H), 6.19 (d, ³J_{H,H} = 9 Hz, 6 H, C₆H₄), 5.65 (d, ³J_{H,H} = 9 Hz, 6 H, C₆H₄), 3.86 (br. s, 3 H, =C=CH–), 2.97 (m, 12 H, CH₂ dppe), 2.84 (m, 12 H, CH₂ dppe) ppm. ³¹P NMR: δ = 38.4 (s, PPh₂), –143.1 (sept, PF₆) ppm.

trans,trans,trans-[(dppe)₂ClRu(C≡C-4-C₆H₄)₃N] (6**):** Compound **5** (0.444 g, 0.125 mmol) was dissolved in CH₂Cl₂ (25 mL), NEt₃ (0.52 mL, 3.75 mmol) was added, and the solution was stirred for 5 min. The reaction mixture was filtered and concentrated under reduced pressure to 5 mL. The extract was adsorbed onto a chromatography column (basic alumina, 3.5 × 10 cm) and eluted with CH₂Cl₂ to afford a yellow band. The solvent was reduced to 5 mL and MeOH was added to afford **6** as a yellow powder, which was collected by filtration, washed with MeOH (5 mL three times) and hexane (5 mL three times), and dried in vacuo (0.272 g, 70%). Complex **6** has been prepared previously by means of a different route.^[12] C₁₈₀H₁₅₆Cl₃NP₁₂Ru₃ (3114.47): calcd. C 69.42, H 5.05, N 0.45; found C 69.58, H 5.02, N 0.52. MS (ESI): calcd. 3120 [M – Cl + MeCN]⁺; found 3120. IR: $\tilde{\nu}$ = 2061 (s, Ru–C≡C), 1271 (s, ν_{C-N}) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 373 [7.8] nm. ¹H NMR: δ = 7.69 (m, 24 H, aromatic H), 7.22–6.99 (m, 96 H, aromatic H), 6.91 (d, ³J_{H,H} = 8 Hz, 6 H, C₆H₄), 6.68 (d, ³J_{H,H} = 8 Hz, 6 H, C₆H₄), 2.71 (m, 24 H, CH₂ dppe) ppm. ¹³C NMR: δ = 143.3 (s, C_{ArNPh2}), 141.1 (s, C_{ArNPh2}), 136.9 and 135.5 (2 × m, C_{ipso} dppe),

134.4–120.8 (m, $C_{Ar/dppe}$), 124.3 (m, $Ru\equiv C$), 113.8 (s, $Ru\equiv C$), 30.8 (m, CH_2 , dppe) ppm. ^{31}P NMR: δ = 50.4 (s, PPh_2) ppm.

trans,trans,trans-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(dppe)₂(C $\equiv$ C-4-C₆H₄)₃N] (7): Compound **6** (0.234 g, 0.075 mmol), NaPF₆ (0.151 g, 0.90 mmol), and ethynylferrocene (0.071 g, 0.34 mmol) (Method A); or compound **5** (0.355 g, 0.099 mmol), NaPF₆ (0.202 g, 1.2 mmol), and ethynylferrocene (0.095 g, 0.45 mmol) (Method B) were dissolved in CH₂Cl₂ (50 mL). NEt₃ [0.25 mL, 1.8 mmol (Method A) or 0.33 mL, 2.4 mmol (Method B)] was added, and the resulting suspension was stirred for 24 h at room temperature with exclusion of light. The reaction mixture was filtered, the inorganic salts washed with CH₂Cl₂ (5 mL three times), and the solution was concentrated to 5 mL under reduced pressure. The extract was adsorbed on top of a chromatography column (basic alumina, 3.5 $\times$ 10 cm) and eluted with CH₂Cl₂. An orange band was collected, its volume was reduced to 5 mL, and MeOH was added to precipitate **7** as an orange powder that was collected by filtration, washed with MeOH (5 mL three times) and hexane (5 mL three times), and dried in vacuo [0.220 g, 81% (Method A); 0.290 g, 80% (Method B)]. C₂₁₆H₁₈₃Fe₃NP₂Ru₃ (3635.26): calcd. C 71.37, H 5.07, N 0.39; found C 71.33, H 5.20, N 0.43. MS (ESI): calcd. 1818 [M]²⁺; found 1817. IR: $\tilde{\nu}$ = 2058 (s, $Ru-C\equiv C$), 1275 (m, ν_{C-N}) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 379 [11.5] nm. ¹H NMR: δ = 7.59 (m, 44 H, aromatic H), 7.25–6.92 (m, 82 H, aromatic H), 6.69 (d, ³J_{H,H} = 6 Hz, 6 H, C₆H₄), 3.99, 3.98 [2 $\times$ s (overlapping), 21 H, Fc], 3.95 (s, 6 H, Fc), 2.67 (m, 24 H, CH₂ dppe) ppm. ¹³C NMR: δ = 143.3 (s, C_{ArNP}), 141.0 (s, C_{ArNP}), 137.4 (m, C_{ipso} dppe), 134.5–121.9 (m, $C_{Ar/dppe}$), 124.7 (m, $Ru\equiv C$), 120.7 (m, $Ru\equiv C$), 116.1 (s, $Ru\equiv C$), 110.5 (s, $Ru\equiv C$), 68.6, 68.3, 65.7 (3 $\times$ s, Fc), 31.6 (m, CH₂ dppe) ppm. ^{31}P NMR: δ = 54.2 (s, PPh_2) ppm.

trans,trans,trans-[(η^5 -C₅H₅)Fe(η^5 -C₅H₄-C $\equiv$ C)Ru(dppe)₂(C $\equiv$ C-4-C₆H₄)₃N][PF₆]₃ (7[PF₆]): Compound **7** (0.109 g, 0.030 mmol) and [Fe(η^5 -C₅H₅)][PF₆] (0.030 g, 0.090 mmol) were dissolved in THF (25 mL) and the solution was stirred for 1 h. The solvent was removed and the residue dissolved in a minimal amount of CH₂Cl₂. Compound **7**[PF₆]₃ was precipitated three times by the addition of Et₂O to a CH₂Cl₂ extract, collected by cannula filtration as a black-purple solid, washed with Et₂O (5 mL three times) and hexane (5 mL three times), and finally dried in vacuo (0.111 g, 91%). C₂₁₆H₁₈₃F₁₈Fe₃NP₅Ru₃ (4070.15): calcd. C 63.74, H 4.53, N 0.34; found C 63.79, H 4.63, N 0.51. IR: $\tilde{\nu}$ = 1987 (vs, $Ru=C=C=Fc$), 1283 (m, ν_{C-N}), 838 (s, P–F) cm⁻¹. UV/Vis [ϵ (10⁴ M⁻¹cm⁻¹): λ = 594 [2.3], 364 [6.9] nm.

Crystallography (General): Compounds **2**, **3**, and **4** were recrystallized by slow diffusion of a CH₂Cl₂ solution of the complex into Et₂O (**2**) or *n*-hexane (**3**, **4**), respectively, to give dark green-brown (**2**) and yellow (**3**, **4**) crystals. They were coated with a thin layer of the viscous cryoprotectant Paratone-N (Hampton Research) and attached to a glass fiber. Crystallographically unique data sets were collected with a Nonius Kappa CCD diffractometer.^[39] To determine the unit-cell parameters, ϕ and ω scans of 1.4° (**2**) and 1.2° (**3**, **4**) width were carried out using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). The latter were obtained by least-squares refinement of 15250 (**2**), 14099 (**3**), and 12970 (**4**) unique reflections [N and N_0 of these with $I \geq 2.0\sigma(I)$] using the DENZO package.^[40] The theta range for each data set was 2.6° $\leq$ θ $\leq$ 27.5° (**3**, **4**) and 2.6° $\leq$ θ $\leq$ 26.0° (**7**), respectively, and the temperature during data collection was kept at (200 $\pm$ 2) K in a nitrogen cryostream. After the complete data collection, the crystal faces were measured to allow for numerical absorption corrections by means of the Gaussian method^[41] implemented from within MAXUS.^[42]

Equivalent reflections were merged, and the structures were solved by direct methods using the SIR92 software.^[43,44] peaks of electron density being located by difference Fourier techniques.^[40] The full-matrix least-squares structure refinements were carried out using the CRYSTAL software package.^[43,45–49] Solvent molecules were located in the asymmetric unit of **2** and **3**; since an appropriate model for the solvent moiety could not be found for **2**, the PLATON SQUEEZE function^[50–52] was used to resolve the residual electron density. In all three structures, anisotropic thermal parameters were refined for all non-hydrogen atoms with no restraints or constraints being implemented. The hydrogen atoms were located in difference Fourier maps. Restraints on their bond lengths and angles were applied to systematize their geometry, with C–H bond lengths being set to 0.950 Å and $U_{iso}(H)$ being kept at values that corresponded to 1.2 $\times$ U_{eq} of the parent atoms on which they ride. In the course of the structure refinements, the positions of the hydrogen atoms were refined with riding constraints and recalculated frequently. Residuals R and R_w on $|F|$ are given for reflections with $I \geq 2.0\sigma(I)$. Graphical representations of **2**, **3**, and **4** (Figure 1, Figure 2, and Figure 3) were generated in ORTEP^[53] and refined using the POV-Ray software.^[54] Crystallographic data are summarized in Table S1 in the Supporting Information.

Crystal and Refinement Data of 2: C₇₂H₆₃ClF₆NP₅Ru; M_r = 1347.68 g mol⁻¹; monoclinic, $P2_1/n$ (no. 14); a = 13.5058(1) Å, b = 20.9299(2) Å, c = 23.6011(2) Å, β = 94.5079(5)°; V = 6650.8(1) Å³; Z = 4 (Z' = 1); $D_{calcd.}$ = 1.346 Mg m⁻³; $\mu(Mo-K_\alpha)$ = 0.455 mm⁻¹; T = 200(2) K; green block, 0.12 $\times$ 0.14 $\times$ 0.22 mm³; 151669 measured reflections, 15250 independent measured reflections, F^2 refinement R_1 = 3.55%, wR_2 = 8.91%; 12156 independent reflections with $I > 2.0\sigma(I)$, 2.6° $\leq$ θ $\leq$ 27.5°; 775 parameters; GOF = 0.94, weighting scheme $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 5.16P]$, $P = [\max(F_o^2, 0) + 2F_o^2]/3$.

Crystal and Refinement Data of 3-CH₂Cl₂: C₇₂H₆₂ClNP₄Ru·CH₂Cl₂; M_r = 1286.64 g mol⁻¹; triclinic, $P\bar{1}$ (no. 2); a = 10.7884(1) Å, b = 11.7935(1) Å, c = 25.9510(4) Å, α = 86.967(7)°, β = 84.5233(8)°, γ = 69.5051(8)°; V = 3078.04(6) Å³; Z = 2 (Z' = 1); $D_{calcd.}$ = 1.388 Mg m⁻³; $\mu(Mo-K_\alpha)$ = 0.534 mm⁻¹; T = 200(2) K; yellow plate, 0.06 $\times$ 0.12 $\times$ 0.17 mm³; 70427 measured reflections, 14099 independent measured reflections, F^2 refinement R_1 = 4.46%, wR_2 = 10.7%; 10878 independent reflections with $I > 2.0\sigma(I)$, 2.6° $\leq$ θ $\leq$ 27.5°; 740 parameters; GOF = 0.90, weighting scheme $w = 1.0/[A_0T_0(x) + A_1T_1(x) + \dots + A_{n-1}T_{n-1}(x)]$, A_i = 13.2, 19.1, 9.09, 2.25; $w = [\text{weight}]/[1 < M > - (\delta F/6\sigma F)^2]$.

Crystal and Refinement Data of 4: C₈₄H₇₁FeNP₄Ru; M_r = 1375.31 g mol⁻¹; triclinic, $P\bar{1}$ (no. 2); a = 10.732(1) Å, b = 11.962(1) Å, c = 27.983(1) Å, α = 92.51(1)°, β = 98.20(1)°, γ = 111.39(1)°; V = 3292.8(5) Å³; Z = 2 (Z' = 1); $D_{calcd.}$ = 1.387 Mg m⁻³; $\mu(Mo-K_\alpha)$ = 0.595 mm⁻¹; T = 200(2) K; yellow plate, 0.05 $\times$ 0.13 $\times$ 0.15 mm³; 66822 measured reflections, 12970 independent measured reflections, F^2 refinement R_1 = 4.48%, wR_2 = 8.86%; 9337 independent reflections with $I > 2.0\sigma(I)$, 2.6° $\leq$ θ $\leq$ 26.0°; 820 parameters; GOF = 0.95, weighting scheme $w = 1/[\sigma^2(F^2) + (0.03P)^2 + 5.15P]$, $P = [\max(F_o^2, 0) + 2F_o^2]/3$.

Theoretical Methods: Density functional theory calculations were executed in this study using the Amsterdam Density Functional (ADF) program, version ADF 2010.01,^[55] developed by Baerends et al.^[56,57] Calculations were performed in parallel mode with the VAYU supercomputer housed at the ANU Supercomputer Facility and operated under the National Computational Infrastructure Scheme. Calculations in C_s symmetry were pursued on the structure [*trans*-(η^5 -C₅H₅)Fe(η^5 -C₅H₄- η^1 -C $\equiv$ C)Ru(C $\equiv$ C-4-C₆H₄NPh₂)-(dmpe)₂]^{q+} (q = 0, 1, 2, 3), hereafter identified as **4-Me^{q+}**. Aside

from the imposition of C_s symmetry and the substitution of dppe ligands for dmpe (both simplifications made for reasons of computational expediency), 4-Me^{q+} is structurally identical to 4^{q+} .

In all calculations and for all atoms, the all-electron Slater-type orbital basis sets used were of triple- ζ -plus-polarization quality (TZP). Geometry optimizations employed the gradient algorithm of Versluis and Ziegler.^[58] Functionals used in the optimization calculations were the local density approximation (LDA) to the exchange potential,^[59] the correlation potential of Vosko, Wilk, and Nusair (VWN),^[60] and the nonlocal corrections of Perdew, Burke, and Enzerhof (PBE).^[61] Optimizations were performed in vacuo and, separately, by using the conductor-like screening model (COSMO)^[62] with solvent parameters appropriate to dichloromethane. Time-dependent calculations (TD-DFT) were also pursued on the solvent-corrected PBE/TZP-optimized structures and using the asymptotically correct SAOP functional.^[63]

CCDC-834823 (for **2**), -834822 (for **3-CH₂Cl₂**), -834824 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the crystallographic studies.

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Dyes That Bear Thiazolylazo Groups as Chromogenic Chemosensors for Metal Cations

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A family of dyes (**L**¹–**L**⁶) that contain a thiazolylazo group as signalling subunit and several macrocyclic cavities with different ring sizes and type and number of heteroatoms as binding sites has been synthesized and characterized. Solutions of **L**¹–**L**⁶ in acetonitrile show broad and structureless absorption bands in the 554–577 nm range with typical molar absorption coefficients that range from 20000 to 32000 M^{−1} cm^{−1}. A detailed protonation study was carried out with solutions of **L**¹, **L**² and **L**⁵ in acetonitrile. Addition of one equivalent of protons to **L**¹ and **L**² resulted in the development of a new band at 425 and 370 nm, respectively, which was ascribed to protonation in the aniline nitrogen. In contrast, protonation of **L**⁵ resulted in a bathochromic shift of 25 nm of the absorption band that was conceivable with protonation of one of the nitrogen atoms of the azo moiety. These

results were in agreement with ¹H NMR spectroscopic data. Theoretical studies on the model ligand **L**¹ and on different possible protonation species were also performed by using density functional theory (DFT) quantum mechanical calculations. Colour modulations in solutions of **L**¹–**L**⁶ in acetonitrile in the presence of the metal cations Fe³⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Hg²⁺ have been studied. A selective chromogenic response of **L**⁴ in the presence of Pb²⁺ and **L**⁵ in the presence of Hg²⁺ was observed. To get a better insight into the chromophoric nature in the presence of metal cations, the interaction of Hg²⁺ with the model compound **L**¹ in two different coordination modes was studied theoretically by using density functional theory (DFT) quantum mechanical calculations.

Introduction

Since the discovery of crown ethers by Pedersen in the early sixties, a huge amount of work that deals with the synthesis of selective receptors for positively charged species has been carried out.^[1] In these first stages, the interaction between abiotic receptors and the target cationic species was studied by means of potentiometric and NMR spectroscopic measurements. An important improvement in the field was introduced by Vögtle et al. in 1978 with the synthesis of the first chromogenic receptors for cations.^[2] Us-

ally those receptors are composed by two subunits, namely, the binding site and the signalling unit that are coupled through a covalent bond.^[3] The binding sites are designed to achieve a great complementarity with the target metal cation and usually have a crown ether nature.^[4] Macrocyclic cavities with different sizes and shapes have been synthesized and employed as binding sites.^[5] Selectivity toward certain metal cations can be achieved by varying the size and the number and type of the heteroatoms on the macrocyclic cavity. In this respect, hard cations coordinate well with hard donor atoms such as oxygen, whereas selectivity toward soft cations can be achieved by the use of soft donor atoms in the binding site. Additionally, and to obtain a visual response upon cation binding, one of the heteroatoms of the macrocyclic cavity should be included in the electronic structure of the dye.

Among organic dyes used as signalling subunits in the development of chromogenic receptors,^[6] azo dyes have been widely used due to their simple synthesis and their well-known spectroscopic properties.^[7] Reaction between N,N-disubstituted anilines and diazonium salts of a great variety of aniline derivatives leads to azo dyes with characteristic charge-transfer absorption bands in the 430–480 nm interval and colours that range from light yellow to red-orange. By changing aniline derivatives to 2-aminothiazole

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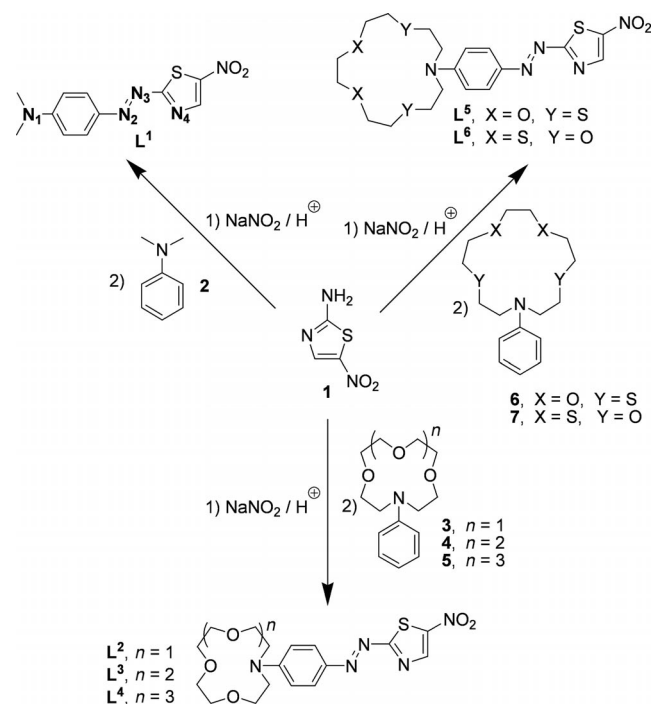
and 2-aminobenzothiazole, a series of thiazolylazo dyes with absorption bands shifted to the 480–650 nm interval can be obtained (with colours that range from orange to deep blue). Some thiazolylazo dyes have been reported to form coloured chelates with a great variety of transition-metal cations (Fe^{3+} , Hg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Mn^{2+} , Pd^{2+} and Cd^{2+}) through interaction with nitrogen atoms from the thiazole and azo moieties and with oxygen atoms usually presented in benzene rings.^[8] Several thiazolylazo dyes have been used for the remediation of the environmentally pollutant Hg^{2+} and Co^{2+} cations.^[9] The use of these azo dyes has also been reported in capillary electrophoresis separations of Co^{2+} , Ni^{2+} , Zn^{2+} and Fe^{2+} and as masking agents in several analytical determinations.^[10] Nevertheless, thiazolylazo dyes have barely been used as signalling subunits in the development of cation receptors based on supramolecular chemistry concepts.

Following our interest in the design of electrochemical and chromo-fluorogenic probes for target guests,^[11] herein we report the synthesis, coordination and chromogenic properties in the presence of metal cations of six receptors that contain a thiazolylazo group as signalling subunit and several macrocyclic cavities with different sizes and numbers and types of heteroatoms as binding sites. Of the six receptors presented here, four (L^2 , L^4 – L^6) are described for the first time; L^1 was used as model because of the lack of macrocyclic subunit and L^3 was synthesized in 1978 by Dix and Vögtle, who studied its coordination behaviour toward alkaline and alkaline-earth cations.^[12] To get a complete understanding of the chromogenic behaviour of this family of thiazolylazo dyes, different possible protonations on L^1 and different coordination modes with Hg^{2+} have also been studied theoretically using density functional theory (DFT) quantum mechanical calculations.

Results and Discussion

Receptors L^1 – L^6 were synthesized (see Scheme 1) by diazotization reaction between the diazonium salt of 2-amino-5-nitrothiazole and *N,N*-dimethylaniline (to obtain L^1) or the corresponding 4-(*N*-crown)phenyl derivatives (to obtain L^2 – L^6). The ligands L^2 – L^6 carry different macrocycles that vary in both the ring size and the type and number of heteroatoms. The 4-(*N*-crown)phenyl macrocycles, which contain oxygen and nitrogen atoms, were synthesized by the Richman–Atkins procedure in which *N,N*-phenyldiethanolamine was deprotonated with sodium hydride followed by treatment under high dilution conditions with methanesulfonyl ester derivatives of the corresponding polyethylene glycol.^[13] The macrocycles that contained sulfur atoms, which were used to obtain receptors L^5 and L^6 , were synthesised by a modified procedure in which 3,6-dioxaoctane-1,8-dithiol and 3,6-dithiaoctane-1,8-diol were deprotonated with potassium carbonate and sodium hydride, respectively, followed by treatment with the methanesulfonyl ester of *N,N*-phenyldiethanolamine. The synthesis of the receptors L^1 and L^3 was previously published.

Receptor L^1 has been used by several groups and its UV/Vis behaviour extensively studied,^[14] whereas L^3 was synthesized by Dix and Vögtle who studied how the coordination of alkaline and alkaline-earth cations modified the electronic levels of the dye.^[12] The ^1H NMR spectrum of receptors L^2 – L^6 shows protons of the macrocyclic unit in the $\delta = 2.6$ to 3.8 ppm range with two clearly defined zones for methylene protons adjacent to sulfur atoms ($\delta = 2.6$ –2.9 ppm) and methylene protons adjacent to nitrogen or oxygen atoms ($\delta = 3.5$ –3.8 ppm). The thiazolylazo moieties in L^1 – L^6 show two doublets centred at $\delta \approx 6.8$ and 7.9 ppm and a singlet at $\delta \approx 8.6$ nm that corresponds to the 1,4-disubstituted benzene and 2,5-disubstituted thiazole ring, respectively.



Scheme 1. Synthesis and chemical structure of receptors L^1 – L^6 .

UV/Vis and ^1H NMR Spectroscopic Behaviour upon Coordination with Protons

As stated above, receptors L^1 – L^6 contain an aniline-type donor moiety attached through an azo linker with an acceptor 5-nitrothiazole heterocycle, exhibiting π -electron delocalization over the entire chromophoric system. As a consequence, L^1 – L^6 receptors showed an intramolecular charge-transfer band (vide infra) typical of such donor–acceptor-substituted dyes. These lowest-energy absorption bands are broad and structureless and centred at around 575 nm in acetonitrile. Typical molar absorption coefficients range from 20000 to 32000 $\text{M}^{-1}\text{cm}^{-1}$ (see Table 1). The subtle differences in the optical properties of the different dyes are imposed by the variations in the substituents on the aniline group. In fact, it has been reported that the presence of other heteroatoms in the crown unit attached

to the aniline moiety can have an effect in the electronic properties of the chromophore through an influence in the electron-donor capacity of the aniline moiety.^[15]

Table 1. Absorption maxima and molar absorption coefficients of **L**¹–**L**⁶.

	L ¹	L ²	L ³	L ⁴	L ⁵	L ⁶
λ_{max} [nm]	577	574	575	574	575	554
ϵ [M ^{−1} cm ^{−1}]	21400	29000	24400	23000	31600	20000

Ligands **L**¹–**L**⁶ can act as polibases due to the presence in their structure of several nitrogen atoms that could, in principle, be protonated. However, a closer look into the reported basicity of these nitrogen atoms indicates that most likely the protonation of the thiazole nitrogen is hindered because this is a poorly basic group that shows protonation constants in the range −1.50 to 0.60.^[16] In contrast, the reported protonation constants of azo dyes that bear the thiazole rings are in the range 1.80–2.80 in water and in organic solvents,^[17] whereas the protonation constant for aniline is 4.65 (in water).^[18] These results suggest that protonation will take most likely in the aniline and/or azo groups. The effect that the secondary heteroatoms on the macrocycle can have in relation to the protonation behaviour is an additional issue related with the protonation of these compounds. In a recent report we observed that different sizes and types of atoms in aniline crowns can modulate the basicity of the aniline nitrogen.^[19] Additionally, protonation studies might clarify the coordination preferences of this family of receptors toward transition-metal cations (vide infra).

A detailed protonation study was carried out with compounds **L**¹, **L**² and **L**⁵ in acetonitrile solutions. The addition of protons (up to 1 equiv.) to solutions of **L**¹ led to a reduction in intensity of the band at 577 nm and the development of a new band at 425 nm. When higher acid concentrations were employed, an additional bathochromic shift (around 10 nm) of the band centred at 577 nm occurred. These observed shifts and the fact that no clear isosbestic points were observed in the course of the titration pointed toward the presence of two protonation equilibria for receptor **L**¹. The initial hypsochromic shift was assigned to a preferential protonation in the aniline nitrogen that decreases its donor strength, whereas the second bathochromic shift is conceivable with protonation of one of the nitrogen atoms of the azo moiety. From the titration curves values of logarithms of 4.77 ± 0.04 and 3.01 ± 0.03 were obtained for these protonation processes.^[20]

To confirm the protonation sites, ¹H NMR spectroscopic titration experiments with **L**¹ in deuterated acetonitrile were carried out. The most significant and remarkable change detected upon addition of one equivalent of protons was observed for the methyl signal that was shifted from $\delta = 3.20$ to 4.56 ppm. This downfield shift strongly suggests a quaternization of the aniline nitrogen atom due to protonation. In the presence of an excess amount of protons, the aromatic doublets at $\delta = 7.89$ and 7.02 ppm from the 1,4-disubstituted benzene ring shifted to $\delta = 7.71$ and 6.97 ppm

and the singlet of the proton located in the nitrothiazole ring was shifted from $\delta = 8.83$ to 8.67 ppm. These upfield shifts could be ascribed to a second protonation process in one of the nitrogen atoms of the azo moiety. The fact that larger amounts of protons were required to protonate the azo group is indicative of its lower basicity than the aniline nitrogen.

Receptor **L**² contains a macrocyclic subunit with three oxygen and one nitrogen atoms. Upon addition of increasing amounts of protons to solutions of **L**² in acetonitrile, the charge-transfer band at 574 nm suffered a hypochromic shift in a progressive fashion and at the same time a new absorption band at 370 nm appeared. This significant hypsochromic shift of 204 nm was ascribed to protonation of the aniline nitrogen atom that is embedded in the crown subunit. Additionally, the presence of a clear isosbestic point at 430 nm strongly suggested that protonation only takes place at the aniline nitrogen in **L**². This preferential protonation at the aniline moiety is due to favourable hydrogen-bonding interactions between the protonated nitrogen atom and the oxygen atoms of the crown cavity and it has been already reported in other dyes that also contain this macrocycle.^[15] This stabilization of the protonated species by hydrogen bonding is reflected in the distinctly higher logarithm of the constant found for the protonation process that amounts to 6.88 ± 0.05 for receptor **L**² (obtained from least-square treatment of the titration profiles). ¹H NMR spectroscopic experiments with **L**² in the presence of increasing quantities of protons were also carried out and confirmed the UV/Vis results.

In contrast, receptor **L**⁵ shows a completely different behaviour. In this case, the charge-transfer band centred at 575 nm suffered a hyper- and bathochromic shift of 25 nm upon addition of protons. This shift is conceivable with protonation of the azo unit. Additionally, the presence of two isosbestic points at 565 and 510 nm indicated that only one protonation occurs. In **L**⁵ the two bulky S atoms in the neighbourhood of the aniline nitrogen effectively shield the N atom from protonation and therefore only the nitrogen atom of the azo moiety was able to interact with protons. From the titration curves, and by least-squares treatment of the profiles, a value of the logarithm of the protonation constant of 3.03 ± 0.01 was obtained for the protonation of **L**⁵. The protonation site in receptor **L**⁵ was also confirmed by ¹H NMR spectroscopic titration experiments in deuterated acetonitrile. Upon addition of an excess amount of protons, the signals of the macrocyclic subunit located in the 2.50–3.70 interval remained unaltered, whereas the aromatic signals suffered remarkable shifts. For instance, an upfield shift from $\delta = 8.81$ to 8.70 ppm was observed for the proton of the nitrothiazole ring.

To get a better insight into the chromophoric nature of the title dyes, the model compound **L**¹ was studied theoretically by using density functional theory (DFT) calculations with the Gaussian 09 package (see the Experimental Section for details). Energies and oscillator strengths of the electronic transitions were obtained from calculations based on the time-dependent (TD) formalism. In the most stable

trans conformation of the azo group, TD calculations predicted for **L**¹ the existence of an electronic absorption at 562 nm that corresponded to the more intense electronic excitation observed. This result is in a good agreement with the experimental data (577 nm). This electronic transition involves an electron transfer from the HOMO to the LUMO orbitals (see Figure 1), which entails a π -intraligand charge transfer (ILCT) that moves electronic density from the phenylamino group to the thiazole fragment (see Figure 1).

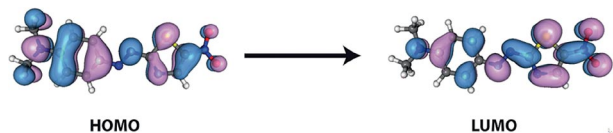


Figure 1. Frontier MOs for **L**¹ compound as obtained from the DFT quantum chemical calculations.

As we have seen before in the spectroscopic studies that involve protons, from the point of view of chemical addressability, ligand **L**¹ possesses four potential protonation sites (i.e., the aniline nitrogen, the two nitrogen atoms from the azo moiety and the thiazole ring). Additionally, to get a better understanding of the protonation behaviour, different possible protonations on **L**¹ were studied theoretically by using DFT calculations, and the energies of the electronic transitions obtained from the TD formalism were compared with the position of the absorption bands found experimentally. Table 2 shows the theoretical energies (λ , in nm) for the ILCT transition associated with the **L**¹ ligand and the corresponding protonated molecules. In the table, species **L**¹, **L**¹₁, **L**¹₂, **L**¹₃ and **L**¹₄ correspond to species protonated in nitrogen atoms 1, 2, 3 and 4, respectively (see Scheme 1).

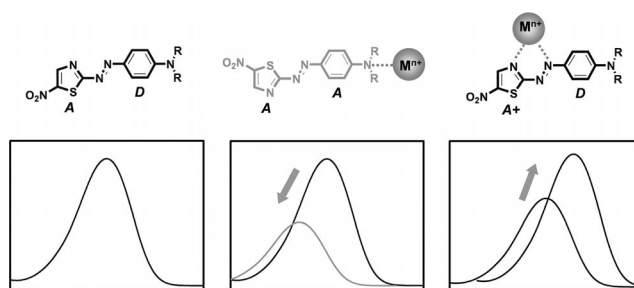
Table 2. Theoretical energies (λ , in nm) for the ILCT electronic transition for **L**¹ ligand, the corresponding protonated molecules and two mercury(II) complexes (see text).

	L ¹	L ¹ ₁	L ¹ ₂	L ¹ ₃	L ¹ ₄	Hg(L ¹)-1	Hg(L ¹)-2
λ_{max} [nm]	567	409	572	477	510	613	407

When comparing the computational results with the experimental spectrum, the absorption bands at 425 and 370 for the protonated derivatives of receptors **L**¹ and **L**², respectively, are in agreement with protonation at the aniline for which a theoretical value of 409 nm for the electronic transition of lower energy was predicted for **L**¹. Other predicted protonations at N3 and N4 suggested lower hypsochromic shifts that were not in agreement with the observed behaviour. Additionally, from the theoretical studies, protonation at N2 is the only protonated species that is predicted to induce a bathochromic shift of the absorption band with respect to the unprotonated species (from 567 to 572 nm). This behaviour is in agreement with that observed experimentally for **L**⁵, which suffered a bathochromic shift of 25 nm, thus strongly suggesting that the protonation in the azo group occurs in the nitrogen that is bonded to the aniline moiety.

UV/Vis Behaviour Upon Coordination with Metal Cations

The behaviour observed in the presence of different metal cations (*vide infra*) for solutions of **L**¹–**L**⁶ in acetonitrile can be rationalized in a similar fashion to that described above for protonation processes. The ILCT transition at approximately 575 nm will be shifted to around 600 nm when the cation is coordinated to the azo group, thereby strengthening its acceptor character. On the contrary, coordination at the aniline nitrogen would result in a hypsochromic shift. Studies of metal coordination were carried out with ligands **L**¹–**L**⁶ in acetonitrile, and three different behaviours were observed (i.e., selective coordination at the aniline, selective coordination at the azo moiety and no coordination). The possible coordination modes and the expected colorimetric behaviour are summarized in Scheme 2.

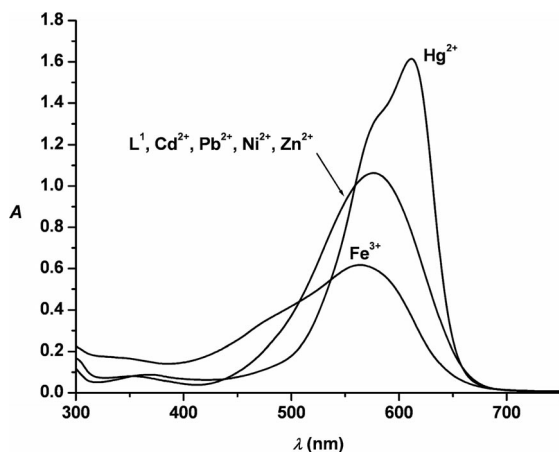


Scheme 2. Coordination modes and colorimetric behaviour of receptors **L**¹–**L**⁶ in the presence of metal cations.

Upon addition of equimolar quantities of Cd²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ cations to a solution of **L**¹ in acetonitrile, negligible changes in the UV/Vis spectrum profile were observed (see Figure 2), thereby indicating that very weak or no interaction of those cations with receptor **L**¹ occurs. In contrast, the addition of equimolar quantities of Hg²⁺ induced the charge-transfer band at 560 nm to be shifted to 612 nm and the appearance of a broad shoulder at 580 nm, which suggests a coordination of this metal cation with the azo-thiazole moiety. On the other hand, the presence of Fe³⁺ induced a blueshift of the absorption band of **L**¹ from 575 to 563 nm and the apparition of a new band at 485 nm. This behaviour suggested an interaction of this cation with the nitrogen of the aniline group. Those observed shifts were reflected in the colour of the **L**¹ solutions that modulated from dark violet to blue and red-magenta for Hg²⁺ and Fe³⁺, respectively. Upon the addition of increasing quantities of Hg²⁺ cation to solutions of **L**¹ in acetonitrile, clear isosbestic points were found that suggested the formation of 1:1 complexes. Monitoring the changes at 610 nm upon Hg²⁺ addition, and through nonlinear least-square treatment of the titration profile, a logarithm of the stability constant of 5.51 ± 0.01 for the formation of the [Hg(**L**¹)]²⁺ complex was obtained (see Table 3). Analogous titration studies with Fe³⁺ (monitoring the changes in the band at 575 nm) were carried out. In this case the complex stability constant log *K* for the formation of the complex [Fe(**L**¹)]³⁺ was determined to be 4.68 ± 0.02 .

Table 3. Logarithms of the stability constants of receptors L^1 – L^6 with Hg^{2+} and Pb^{2+} cations.

	L^1	L^2	L^3	L^4	L^5	L^6
Hg^{2+}	5.51 ± 0.02	4.79 ± 0.02	5.20 ± 0.2	5.33 ± 0.02	7.63 ± 0.09	4.93 ± 0.02
Pb^{2+}	–	–	–	6.17 ± 0.05	–	–

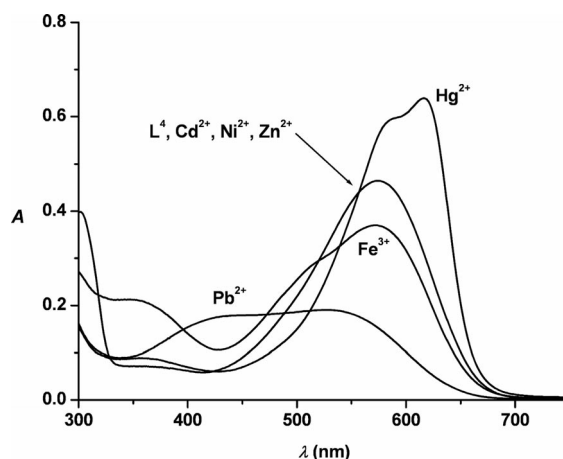
Figure 2. UV/Vis behaviour of receptor L^1 in acetonitrile ($C = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$) in the presence of 1 equiv. of certain metal cations.

The response presented by solutions of L^2 upon addition of equimolar quantities of metal cations was quite similar to that observed for L^1 (i.e., the Hg^{2+} metal cation coordinated the acceptor moiety and induced the apparition of two bands at 623 and 590 nm), whereas Fe^{3+} induced a hypochromic and blueshift from 574 to 568 nm and the development of a shoulder at 490 nm. The presence of other cations (i.e., Ni^{2+} , Zn^{2+} and Cd^{2+}) induced negligible changes in the visible spectrum of L^2 . The presence of isosbestic points in the titration studies of L^2 with Hg^{2+} suggest the formation of well-defined 1:1 complexes with $\log K = 4.79 \pm 0.02$ (see Table 3). Fe^{3+} gave more complicated titration patterns indicative of the formation of different coordination complexes.

Interestingly, receptors L^3 and especially L^4 behave differently in the sense that the inclusion of large crowns induces a change in selectivity trend when compared with L^1 . Receptors L^3 and L^4 contain one and two more oxygen atoms and one and two more ethylene bridges than the macrocycle in L^2 . For L^3 , the most significant feature was a hypochromic effect observed in the presence of Pb^{2+} that could be ascribed to a weak interaction with the nitrogen atom of the macrocyclic moiety. A similar reduction in the intensity of the absorption band was found for L^3 in the presence of Fe^{3+} . The lack of isosbestic points and the existence of complex titration patterns found for Fe^{3+} and Pb^{2+} precluded the determination of the stability constants. Addition of Hg^{2+} to solutions of L^3 resulted in similar behaviour to that found for L^1 and L^2 (i.e., the shift of the 575 nm absorption band of the ligand to 622 nm and the appearance of a new band at 589 nm). From titration studies a logarithm of the stability constant of 5.20 ± 0.2 for the formation of the $[Hg(L^3)]^{2+}$ complex was obtained. As in the

above cases, the redshift observed upon Hg^{2+} addition is ascribed to preferential coordination with the thiazolyazo acceptor moiety.

The hesitant selectivity trend towards Pb^{2+} found for L^3 is fully developed when using L^4 . This ligand contains the largest macrocyclic cavity that is able to accommodate a large cation such as Pb^{2+} (anionic radius 1.19 Å).^[21] In fact, the addition of equimolar quantities of Pb^{2+} to solutions of L^4 in acetonitrile induced the apparition of blueshifted bands at 526 and 430 nm together with an important reduction in the absorbance intensity (see Figure 3). This strongly suggests strong coordination with the lone pair of the nitrogen atom imbedded in the macrocycle. Least-squares treatment of the titration profiles allowed us to determine a logarithm of the stability constant of 6.17 ± 0.05 for the formation of the $[Pb(L^4)]^{2+}$ complex. It has to be noted that Pb^{2+} cation does not interact with L^1 and L^2 receptors. Apart from this distinct response towards Pb^{2+} cation, the presence of Hg^{2+} induced a similar behaviour to that found for receptors L^1 , L^2 and L^3 . From titration experiments a logarithm of the stability constant of 5.33 ± 0.02 for the formation of the $[Hg(L^4)]^{2+}$ complex was determined.

Figure 3. UV/Vis behaviour of receptor L^4 in acetonitrile ($C = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$) in the presence of 1 equiv. of certain metal cations.

Remarkably, L^5 behaves very differently to L^1 – L^4 and shows a selective response to Hg^{2+} due to the presence of sulfur atoms in the crown. In fact, several examples of chromogenic and fluorogenic receptors functionalized with macrocycles that contain two or more than two S atoms in its structure that selectively recognize Hg^{2+} cations have been described.^[22] In particular, the macrocycle **6** has been reported by us and others to selectively coordinate Hg^{2+} over other transition-metal cations.^[23] The presence in this macrocycle of two sulfur atoms close to the aniline nitrogen

atom has the ability to strongly shield the site against complexation with nonthiophilic cations. Solutions of **L**⁵ in acetonitrile show a charge-transfer band at 575 nm. Addition of equimolar amounts of Hg²⁺ induced a pronounced blueshift of the band to 406 nm with a colour change from blue to pale yellow (see Figure 4). This blueshift together with a high hypochromic effect is indicative of Hg²⁺ coordination within the macrocyclic subunit. This strong coordination with the crown was reflected in the high stability constant ($\log K = 7.63 \pm 0.09$) for the formation of [Hg(**L**⁵)]²⁺ complex calculated from titration profiles. This behaviour is clearly different to those shown by receptors **L**¹–**L**⁴. The presence of the two S atoms in the macrocycle also induces a different behaviour in receptor **L**⁵ in the presence of the Fe³⁺ in the sense that, in this case, preferential coordination with the thiazolylazo moiety occurs. This was reflected in a slight redshift of the absorption band that was observed upon addition of Fe³⁺ to solutions of **L**⁵. Titration profiles of receptor **L**⁵ with Fe³⁺ showed clear isosbestic points and least-squares treatment of the titration profiles indicated the formation of 1:1 complexes and a logarithm of the stability constant of 4.27 ± 0.08 for the formation of complex [Fe(**L**⁵)]³⁺ was calculated. As can be seen in Figure 4, receptor **L**⁵ acts as a selective chromogenic chemosensor for Hg²⁺ cation.

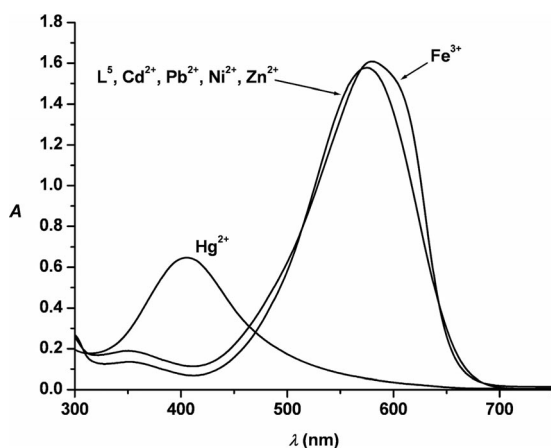


Figure 4. UV/Vis behaviour of receptor **L**⁵ in acetonitrile ($C = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$) in the presence of 1 equiv. of certain metal cations.

The change in the position of the S atoms in the macrocycle between **L**⁵ and **L**⁶ induced a remarkable change in the coordination behaviour of the latter. In this case, upon addition of one equivalent of Hg²⁺, the charge-transfer band at 560 nm was shifted to 570 nm and a broad shoulder appeared at 650 nm. Also a band at 375 nm was observed. The presence of these bands at longer and lower wavelengths seems to be indicative of the simultaneous formation of metal–aniline and metal–thiazolylazo complexes, although from the intensities of the bands, the formation of the thiazolylazo complexes appeared to be predominant. The remote position of the sulfur atoms with respect to the nitrogen in the macrocycle induced, upon coordination of

Hg²⁺ cation with the macrocyclic subunit in **L**⁶, poor interactions with the lone pair and a poor spectral response. Neither of the other cations tested induced significant changes in the visible spectrum of **L**⁶.

To get a better insight into the chromophoric nature in the presence of metal cations, the interaction of Hg²⁺ with compound **L**¹ in two different coordination modes was studied theoretically by using DFT quantum mechanical calculations. As carried out before for protonations, the energies of the electronic transitions for the different complexes were obtained from calculations based on the time-dependent (TD) formalism. As we have seen, the metals studied and the protons have a similar electronic effect when binding a given ligand. Both metal and protons accept electronic density that results in changes in the energies of HOMO and LUMO orbitals, therefore they have direct consequences on the energy of the ICLT band. In the interaction of the model compound **L**¹ with Hg²⁺, two coordination complexes were studied. In one model the Hg²⁺ cation was coordinated by the N2 and N4 atoms of **L**¹, whereas in the second model the Hg²⁺ cation coordinated the aniline N1. In the theoretical calculations the remaining positions of the coordination sphere of Hg²⁺ (tetrahedral geometry) were occupied by solvent (acetonitrile) molecules. TD calculations for the chelation by coordination in N2 and N4 predict moderate and intense ILCT electronic transitions at 613 and 576 nm that are very close to those experimentally observed (610 and 578 nm) for complexes of Hg²⁺ with ligands from **L**¹, **L**², **L**³, **L**⁴ and **L**⁶. Moreover, TD calculations for the complex with the Hg²⁺ coordination at the aniline anticipated the appearance of a band at 407 nm. This result is in very good agreement with that found for the interaction of Hg²⁺ with **L**⁵ that resulted in and electronic transition at 406 nm.

Conclusion

In summary, we have prepared and characterized a family of dyes (**L**¹–**L**⁶) that contain a thiazolylazo group as signalling subunit and several macrocyclic cavities with different ring sizes and type and number of heteroatoms as binding sites. Solutions of receptors **L**¹–**L**⁶ in acetonitrile showed absorption bands in the 554–577 nm range with typical molar absorption coefficients that ranged from 20000 to 32000 M^{−1} cm^{−1}. In these spectroscopic studies that involved protons, from the point of view of chemical addressability, ligands **L**¹–**L**⁶ possess four potential protonation sites (i.e., the aniline nitrogen, the two nitrogen atoms from the azo moiety and the thiazole ring). From experimental ¹H NMR spectroscopy data and theoretical studies carried out using DFT quantum mechanical calculations on the model ligand **L**¹, it was found that hypsochromic shifts were related to protonation at the aniline nitrogen, whereas bathochromic shifts dealt with coordination at the nitrogen of the azo moiety that is closer to the aniline group. A similar behaviour (hypsochromic and bathochromic shifts) were observed in solutions of **L**¹–**L**⁶ in acetonitrile in the

presence of the metal cations Fe^{3+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} . Additionally, a remarkable selective chromogenic response for L^4 in the presence of Pb^{2+} and for L^5 in the presence of Hg^{2+} was observed. Finally, the experimental chromogenic data found for L^1 – L^6 in the presence of Hg^{2+} cation was studied more in detail by using DFT calculations. Two different coordination modes were selected: coordination of the Hg^{2+} cation with the aniline that induced a hypsochromic shift and coordination of Hg^{2+} by two nitrogen atoms from the thiazolylazo group that resulted in a bathochromic shift. The calculations were in very good agreement with the experimental results.

Experimental Section

General Remarks: All commercially available reagents were used without further purification. Air-/water-sensitive reactions were performed in flame-dried glassware under argon. Acetonitrile was dried with CaH_2 and distilled prior to use.

Physical Measurements: Metal cations (Cd^{2+} , Fe^{3+} , Hg^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} as perchlorate or triflate salts) were used to obtain solutions of approximate concentration of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ in acetonitrile. Protonation studies were carried out with solutions of perchloric acid in acetonitrile. Photophysical studies of the behaviour of solutions of all the ligands in acetonitrile in the presence of the metal cations cited above and protons were carried out. The UV/Vis behaviour was studied with a Perkin–Elmer Lambda 35 spectrometer. The concentration of ligands used in the UV/Vis measurements was around $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile. UV/Vis spectra were recorded in the presence of equimolar quantities of all the ligands and the corresponding metal cations.

The ^1H and ^{13}C NMR spectra were recorded with a Varian–Gemini spectrometer. Chemical shifts are reported in ppm downfield from the TMS signal. Spectra taken in CDCl_3 were referenced to residual CHCl_3 . ^1H NMR spectroscopic studies in the presence of increasing quantities of protons were also carried out. For these protonation studies, the correspondent receptor (concentration of around $1.0 \times 10^{-2} \text{ mol dm}^{-3}$) were dissolved in deuterated acetonitrile and then titrated with perchloric acid.

Synthetic Procedures: The synthesis of macrocyclic subunits 3–7 were previously published.^[24] The synthesis of receptors L^1 and L^3 was also previously published.^[14,12]

General Procedure for the Synthesis of Thiazolylazo Derivatives L^1 – L^6 : Compound **1** was diazotated with NaNO_2 and HCl and subsequently treated with **2** or the corresponding phenyl macrocycle (3–7) dissolved in water solutions that contained acetic acid to give the correspondent receptors L^1 – L^6 as blue solids.

Synthesis of L^1 : In a round-bottomed flask, compound **1** (1320 mg, 9.1 mmol) was dissolved in a mixture (50 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO_2 (628 mg, 9.1 mmol) dissolved in water (15 mL) was added. After 10 min, compound **2** (1000 mg, 8.26 mmol) dissolved in HCl /water (5:1 v/v, 50 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH_2Cl_2 and the organic phase washed with aqueous NaHCO_3 solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1 v/v) as eluent. The final receptor L^1 (1373 mg, 4.96 mmol) was iso-

lated as a dark blue solid; yield 60%. ^1H NMR (300 MHz, $[\text{D}_6]$ -DMSO): δ = 3.20 [s, 6 H, $\text{N}-(\text{CH}_3)_2$], 6.77 (d, 2 H, C_6H_4), 7.91 (d, 2 H, C_6H_4), 8.58 (s, 1 H, thiazole) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 40.3, 112.7, 143.1, 143.8, 147.0, 154.2, 181.4 ppm. HRMS calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_5\text{O}_2\text{S}$ 207.0633; found 207.0689.

Synthesis of L^2 : In a round-bottomed flask, compound **1** (100 mg, 0.69 mmol) was dissolved in a mixture (5 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO_2 (47.6 mg, 0.69 mmol) dissolved in water (1.5 mL) was added. After 10 min, macrocycle **3** (158 mg, 0.63 mmol) dissolved in HCl /water (5:1 v/v, 5 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH_2Cl_2 and the organic phase washed with aqueous NaHCO_3 solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1 v/v) as eluent. The final receptor L^2 (102.5 mg, 0.25 mmol) was isolated as a dark blue solid; yield 40%. ^1H NMR (300 MHz, $[\text{D}_6]$ -DMSO): δ = 3.65 (s, 8 H, $\text{O}-\text{CH}_2-\text{O}$), 3.76 (t, 4 H, $\text{N}-\text{CH}_2-\text{O}$), 3.80 (t, 4 H, $\text{O}-\text{CH}_2-\text{O}$), 6.78 (d, 2 H, C_6H_4), 7.91 (d, 2 H, C_6H_4), 8.58 (s, 1 H, thiazole) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 53.5, 70.0, 70.4, 71.3, 112.7, 143.1, 143.8, 147.0, 154.2, 181.4 ppm. HRMS calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_5\text{O}_5\text{S}$ 407.1263; found 407.1275.

Synthesis of L^3 : In a round-bottomed flask, compound **1** (100 mg, 0.69 mmol) was dissolved in a mixture (5 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO_2 (47.6 mg, 0.69 mmol) dissolved in water (1.5 mL) was added. After 10 min, macrocycle **4** (186 mg, 0.63 mmol) dissolved in HCl /water (5:1 v/v, 5 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH_2Cl_2 and the organic phase washed with aqueous NaHCO_3 solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1 v/v) as eluent. The final receptor L^3 (117 mg, 0.26 mmol) was isolated as a dark blue solid; yield 41%. ^1H NMR (300 MHz, $[\text{D}_6]$ -DMSO): δ = 3.65 (s, 4 H, $\text{O}-\text{CH}_2-\text{O}$), 3.68 (m, 12 H, $\text{O}-\text{CH}_2-\text{O}$ and $\text{N}-\text{CH}_2-\text{O}$), 3.83 (t, 4 H, $\text{O}-\text{CH}_2-\text{O}$), 6.79 (d, 2 H, C_6H_4), 7.89 (d, 2 H, C_6H_4), 8.56 (s, 1 H, thiazole) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 53.1, 68.3, 70.1, 70.5, 71.3, 112.9, 142.8, 143.6, 147.2, 154.1, 181.7 ppm. HRMS calcd. for $\text{C}_{19}\text{H}_{25}\text{N}_5\text{O}_6\text{S}$ 451.1526; found 451.1511.

Synthesis of L^4 : In a round-bottomed flask, compound **1** (100 mg, 0.69 mmol) was dissolved in a mixture (5 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO_2 (47.6 mg, 0.69 mmol) dissolved in water (1.5 mL) was added. After 10 min, macrocycle **5** (213.6 mg, 0.63 mmol) dissolved in HCl /water (5:1 v/v, 5 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH_2Cl_2 and the organic phase washed with aqueous NaHCO_3 solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1 v/v) as eluent. The final receptor L^4 (139 mg, 0.28 mmol) was isolated as a dark blue solid; yield 45%. ^1H NMR (300 MHz, $[\text{D}_6]$ -DMSO): δ = 3.71–3.85 (m, 24 H, $\text{O}-\text{CH}_2-\text{O}$ and $\text{N}-\text{CH}_2-\text{O}$), 6.80 (d, 2 H, C_6H_4), 7.93 (d, 2 H, C_6H_4), 8.60 (s, 1 H, thiazole) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 51.2, 68.4, 70.7, 70.9, 113.0, 143.5, 144.2, 147.6, 153.9, 183.5 ppm. HRMS calcd. for $\text{C}_{21}\text{H}_{29}\text{N}_5\text{O}_7\text{S}$ 495.1788; found 495.1769.

Synthesis of L⁵: In a round-bottomed flask, compound **1** (100 mg, 0.69 mmol) was dissolved in a mixture (5 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO₂ (47.6 mg, 0.69 mmol) dissolved in water (1.5 mL) was added. After 10 min, macrocycle **6** (206 mg, 0.63 mmol) dissolved in HCl/water (5:1 v/v, 5 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH₂Cl₂ and the organic phase washed with aqueous NaHCO₃ solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and CH₂Cl₂/CH₃CN (9:1 v/v) as eluent. The final receptor L⁵ (145 mg, 0.3 mmol) was isolated as a dark blue solid; yield 48%. ¹H NMR (300 MHz, [D₆]-DMSO): δ = 2.76 (t, 4 H, S-CH₂-S), 2.93 (t, 4 H, S-CH₂-S), 3.63 (s, 4 H, O-CH₂-O), 3.80 (m, 8 H, S-CH₂-N, O-CH₂-O), 6.78 (d, 2 H, C₆H₄), 7.92 (d, 2 H, C₆H₄), 8.60 (s, 1 H, thiazole) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 29.6, 31.7, 52.4, 70.8, 74.4, 112.4, 143.5, 144.5, 147.6, 154.7, 182.1 ppm. HRMS calcd. for C₁₉H₂₅N₅O₄S₃ 483.1069; found 483.1075.

Synthesis of L⁶: In a round-bottomed flask, compound **1** (100 mg, 0.69 mmol) was dissolved in a mixture (5 mL) of acetic acid and water (5:1 v/v). The crude material was cooled with an ice bath. Then NaNO₂ (47.6 mg, 0.69 mmol) dissolved in water (1.5 mL) was added. After 10 min, macrocycle **7** (206 mg, 0.63 mmol) dissolved in HCl/water (5:1 v/v, 5 mL) was added dropwise to the crude reaction mixture. Then the crude mixture was allowed to react for 30 min in an ice bath and for 60 min at room temperature. The crude reaction mixture was extracted with CH₂Cl₂ and the organic phase washed with aqueous NaHCO₃ solution. The crude reaction mixture was purified with column chromatography by employing aluminium oxide as the stationary phase and CH₂Cl₂/CH₃CN (9:1 v/v) as eluent. The final receptor L⁶ (121 mg, 0.25 mmol) was isolated as a dark blue solid; yield 40%. ¹H NMR (300 MHz, [D₆]-DMSO): δ = 2.80 (t, 4 H, S-CH₂-S), 2.91 (t, 4 H, S-CH₂-S), 3.73 (s, 4 H, O-CH₂-O), 3.87 (m, 8 H, S-CH₂-N, O-CH₂-O), 6.77 (d, 2 H, C₆H₄), 7.93 (d, 2 H, C₆H₄), 8.59 (s, 1 H, thiazole) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 31.8, 33.0, 51.6, 70.5, 72.7, 112.4, 142.7, 143.8, 147.3, 154.7, 182.3 ppm. HRMS calcd. for C₁₉H₂₅N₅O₄S₃ 483.1069; found 483.1057.

Computational Details: Calculations were performed with the Gaussian 09 package using the B3LYP functional and the quadratic convergence approach.^[25] Double- ζ all-electron basis sets proposed by Ahlrichs et al. were used for all atoms except for the mercury atom, for which valence double- ζ proposed by Dunning and Huzinaga and Los Alamos electron core pseudopotential were used.^[26] Molecular geometries were optimized for the used molecules. To optimize the computational time, the organic skeleton involved in the studied charge-transfer band – formed by aniline, azo and thiazole groups – was frozen in metallic complexes. Energies and oscillator strengths of the electronic transitions were obtained from calculations based on the time-dependent formalism.^[27] In such cases, a polarizable continuum model (PCM) with the parameters that correspond to the acetonitrile was used to simulate the electronic effects of the solvent.^[28]

Supporting Information (see footnote on the first page of this article): ¹H NMR and UV/Vis titrations.

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Iron Coordination Chemistry of N₂Py₂ Ligands Substituted by Carboxylic Moieties and Their Impact on Alkene Oxidation Catalysis

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A biomimetic approach based on Rieske dioxygenase mimics has been undertaken, which uses the tetradentate N₂Py₂ ligand platform that contains two pyridine moieties linked to a 1,2-diaminoethane or a *trans*-1,2-diaminocyclohexane backbone. Here we report the impact of the incorporation of carboxylic functionalities with the N₂Py₂ ligand on the catalytic efficiency of its Fe^{II} complexes during epoxidation with H₂O₂ as the oxidant. Five complexes have been characterized in the solid state and solution. The X-ray structure of a ferrous complex with a ligand that contains two carboxylic acid moieties shows an unexpected N₄O₃-type iron coordina-

tion sphere. Moreover, the two carboxylic groups of the ligand remain protonated and bound by its sp² oxygen atom. Two substitutions of the ligand with carboxylic moieties was found to be deleterious to the reactivity of the complex during alkene oxidation, whereas monosubstitution led to a slight change in the reactivity. Moreover, the catalyst built from the optically active *trans*-1,2-diaminocyclohexane backbone, **L**³, catalyzes the asymmetric epoxidation of *trans*-2-heptene with up to 17 % yield. The addition of acetic acid leads to better selectivity, enantioselectivity (38 %), and yield of the epoxidation of nonaromatic alkenes.

Introduction

The design of homogeneous catalysts for oxidation remains a great challenge. In general, the state-of-the-art consists of catalytic processes that are environmentally friendly, use inexpensive catalysts, less energy-consuming protocols, and the use of sustainable oxidants.^[1] One strategy lies in mimicking metalloenzymes, by tentatively reproducing the environment of mono- or dioxygenase active sites. The targeted active site of nonheme iron oxygenases, which consists of a mononuclear iron(II) center coordinated by the so-called 2-His-1-carboxylate facial triad, has been a great source of inspiration (Figure 1).^[2]

For instance Rieske dioxygenases, such as naphthalene dioxygenase (NDO), catalyze a stereospecific *cis*-dihydroxylation during the biodegradation of arenes.^[2b,3] This metal-promoted biological oxidation has been particularly targeted for the development of bioinspired catalysts because they fulfill some of the requirements listed above and

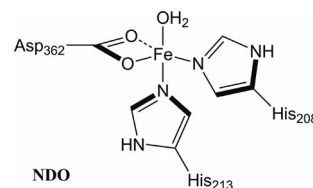


Figure 1. Representation of the catalytic iron site of NDO from *Pseudomonas* sp. NCIB 9816-4.^[2b]

perform the consumption of very inert substrates. A large number of synthetic nonheme complexes has been developed as potential oxidation catalysts. Among them, catalysts based on the full reproduction of the active site of Rieske dioxygenases were found to be poorly active with H₂O₂ as the oxidant, which suggests that the presence of carboxylic groups plays an important role on the reactivity.^[4] These outcomes contrast with the promising development of iron catalysts that contain tetradentate pyridine/amine (N₂Py₂) ligands with H₂O₂ as the oxidant.^[5] Indeed, selective alkane functionalization has been reported with Fe[(*S,S*)-PDP] [(*S,S*)-PDP = 2-((*S*)-2-[(*S*)-1-(pyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl)methylpyridine]^[6] and [Fe(*S,S,R*)-mcpp](CF₃SO₃)₂ [mcpp = *N,N'*-dimethyl-*N,N'*-bis(4,5-pinen-2-picolyl)cyclohexane-1,2-diamine].^[7] Alkene oxidation has also been extensively studied,^[8] which revealed that the product formation, epoxide^[8d–8f] or *cis*-diols,^[8g,8h] can be controlled by Fe(BPMEN) [BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-di-

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amine],^[8d] Fe(bispidine),^[8e] Fe(terpyridine),^[8f] Fe(TPA),^[8g] or Fe(diazapyridinophane)^[8h] as catalysts. A chiral N₂Py₂ ligand has led to enantioselective *cis*-dihydroxylation up to 99% *ee*, but this family of catalysts remains inefficient for enantioselective epoxidation.^[9] The selectivity for epoxidation versus *cis*-dihydroxylation is partly dependent on the presence of carboxylic acids in the reaction medium, but their effect on the enantioselectivity has not been reported. This additive was proposed to control the active species by the coordination of its acid form to a η^1 -Fe-peroxo species, which is a precursor of the oxidizing iron species. This helped to favor heterolytic cleavage of the O–O bond by the transfer of its proton to the distal oxygen atom of the hydroperoxo adduct. The resulting high-valent iron species epoxidized the alkene substrate with retention of configuration.^[10]

Carboxylic functionalities have controversial effects on the efficiency of iron catalysts for the epoxidation of alkenes. The acidic form is of great interest for selectivity but the basic form may bind to iron, which leads to the drastic change to the electronic properties of the iron and then to a well documented loss of catalyst efficiency.^[11] To circumvent this antagonistic effect, we have undertaken the design of iron catalysts using the N₂Py₂ platform [BPMEN or BPMCN, BPMCN = *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-*trans*-1,2-diaminocyclohexane],^[8c] to which one or two carboxylic moieties have been introduced (Figure 2). Three new ligands have been synthesized, which differ in the number of carboxylic functional groups and/or the nature of the strap connecting the two 2-pyridylmethylamine units (Figure 2). Achieving the aim of this work relies on the design of complexes in which a carboxylic acid func-

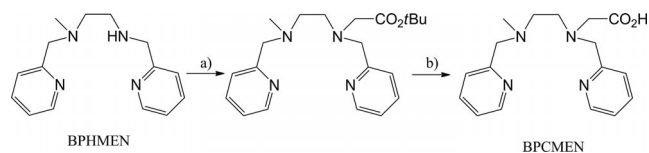
tional group is maintained close to the iron center in order to mimic the proposed essential catalytic transition state.^[10] Ferrous, instead of ferric, complexes were targeted, which enabled us to retain the acidic form of the carboxylic moieties of the ligand as the Lewis acidity of the ferrous state is lower than that of the ferric state.

Herein we report the synthesis and characterization of five new ferrous complexes with **L**¹, **L**², **L**³, and **L**⁴. The synthesis of the ferrous complexes was found to be counteranion dependent, and the complexes were formed with chloride or more weakly coordinating (ClO₄) ligands. All the complexes were characterized by various spectroscopic techniques in solution and in the solid state, which support the description of the complexes as hexa- or hepta-coordinate with bound carboxylic moieties. The complexes were tested in epoxidation catalysis, which revealed the impact of the intrinsic carboxylic group on the reactivity and enantioselectivity.

Results and Discussion

Ligands Syntheses

The synthesis of **L**¹ has already been described,^[12] but as the direct insertion of a carboxymethyl arm to BPMEN gave neither satisfactory yield, purity, or degree of protonation, we decided to insert the carboxylic moiety by a two-step route: alkylation by *tert*-butyl 2-bromoacetate followed by smooth, quantitative hydrolysis by trifluoroacetic acid (Scheme 1). The sensitivity of *tert*-butyl 2-bromoacetate precludes the use of strong bases. Because of its intrinsic basicity, BPMEN was converted into its insoluble hydrobromide salt, which led to a limitation of the yield of 50% for the alkylation step. Nevertheless, BPMEN·HBr was recycled. This afforded a suitable synthetic pathway that was applied to the synthesis of **L**², **L**³, and **L**⁴. **L**³ and **L**⁴ incorporate the chiral *trans*-diaminocyclohexane backbone, (1*S*,2*S*) for **L**³ and (1*R*,2*R*) for **L**⁴. The chiral diamines were used directly for the corresponding synthesis of **L**³ and **L**⁴.



Scheme 1. a) *tert*-Butyl 2-bromoacetate, K₂CO₃, CH₃CN, 0 °C, 3 h. b) CF₃CO₂H, CH₂Cl₂, 0 °C/30 min, room temp./17 h.

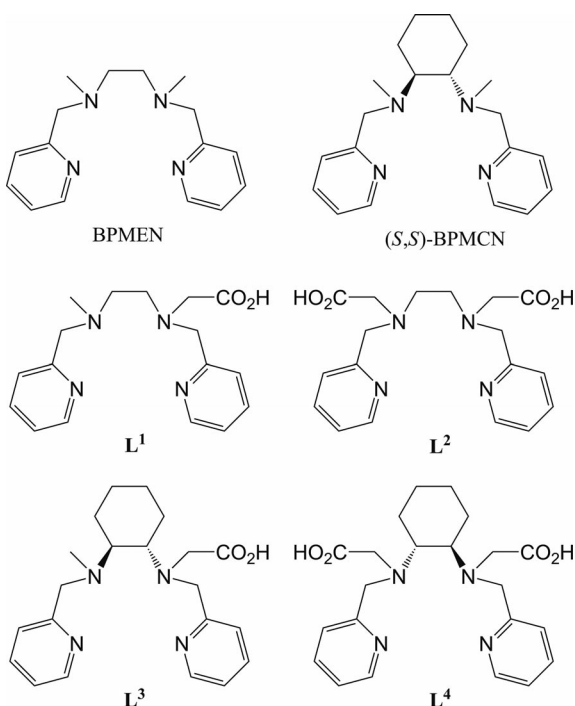


Figure 2. Representation of the ligands described in this study.

Characterization of the Iron Complexes

New mononuclear complexes with potentially hexadentate **L**² and **L**⁴ and pentadentate **L**¹ and **L**³ ligands have been prepared. We tackled ferrous complexes as the Lewis acidity of the oxidation state is lower than that of the ferric one. Consequently, the ferric state of the complexes excludes the retention of carboxylic forms, whereas the ferrous state allows them to coexist in the same complex. To

prevent oxidation of the iron(II) complexes, they were all synthesized in a glove box. Initially, FeCl_2 was used to ensure a stable coordination sphere. As the formed chlorinated complexes did not precipitate in some cases, we switched to the use of $\text{Fe}(\text{ClO}_4)_2$ salts. The complexes were synthesized by reacting 1 equiv. of $\text{Fe}(\text{ClO}_4)_2$ with 1 equiv. of the ligand. When FeCl_2 was used, 2 equiv. of iron salt were required to maximize the yield. In some cases, powder was deposited as a function of time, otherwise diethyl ether was added to precipitate the product. All the complexes were characterized by IR, UV/Vis, and NMR spectroscopy, ESI-MS, and elemental analysis. The presence of $[\text{FeCl}_4]^{2-}$ as a counteranion for $[\text{Fe}(\text{BPMCn})(\text{C}_3\text{H}_6\text{O})]^{2+}$ and $[\text{Fe}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})]^{2+}$ was deduced from spectroscopic studies (vide infra) and supported by satisfactory elemental analyses, in which the presence of the $\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3$ dianion, which is the product of the air oxidation of $[\text{FeCl}_4]^{2-}$, was determined. Thanks to elemental analysis we were also able to propose stoichiometries between FeL^n and the FeCl_4 counteranion. For example, in the case of the coordination of L^4 to iron, the presence of an extra chloride ligand to complete the coordination sphere led to the presence of a FeCl_4 counteranion for two cationic species. The structures of all the complexes were deduced by comparison of their spectroscopic properties with those of the crystallographically characterized $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$.

X-ray Crystallography of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$

Colorless crystals of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ suitable for X-ray analysis were obtained from the slow evaporation of an acetone solution of the complex in a glove box. The ORTEP representation of the cation is displayed in Figure 3. L^4 wraps around the ferrous ion, which is heptacoordinate. The polyhedron of the iron atom is a distorted pentagonal bipyramid, in which the two nitrogen atoms from the amine moieties, the sp^2 oxygen atoms of the two carboxylic moieties of the ligand, and the acetone solvent molecule form the equatorial plane. The two pyridyl rings occupy the axial positions and have a dihedral angle of 82.4° . This unexpected N_4O_3 coordination derives from the full coordination of the ligand, of which the four nitrogen atoms are in a “cis α ” topology and the two oxygen atoms are from the protonated form of the carboxylic ligand moieties, with an oxygen atom from a solvent molecule (this topology was based on a previously reported N_2Py_2 complex).^[8c,13] The Fe–N distances range from 2.161(3) Å, which are associated with the pyridine nitrogen atoms, to 2.308(3) Å, which are associated with the amino nitrogen atoms (Table 1). These values are different to those reported for $[\text{Fe}^{\text{II}}(\text{BPMCn})](\text{CF}_3\text{SO}_3)_2$ or $[\text{Fe}^{\text{II}}(5\text{-Me-BPMCn})](\text{CF}_3\text{SO}_3)_2$, as longer Fe– N_{amine} bonds were measured in $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$, although the variation between the different Fe–N bonds (pyridine or amine functionalities) followed the same trend.^[8c] The lower symmetry of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ and the protonation of the ligand may be responsible for the longer bonds. The Fe–O bonds are mostly long (around 2.39 Å) with the exception of that involving the acetone ligand [2.172(2) Å]. These values indicate that the carboxylic

moieties of the ligand are protonated as Fe^{II}–O distances of 2.00–2.15 Å are generally reported for carboxylate ligands.^[4a] The coordination mode of the carboxylic groups is rare in a discrete iron complex and has only been reported with two polynuclear species in which the carboxylic moiety connects two iron sites.^[14] Finally, the Fe–O bond length in $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ is long compared to that of another sp^2 oxygen atom–Fe^{II} bond, which involves an amido ligand.^[15] Taken together, the ligand distances agree with a high-spin configuration of the ferrous ion in the solid state. Seven-coordinate iron complexes are unusual, even if iron complexes have been more extensively described than their congeners.^[16] Usually, examples of ferric complexes predominate over ferrous complexes.^[17]

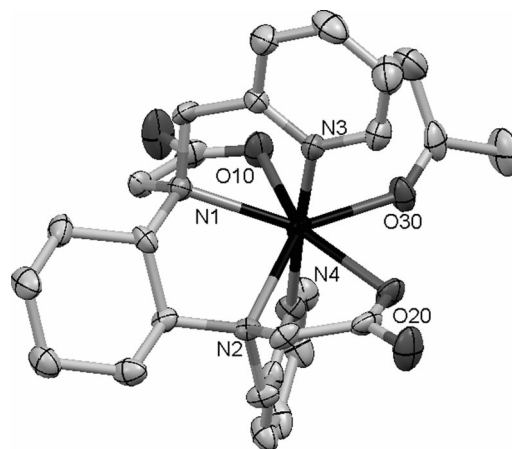


Figure 3. ORTEP representation of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})]^{2+}$. Hydrogen atoms are omitted for clarity.

Table 1. Bond lengths [Å] and angles [°] for $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$.

Fe ¹ –N ¹	2.308(3)	Fe ¹ –N ²	2.300(3)
Fe ¹ –N ³	2.162(3)	Fe ¹ –N ⁴	2.163(3)
Fe ¹ –O ¹⁰	2.292(2)	Fe ¹ –O ²⁰	2.288(2)
Fe ¹ –O ³⁰	2.172(2)		
N ¹ –Fe ¹ –N ²	76.96(10)	N ¹ –Fe ¹ –N ³	75.64(11)
N ¹ –Fe ¹ –N ⁴	106.94(10)	N ² –Fe ¹ –N ³	104.47(11)
N ² –Fe ¹ –N ⁴	76.50(11)	N ³ –Fe ¹ –N ⁴	177.41(11)
N ¹ –Fe ¹ –O ¹⁰	70.27(10)	N ¹ –Fe ¹ –O ²⁰	136.65(10)
N ¹ –Fe ¹ –O ³⁰	142.95(10)	N ² –Fe ¹ –O ¹⁰	133.05(10)
N ² –Fe ¹ –O ²⁰	70.80(9)	N ² –Fe ¹ –O ³⁰	140.01(10)
N ³ –Fe ¹ –O ¹⁰	99.00(11)	N ³ –Fe ¹ –O ²⁰	85.06(10)
N ³ –Fe ¹ –O ³⁰	92.27(10)	N ⁴ –Fe ¹ –O ¹⁰	81.87(11)
N ⁴ –Fe ¹ –O ²⁰	93.05(10)	N ⁴ –Fe ¹ –O ³⁰	85.53(11)
O ¹⁰ –Fe ¹ –O ²⁰	152.23(8)	O ¹⁰ –Fe ¹ –O ³⁰	77.48(9)
O ²⁰ –Fe ¹ –O ³⁰	74.90(9)		

Solid-State IR Spectroscopy

All the IR spectra of the complexes displayed characteristic features in the 1400–1750 cm^{-1} region (Figure 4). In the case of $[\text{Fe}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$, three resonances were observed, two narrow ones at 1676 and 1607 cm^{-1} that flank a broader one around 1650 cm^{-1} (Figure 4, A). The low energy peak is attributed to the asymmetric C=O vibrations of the bound acetone by comparison with literature values,^[18] that at 1607 cm^{-1} to $\nu_{\text{C}=\text{N}}$ of the pyridine

rings, whereas the broad band corresponds to $\nu_{\text{COOH}_{\text{as}}}$ of the bound carboxylic groups in the complex. This energy value is between that of free ν_{COOH} (above 1750 cm^{-1}) and coordinated ν_{COO^-} ($1700\text{--}1510\text{ cm}^{-1}$).^[19] In addition, $\nu_{\text{COOH}_{\text{s}}}$ is located at 1437 cm^{-1} , which implies a $\Delta(\nu_{\text{s}}-\nu_{\text{as}})$ of 213 cm^{-1} , a value characteristic of monodentate binding modes. In the case of $[\text{Fe}^{\text{II}}(\text{L}^2)](\text{ClO}_4)_2$, the same ν_{COOH} resonance was observed at 1635 cm^{-1} but no narrow peak was detected in this region, which indicates the absence of acetone as a ligand.

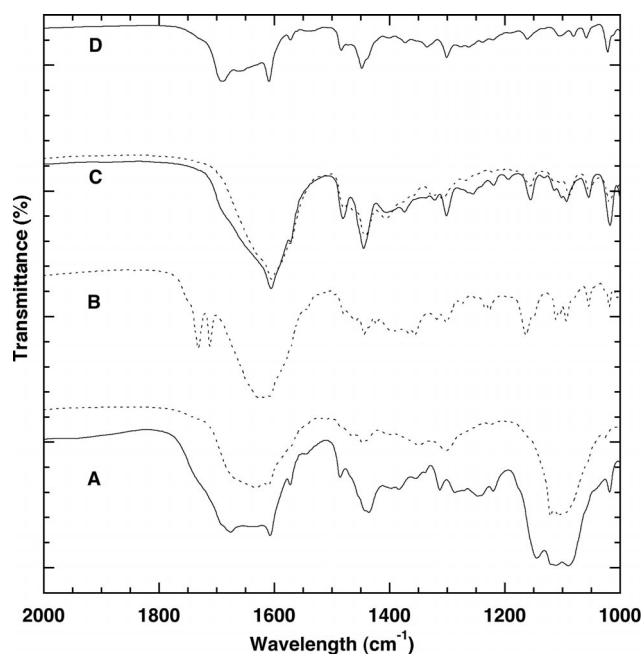


Figure 4. IR spectra of the iron complexes (solid lines for ligands with a cyclohexane moiety and dashed for ligands with an ethane moiety): **A** for $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ and $[\text{Fe}^{\text{II}}(\text{L}^2)](\text{ClO}_4)_2$; **B** for $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{Cl})]_2(\text{FeCl}_4)$; **C** for $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ and $[\text{Fe}^{\text{II}}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$; **D** for $[\text{Fe}^{\text{III}}(\text{L}^3)(\text{Cl})](\text{Fe}^{\text{III}}\text{Cl}_4)$.

In the spectrum of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{Cl})]_2(\text{FeCl}_4)$, two ν_{COOH} bands were observed, one at 1732 cm^{-1} , which is characteristic of a free carboxylic acid, and the other broad one around 1640 cm^{-1} , which is common to these species (Figure 4, B). The latter component was also observed in the spectra of $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ and $[\text{Fe}^{\text{II}}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ (Figure 4, C). The change in oxidation state of the metal in $[\text{Fe}^{\text{III}}(\text{L}^3)](\text{FeCl}_4)$ caused the slight shift of this transition to 1690 cm^{-1} , which indicates a different coordination mode or a different protonation state of the carboxylic/carboxylate moiety (Figure 4, D) (see below).

ESI-MS in Acetone

All the MS of the deoxygenated solutions of the complexes displayed a $[\text{Fe}^{\text{II}}\text{L} - \text{H}]^+$ fragment in the positive mode, which confirms the mononuclearity of the complex in solution. For $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$, a dicationic $[\text{FeL}]^{2+}$ fragment was observed as well as a fragment that contains the ClO_4 counteranion, which suggests that the carboxylic functionalities of the ligand were totally protonated in the starting solution. In the spectra of $[\text{Fe}^{\text{II}}(\text{L}^3)-$

$(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ and $[\text{Fe}^{\text{II}}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$, a peak at $m/z = 160.8$ was detected in the negative mode, which was attributed to $[\text{Fe}^{\text{II}}\text{Cl}_3]^-$, a footprint of the unstable $[\text{Fe}^{\text{II}}\text{Cl}_4]^{2-}$ fragment. This was replaced in the spectrum of $[\text{Fe}^{\text{III}}(\text{L}^1)(\text{Cl})](\text{FeCl}_4)$ with a peak at $m/z = 197.2$, which corresponds to $[\text{Fe}^{\text{III}}\text{Cl}_4]^-$. No evidence of a $\text{Cl}_6\text{Fe}_2\text{O}$ fragment (deduced from the elemental analysis) was found.

UV/Vis Spectroscopy in Acetone

Two patterns of transitions were observed in the electronic spectra recorded under argon. First, only one transition in the near UV was observed for the perchlorate complexes, at 342 nm for $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ and 310 nm for $[\text{Fe}^{\text{II}}(\text{L}^2)](\text{ClO}_4)_2$ with similar extinction coefficients in the $1500\text{--}4000\text{ cm}^{-1}\text{ m}^{-1}$ range, which is attributed to iron-to-nitrogen metal-to-ligand charge transfer.^[20] Second, the UV/Vis spectra of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{Cl})]_2(\text{FeCl}_4)$, $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$, and $[\text{Fe}^{\text{II}}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ are dominated by two transitions at 360 and 310 nm with extinction coefficients of around $2000\text{ cm}^{-1}\text{ m}^{-1}$, which are absent in the spectra of their ClO_4^- counterparts. Interestingly, these bands were also present but more intense in the spectrum of $[\text{Fe}^{\text{III}}(\text{L}^1)(\text{Cl})](\text{FeCl}_4)$, which suggests that they originate from the counteranion (Figure 5). The energy values of these transitions were found to be identical to those found in literature for the $\text{Fe}^{\text{III}}\text{Cl}_4^-$ anion.^[21] However, the extinction coefficients are lower in our case, which indicates that the ferrous anion (FeCl_4) was partly oxidized during the measurements.

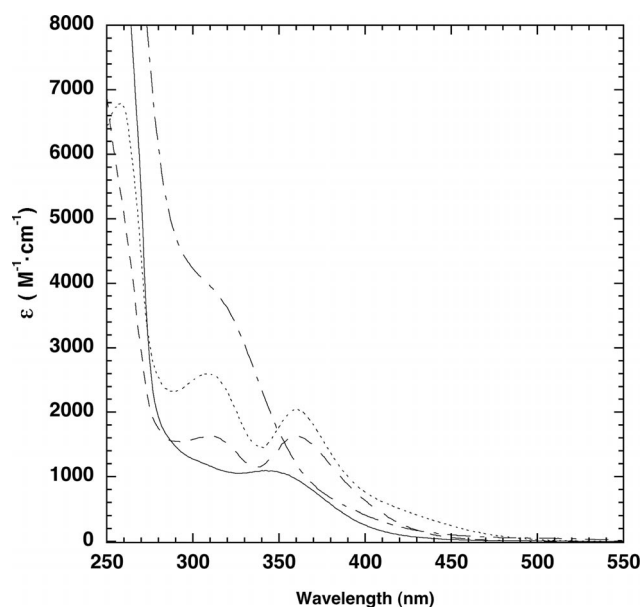


Figure 5. UV/Vis spectra of acetonitrile solutions of $[\text{Fe}^{\text{II}}(\text{L}^2)](\text{ClO}_4)_2$ (---), $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ (-.-.-), $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{Cl})]_2(\text{Fe}^{\text{II}}\text{Cl}_4)$ (····), and $[\text{Fe}^{\text{II}}(\text{BPMCN})](\text{Fe}^{\text{III}}\text{Cl}_4)$ (—).

This outcome was confirmed by oxygenation of the acetonitrile solutions of the ferrous complexes (Figure 6). We observed the increase in intensity of the two transitions at 360 and 310 nm for all the chlorinated complexes to the level of the exact extinction coefficient of the $\text{Fe}^{\text{III}}\text{Cl}_4^-$ anion

itself. Consequently, the formation of the ferric anion arises from the oxidation of the $\text{Fe}^{\text{II}}\text{Cl}_4$, which does not have visible transitions.^[21–22] The absorbance measured at 360 and 310 nm is in accordance with a ratio of 1:1 between the iron cation and its counteranion.

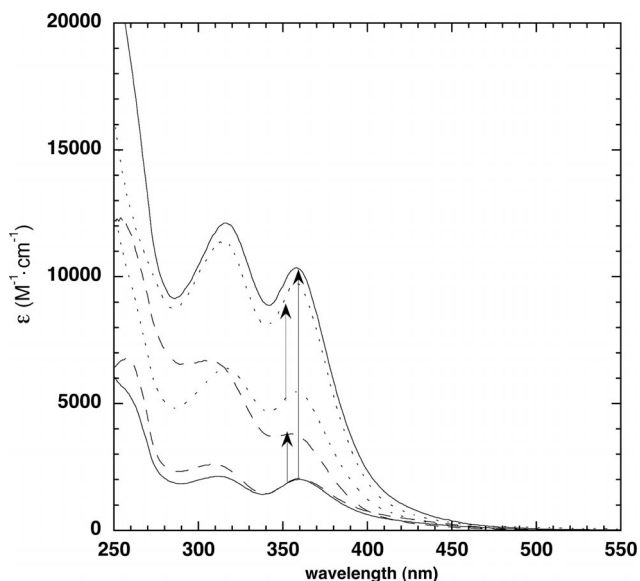


Figure 6. UV/Vis spectra of acetonitrile solutions of $[\text{Fe}(\text{BPMCN})](\text{FeCl}_4) \pm \text{O}_2$ (—); $[\text{Fe}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4) \pm \text{O}_2$ (···); $[\text{Fe}(\text{L}^4)(\text{Cl})]_2(\text{FeCl}_4) \pm \text{O}_2$ (---). Arrows indicate the absorption changes in the presence of dioxygen.

¹H NMR Spectroscopy in $[\text{D}_6]$ Acetone

¹H NMR spectroscopy has been shown to be a powerful tool for probing the structural and magnetic properties of iron complexes.^[17,23] All the spectra (Figure 7) spanned between 170 to -40 ppm, which attests that all the complexes contain high-spin ferrous species in solution. As the resonance pattern of the NMR spectra of the complexes is reminiscent of the ligand conformation, it was possible to propose a structural topology of the ligand for most of them. First, the spectra of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ and its analog $[\text{Fe}^{\text{II}}(\text{L}^2)](\text{ClO}_4)_2$ consist of broad resonances above 70 ppm, which are assigned to *o*-H of the pyridine rings and the methylene proton resonances (Figure 7). The two narrow resonances that flank a broader one in the 40–60 ppm region, are attributed to *m*-H of the pyridine rings and the methylene protons. The upfield resonance at -12 ppm is tentatively assigned to *p*-protons by comparison with earlier studies.^[20] The difference in the pattern of the two spectra in the 0–110 ppm region is attributed to the presence of the extra methylene protons of the strap between the two nitrogen atoms in L^2 compared to L^4 .

The *o*-protons are all equivalent and show a resonance at 130 ppm, which indicates that the complexes have a high symmetry. This is in agreement with the conservation of the *cis* α topology in solution. The presence of bound acetone could not unambiguously be attributed in the spectrum of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$, which indicates its facile exchange with a solvent molecule.

The ¹H NMR spectrum of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{Cl})]_2(\text{FeCl}_4)$ was different to that of its ClO_4^- congener (Figure 7). The resonance pattern looked similar, except the loss of low-field resonances above 50 ppm, which was attributed to a change in ligand topology as *o*-H pyridine proton resonances are the most affected by the relative positions of the pyridine rings.^[13] We propose that the ligand conformation was *cis* β , which leads to distinct pyridine positions in the complex structure. This leads to each *o*-H resonance becoming distinct and merging with the baseline. Moreover, the spectrum looked similar to that of the ferrous BPMCN complex, which was prepared by adding FeCl_2 to BPMCN in acetone. Despite the absence of X-ray structural analysis, the topology of the BPMCN complex can be deduced from an anion metathesis experiment to exchange the Cl^- ion by triflate (OTf). It has been reported that BPMCN isomers do not interconvert, which allows the structural characterization of both *cis*- α - and *cis*- β - $[\text{Fe}^{\text{II}}(\text{BPMCN})](\text{OTf})_2$.^[13,24] Interestingly, their syntheses involved the metathesis reaction pathway with its chlorinated analog in CD_3CN .^[13] Using the same procedure, the ¹H NMR spectroscopic pattern observed after metathesis was identical to that of β - $[\text{Fe}^{\text{II}}(\text{BPMCN})(\text{CD}_3\text{CN})_2]^{2+}$, which indicates a *cis* β topology for the BPMCN complex (Figure S3).^[13,24]

The ¹H NMR spectrum of $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$ has a complex pattern of resonances spanning between 160 and -10 ppm (Figure 7), which was attributed to the superposition of two close but distinct spectra with at least 26 proton resonances for each. It is tempting to relate this signature to the coexistence of two related topologies of the ligand. As both substituents on the amino nitrogen atoms of the ligand are different (Me versus carboxymethyl), two topologies in a similar proportion are generated only for the asymmetric geometry, i.e. *cis* β (opposite to *trans* and *cis* α). In the case of L^1 , the spectrum was also very complex, which indicated that several isomers were present. In this case, the broadness of some peaks precluded an extensive interpretation of the pattern. At least we can suggest the presence of *cis* α and β conformations in nonequivalent proportions as the *trans* topology has not been observed for this type of ligand.

Based on a comparison of the solution and solid-state spectroscopic studies of all the complexes, we propose the structures of the complexes with the new ligands as depicted in Figure 8.

Catalytic Studies for Alkene Oxidations

The complexes were tested for the catalytic oxidation of several different alkenes in acetonitrile solution with H_2O_2 as the oxidant with a catalyst:substrate: H_2O_2 ratio of 1:200:300. The catalytic properties of the new complexes were compared to their BPMCN or BPMEN analogs and evaluated as a function of acetic acid or perchloric acid addition. The catalysis experiments performed in acidic conditions have been the subject of extensive studies as they determine the high selectivity for epoxides.^[8d,8g]

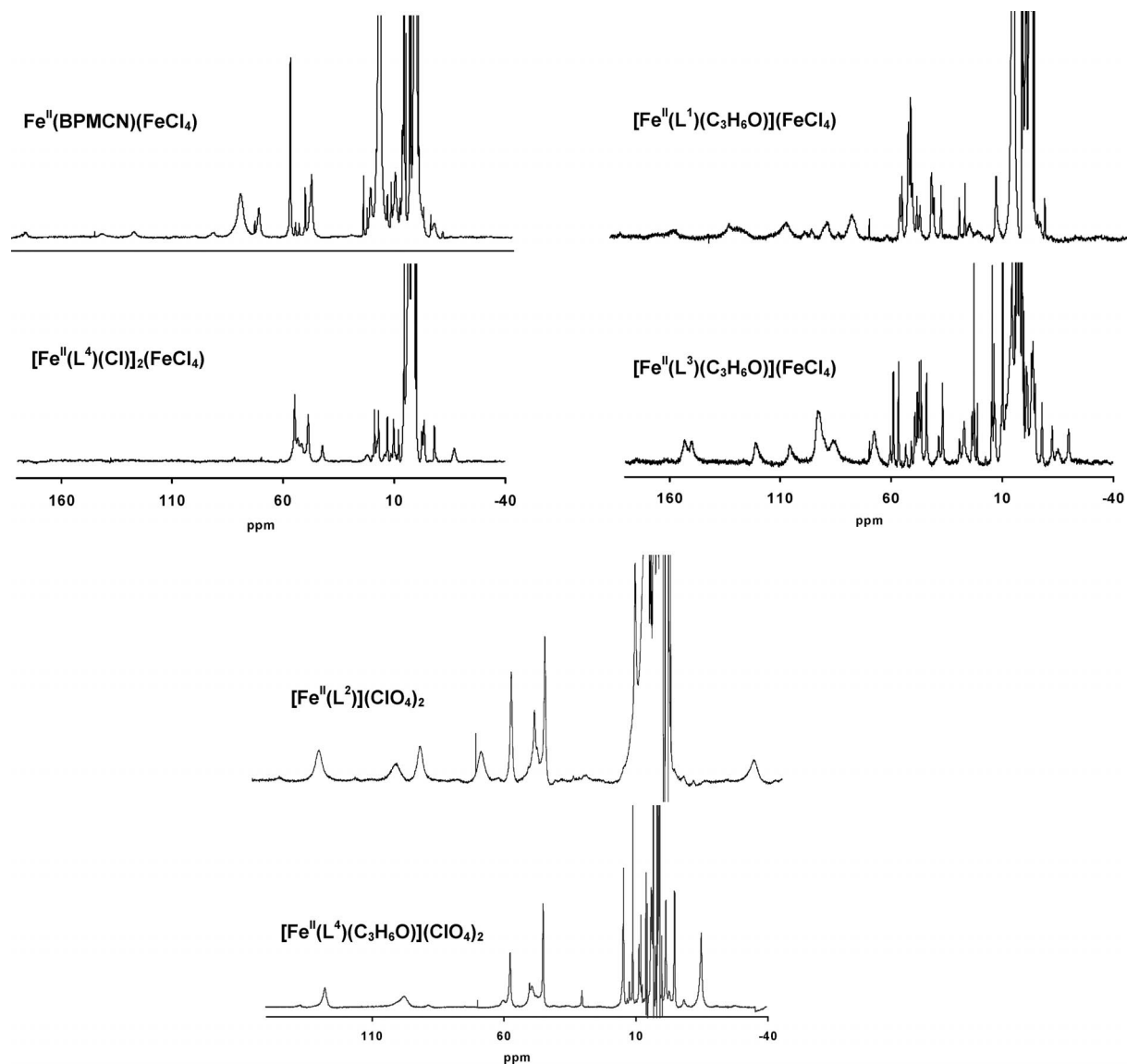


Figure 7. ^1H NMR spectra of iron complexes in $[\text{D}_6]\text{acetone}$.

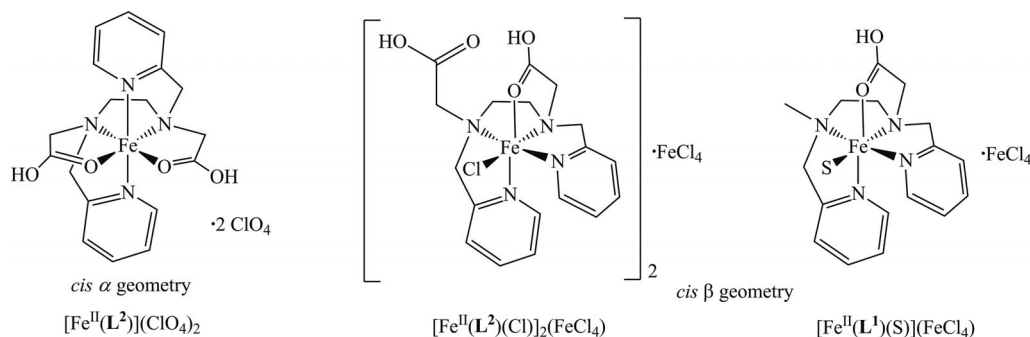


Figure 8. Proposed structures for the new iron complexes (S stands for acetone or solvent). A mixture of the *cis* α and *cis* β forms coexist in $[\text{Fe}^{\text{II}}(\text{L}^1)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$.

The experiments were performed at room temperature in air. The oxidant was delivered by dropwise addition over 30 min using a syringe pump in order to reduce H_2O_2 disproportionation. The yield was measured 30 min after the

end of the oxidant addition. The presence of air did not affect the yield or selectivity of the epoxidation reaction. As most complexes contain either a chloride ligand and/or an $\text{Fe}(\text{II})\text{Cl}_4$ or $\text{Fe}(\text{III})\text{Cl}_4$ counteranion, five equivalents of

Table 2. Cyclooctene oxidation catalyzed by [FeL](FeCl₄) complexes under various conditions with 0.5 mol-% catalyst.^[a]

Catalyst [FeL] L	CH ₃ CN ^[a]		+ 100 equiv. CH ₃ CO ₂ H		CH ₃ CN/CH ₃ CO ₂ H 1:2		+ 1 equiv. HClO ₄	
	Epoxide ^[b] [%]	Conv. [%]	Epoxide ^[b] [%]	Conv. [%]	Epoxide ^[b] [%]	Conv. [%]	Epoxide ^[b] [%]	Conv. [%]
None	0	4	1	20	1	20	—	—
FeCl ₂	3	22	1	18	—	—	—	—
BPMEN	32	68	95	98	92	98	44	85
L ¹	27	68	82	97	31	51	29	66
L ²	3	37	3	37	4	37	—	—
BPMC	56	92	64	98	63	100	38	90
L ³	37	78	59	95	80	99	43	91
L ⁴	1	1	1	1	4	16	—	—

[a] Ratio catalyst:substrate:H₂O₂ = 1:200:300, in CH₃CN, oxidant delivered by a syringe pump over 30 min and 30 extra minutes of stirring were allowed before GC injection. [b] Yield based on substrate consumption.

Ag(CF₃SO₃) were added prior to the addition of the oxidant, which accounts for the removal of these chloride anions from the solution as they may compete with the oxidant to bind to the metal ion. This experimental requirement was supported by the total loss of epoxide formation during catalysis with these complexes in the absence of silver salts. Furthermore, [Fe^{III}Cl₄][−], Fe^{III}Cl₃, or Fe^{III}(ClO₄)₃ were found to be inactive for epoxide formation under standard conditions, although a small conversion yield was measured. These control experiments guaranteed that the results obtained are attributed to the starting ferrous FeLⁿ dication.

In the absence of either the catalyst or the oxidant, no epoxide products were detected, although the substrate was partially converted in some cases. This is particularly true when acetic acid was added to the reaction medium; up to 20% conversion was measured when 100 equiv. were added (Table 2, Column 4).

In the absence of acetic acid, [Fe^{II}(L⁴)(C₃H₆O)](ClO₄)₂ and [Fe^{II}(L²)](ClO₄)₂ were found to be quasi-inactive for cyclooctene oxidation. Conversely, reasonable epoxide yields were reached with [Fe^{II}(L³)(C₃H₆O)](FeCl₄) and [Fe^{II}(L¹)(C₃H₆O)](FeCl₄) (27 and 37% yield, respectively) under the same conditions (Table 2 and Figure 9). For comparison, the BPMEN and BMCN analogs were found to be more efficient (32^[13] and 56% yield, respectively). Under our conditions, the epoxide selectivity reached 60%, although only a small amount of the corresponding diols were detected (Figure 9). As the conversion ranged from 68–92% depending on the catalyst, other secondary products were formed. ¹H NMR spectroscopic studies of the reaction media confirmed the presence of cyclooctene oxide and trace amounts of diols (less than 4%) as the major products but no other oxygenated products, such as octanedioic acid, were detected.

The presence of acetic acid increased the efficiency of the catalysts that contain L¹ and L³, whereas those with L² and L⁴ remained unreactive. For example, the epoxide and conversion yields increased significantly (from 37 to 80% and 78 to 100%, respectively) as acetic acid concentration increased and reached 81% selectivity with [Fe^{II}(L³)(C₃H₆O)](FeCl₄). By comparison, [Fe^{II}(BPMC)](FeCl₄) was unaffected under these conditions. Interestingly,

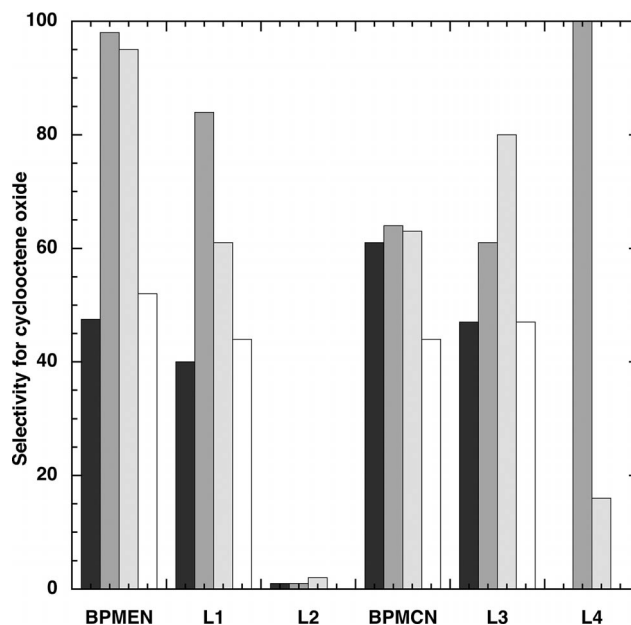


Figure 9. Selectivity for cyclooctene epoxide depending on the ligand of the iron(II) catalyst (black), in the presence of 100 equiv. acetic acid (grey), in a CH₃CN/CH₃CO₂H (1:2) solution (light grey), and in the presence of 1 equiv. of H⁺ (white).

[Fe^{II}(BPMEN)](FeCl₄) showed a stimulation of its reactivity (37 to 98%) with a 100% selectivity (Figure 9).^[10] These results underline a difference in catalytic behavior that is related to the nature of the diamine (cyclohexanediamine vs. ethylenediamine).

The addition of 1 equiv. of HClO₄ was totally ineffective in stimulating the epoxidation catalysis, which implicates that protons alone are not sufficient to account for the enhancement of the reaction by acetic acid. This result suggests that acetic acid has to bind into the oxidizing species, which has been proposed earlier.^[10]

The complex that contains a chiral substructure, i.e. (S,S)-cyclohexanediamine, performed enantioselective epoxidations, and the results are shown in Table 3. Interestingly, the enantioselectivity of the reaction depended on the presence of acetic acid in the reaction medium; a large increase from 15 to 34% was observed in the case of enantiomeric excess for the H₂O₂ oxidation of the *trans*-2-heptene

Table 3. Asymmetric alkene oxidation catalyzed by $[\text{Fe}^{\text{II}}\text{L}](\text{FeCl}_4)$ with 0.5 mol-% catalyst.^[a]

Catalyst ($[\text{FeL}]$) L	$\text{CH}_3\text{CN}^{\text{[a]}}$ Epoxide [%]	<i>ee</i> [%]	+ 100 equiv. $\text{CH}_3\text{CO}_2\text{H}$ Epoxide [%]	<i>ee</i> [%]	1:2 $\text{CH}_3\text{CN}/\text{CH}_3\text{CO}_2\text{H}$ Epoxide [%]	<i>ee</i> [%]
<i>trans</i> -2-Heptene						
None	1	0	—	—	1	0
BPMC	31	14	52	38	42	30
L^3	18	17	29	30	40	34
<i>trans</i> - β -Methylstyrene						
None	3	0	3	0		
L^3	7	0	6	0		
<i>cis</i> - β -Methylstyrene						
None	0	0	0	0		
L^3	13	13	21	18		
(<i>R</i>)-Carvone						
None	0	0	0	0		
L^3	17	5 ^[b]	27	15 ^[b]		

[a] Ratio catalyst:substrate: H_2O_2 = 1:200:300 in CH_3CN , oxidant delivered by a syringe pump over 30 min and 30 extra minutes of stirring were allowed before GC injection. Yield based on substrate. [b] A diastereomeric excess was measured by integration of the relevant ^1H NMR spectroscopic signals.

when 100 equiv. of acid was present. The presence of the carboxylic moiety on the ligand did not impact on the enantioselectivity of this reaction as similar values were observed with $[\text{Fe}^{\text{II}}(\text{L}^3)](\text{FeCl}_4)$ and $[\text{Fe}^{\text{II}}(\text{BPMC})](\text{FeCl}_4)$. It may suggest that the carboxylic ligand does not bind the active catalyst or does not bind in a position that affords H-bonding with the peroxide adduct. This role is devoted to the exogenous acid.

The electron richness of the substrate drastically affects the enantiomeric excess; it was found that the chiral complex was a poor catalyst for the oxidation of *cis*- or *trans*- β -methylstyrene but afforded retention of the configuration. Low but remarkable *ee* values for complexes with the N_2Py_2 ligand platform were measured,^[8c] which are affected by the presence of acetic acid. Furthermore, discrimination between both diastereoisomers of the alkene by the catalyst was observed in terms of *ee* and yield. Although a racemic mixture of the corresponding epoxide was found with *trans*-(*E*)- β -methylstyrene, a noticeable enantiomeric excess was detected when *cis*-(*Z*)- β -methylstyrene was used as a substrate. Finally, benzaldehyde, propiophenone, and traces of diol were detected in less than 5% total yield, which means a poor selectivity for the epoxide. However, even if styrenes undergo competing aromatic hydroxylation reactions, which is well documented for $\text{Fe}(\text{BPMEN})$ and $\text{Fe}(\text{TPA})$,^[25] such hydroxylated species were not detected here.

The selective epoxidation of (*R*)-carvone was catalyzed by $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$, which proceeded by exclusive attack on the electron-rich, external C=C bond. This indicates that the oxidizing species has an electrophilic character. Moreover, the presence of acetic acid in the medium did not enhance greatly the yield of epoxide (17 versus 27% in the presence of 100 equiv. of acid) but affected the diastereomeric excess (from 5 to 15% with 100 equiv. of acetic acid). Moreover, the selectivity for the epoxide was only of 62% as two other oxygenated products were detected, one of which was definitively identified as 2-(4-methyl-5-oxocyclohex-3-en-1-yl)propanal (see Supporting Information). The other could be the alcohol analog of the latter species,

which could result from Markovnikov addition of hydroxyl radicals to the double bond.^[26]

Discussion

The design of complexes with carboxylic ligands was successful, thanks to the use of ferrous salts and acetone as the solvent. The new mononuclear complexes present an original property of a monodentate coordination mode of a carboxylic functionality of the ligand, which was proven by IR spectroscopy (a broad peak at 1640 cm^{-1}) for all the complexes and confirmed by the X-ray structure of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$. The state of protonation of the carboxylic group leads to a Fe–O bond, which implies the presence of an sp^2 oxygen atom. Another characteristic of the complexes was the unexpected formation of the metallic anion $\text{Fe}^{\text{II}}\text{Cl}_4^-$, which was indirectly detected by ESI-MS and UV/Vis spectroscopy.

The geometries of the six original complexes were found to be anion dependent in acetone. The presence of a noncoordinating anion leads to the formation of *cis* α complexes, in which the pyridine rings are *trans* to each other and the carboxylic moieties are *cis* to each other (Figure 8). However, with a chloride anion, the major topology, deduced from NMR spectroscopic studies, seems to be *cis* β whatever the ligand used. We propose that the chloride ions first bind to FeL , which induces a preferred topology, before being exchanged by the carboxylic arm combined with the presence of extra coordination sites in FeCl_2 ($[\text{FeCl}_4]^{2-}$ is thermodynamically more stable than the expected FeLCl_2 complex). The geometry is also related to the lower acidity of carboxylic acids compared to HCl, which prevents deprotonation of the carboxylic acid during the synthesis. Such a phenomenon has been observed previously.^[27] In one report, the degree of protonation of the ligand influenced the synthesis of the tetrachloride ferrous anion.

In terms of complex geometry, the propensity for this *cis* β topology remains puzzling but seems to be driven by the

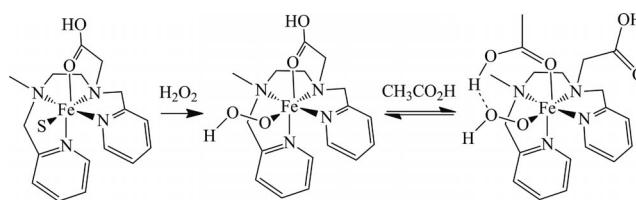
constraints imposed by the diamine part of the ligand. A mixture of isomers was found with a more flexible diamine in an analogous complex.^[24] Moreover, the cyclohexanediamine guarantees the topology in solution as it is more constrained than ethylenediamine.

In $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$, the ligand in the sixth coordination position could not be unambiguously determined but Cl^- anions are excluded. We were able to compare its O_2 -oxidized form with $[\text{Fe}^{\text{III}}(\text{L}^3)(\text{Cl})](\text{FeCl}_4)$, which was synthesized separately. The latter complex was characterized as hexacoordinate, in which one chloride anion completed the iron coordination sphere in addition to the anionic form of the carboxylic group. Although both complexes displayed similar UV spectroscopic signatures that arise from $\text{Fe}^{\text{III}}\text{Cl}_4^-$, their ^1H NMR spectra (which were in agreement with mononuclear species) were different (Figure S5). This behavior implies a different environment around the ferric atom, which suggests that the Cl ligand is absent in the ferrous complex. We propose that the solvent, in solution, or an acetone molecule, in the solid state, is coordinated in the complex.

The catalytic properties of the original complexes were then compared to those of the BPMEN and BPMCN complexes. Initially, the use of silver salt allows the exchange of a chloride anion with acetonitrile in order to be under the previously reported catalytic conditions for the BPMEN and BPMCN complexes. The general outcome under these conditions is that the substitution of a methyl group by a carboxylic moiety on the ligand does not alter the capacity of the N_2Py_2 iron catalyst. However, two substitutions of the methyl groups by carboxylic moieties in the ligand totally poisoned the iron catalyst, which indicates that i) these moieties still bind to the oxidizing metal species or oxidant activating species and ii) they hamper the ability of the oxidant to bind. Similar results were obtained with catalysts that contain dicarboxylic ligands^[4b] and, to some extent, with a system that contains one bidentate carboxylate ligand.^[15] The existence of one labile site is required for catalytic activity and accounts partly for the selectivity of the alkene oxidation.^[5] The high selectivity for epoxide over diol is typical of pentadentate iron catalysts, as two direct oxygen atom transfers are precluded.^[28] The catalytic stimulation by acetic acid is more complicated to assess. In all cases, it had a positive effect on the conversion, the selectivity, and the epoxide yields, with the exception of the complex with BPMCN. Acetic acid has been proposed to assist the heterolytic cleavage of a transient hydroperoxo ferric intermediate, which is generally accepted as the key feature to generate the active oxidant in the cytochrome P450 mechanism.^[29] In our case, proton assistance should be driven by the carboxylic moieties and/or acetic acid, which displaces the carboxylic moiety. The absence of an effect of protons alone (HClO_4) suggests that the acetic acid has to bind to the complex. The observed stimulation of the catalysis was modulated by the exchange between a carboxylic ligand and exogenous acetic acid in the iron coordination sphere and also depended on the orientation of carboxylic ligand towards the hydroperoxide ligand. Accordingly, the

rigidity of the ligand may exclude the formation of H-bonding between the hydroperoxide and the endogenous carboxylic ligand. Moreover, this substitution process depends on the strength of the $\text{Fe}-\text{O}_{\text{carb}}$ bond. The reorganization of the coordination sphere during the process is probably more difficult for more rigid cyclohexanediamine-based complexes compared to the ethanediamine series, which generates a lower stimulating effect (Figure 9). We proposed that the easier it is for the acetic acid to bind, the higher the reactivity.

The catalyst that incorporates the optically active *trans*-1,2-diaminocyclohexane backbone into its ligand framework, i.e. complexes of L^3 , catalyzed the asymmetric epoxidation of *trans*-2-heptene with enhanced *ee* values in the presence of an external acid. Again, the presence of this intramolecular carboxylic group was not deleterious for the enantioselective control as similar *ee* values were obtained with $[\text{Fe}^{\text{II}}(\text{BPMCN})](\text{FeCl}_4)$ and $[\text{Fe}^{\text{II}}(\text{L}^3)(\text{C}_3\text{H}_6\text{O})](\text{FeCl}_4)$. The similar value obtained in the presence of acetic acid confirms that the intrinsic carboxylic group was not involved in the catalytic process (Scheme 2). The existence of an asymmetric control emphasizes the existence of a metal-based mechanism. The formation of the oxidizing species and its structure is controlled by the presence of external acetic acid. It still remains to be established if a high-valent iron species^[10] is involved in the process. Further studies will be undertaken to shed light on the nature of this species in order to gain insight into the oxidation mechanism. Among the results obtained with mono- or dimeric iron catalysts for the stereoselective epoxidation of various alkenes, this is the first time that a noticeable enantiomeric excess has been obtained with a nonheme iron mononuclear catalyst and a nonelectron-rich substrate.^[30]



Scheme 2. Possible activation of hydrogen peroxide by the ferrous complex of L^1 (and/or L^3).

Conclusions

A new N_4O environment for an iron complex derived from N_2Py_2 ligands (BPMEN or BPMCN) affords a good efficiency for epoxidation, thanks to the protonation of its carboxylic group, whereas a more oxygenated N_4O_2 environment drastically affects the catalytic activity. The presence of an available, internal carboxylic functionality in the complex slightly competes with the coordination of external acetic acid, which is known to stimulate epoxidation catalysis observed with N_2Py_2 catalysts such as $[\text{Fe}(\text{BPMCN})_2(\text{CH}_3\text{CN})_2](\text{CF}_3\text{SO}_3)_2$. Interestingly, the stimulating effect of acetic acid combined with the weak effect of the carbox-

ylic moiety ligands was also observed for the first time for the enantioselective reaction with *trans*-2-heptene.

The presence of carboxylic functionalities may be tolerated for the design of bioinspired catalysts.

Experimental Section

General: All reagents were purchased from commercial sources and were used as received unless noted otherwise. Solvents were dried and degassed before use.

Crystallographic Studies: Data collection of $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$ were conducted with a Bruker SMART CCD system at the crystallography service of the SCIB laboratory (CEA-Grenoble). Experimental conditions for $[\text{Fe}^{\text{II}}(\text{L}^4)(\text{C}_3\text{H}_6\text{O})](\text{ClO}_4)_2$: ($\text{C}_{25}\text{H}_{34}\text{Cl}_2\text{FeN}_4\text{O}_{13}$) $M = 725.31 \text{ g mol}^{-1}$, yellow plate $0.26 \times 0.17 \times 0.13 \text{ mm}$, orthorhombic, collection wavelength $0.71073 \text{ \AA}$; collection temperature $150(2) \text{ K}$, space group $P2_12_12_1$, $a = 12.1116(4) \text{ \AA}$, $b = 15.7961(6) \text{ \AA}$, $c = 16.4185(6) \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 90.0^\circ$, $\gamma = 90.0^\circ$, $V = 3141.11(19) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.534 \text{ g cm}^{-3}$; Reflections collected = 10236 and 6361 independent reflections collected; $R1 = 0.0412$ [$I \geq 2\sigma(I)$]. Pertinent crystallographic data are reported in Table 1. The structure was solved by direct methods using the SHELXTL 5.03 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group) isotropic displacements.

CCDC-809749 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical Studies: ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer. ^1H NMR chemical shifts are reported in ppm with the solvent as the internal reference. ESI-MS studies were performed with an LXQ-linear ion trap (Thermo Scientific, San Jose, CA, USA) equipped with an electrospray source in an aqueous or aqueous/acetone mixture. Electrospray full scan spectra in the range $m/z = 50\text{--}2000$ were obtained by infusion through fused silica tubing at $2\text{--}10 \mu\text{L min}^{-1}$. The LXQ calibration was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine/MRFA and Ultramark 1621). The temperature of the heated capillary of the LXQ was set to $150\text{--}200^\circ\text{C}$, and the ion spray voltage was in the range $1\text{--}3 \text{ kV}$. The experimental isotopic profile was compared in each case to the theoretical one. UV/Vis spectroscopic studies were carried out with a Shimadzu UV-1800 spectrophotometer. IR spectra of the complexes as KBr discs were measured with a Perkin-Elmer Spectrum 100 FT-IR spectrometer. GC was performed with a Perkin-Elmer Autosystem XL instrument with a FID detector, which used an SE 30 column coupled to a Perkin-Elmer Turbomass EI spectrometer. Enantiomeric excesses were measured by GC with a ChiralDEX TA column. The values are the average of three separate samples. The diastereoisomeric excess for carvone epoxide was measured by ^1H NMR spectroscopy and was based on the average of the splitting of the epoxide peak at 2.68 ppm and the methyl peak at 1.30 ppm . Elemental analyses were performed by the Microanalysis Service of CNRS (Vernaison).

Synthesis of Ligands

***N*-Methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine ("BPHMEN"):** Synthesized according to the method reported by Baffert et al.^[12]

(1*S*,2*S*)-*N*-Methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine ("BPHMCN"): Synthesized by an adaptation of a previously published procedure.^[31] (1*S*,2*S*)-*N,N'*-Bis(2-pyridylmethyl)-1,2-cyclohexanediamine (1.6 g, 5.39 mmol) was dissolved in aqueous formic acid (50 mL, 90%). Formaldehyde (9.92 mL, 25 equiv., 37%) was added and the resulting solution was stirred at 90°C for 24 h. The mixture was cooled to 20°C and the pH was adjusted to 12 by addition of aqueous sodium hydroxide (3 M) with constant cooling. The aqueous layer was extracted into dichloromethane, and the combined organic layers were dried with anhydrous Na_2SO_4 , filtered, and evaporated to give a brown oil. Purification on a column of neutral aluminium oxide using a pentane/ethyl acetate/triethylamine mixture (50:50:1 v/v) as eluent afforded the title product (1.412 g, 85%) as a clear oil in addition to dimethylated BPMCN (15%). ^1H NMR (300 MHz, CDCl_3): BPMCN: $\delta = 8.55$ (d, $J = 4.8 \text{ Hz}$, 2 H, Py), 7.63 (m, 4 H, Py), 7.17 (m, 2 H, Py), 3.98 and 3.86 (d, $J = 14.7 \text{ Hz}$, $2 \times 2 \text{ H}$, CH_2), 2.71 (m, 2 H), 2.33 (s, 6 H, $2 \times \text{CH}_3$), 2.02 (m, 2 H), 1.81 (m, 2 H), 1.26 (m, 4 H) ppm. BPHMCN: $\delta = 8.43$ (d, $J = 4.2 \text{ Hz}$, 2 H, Py), 7.56 (m, 3 H, Py), 7.23 (m, 1 H, Py), 7.07 (m, 2 H, Py), 3.97 (d, $J = 14.1 \text{ Hz}$, 1 H, CH_2), 3.78 and 3.73 (ddd, $J = 4.5$, $J = 4.8 \text{ Hz}$, 2 H, CH_2), 3.54 (d, $J = 14.4 \text{ Hz}$, 1 H, CH_2), 2.43 (m, 2 H), 2.24 (m, 1 H), 2.15 (s, 3 H, CH_3), 1.89 (m, 1 H), 1.76 (m, 1 H), 1.67 (m, 1 H), 1.17 (m, 5 H) ppm.

(1*S*,2*S*)-*N*-Carboxymethyl-*N'*-methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (L^3) (General Procedure): BPHMCN (1.006 g, 3.26 mmol) was dissolved in a mixture of anhydrous MeCN (20 mL) and K_2CO_3 (720 mg, 5.22 mmol) under an inert atmosphere. *tert*-Butyl 2-bromoacetate (723 μL , 4.89 mmol) in anhydrous MeCN (20 mL) was added dropwise with a syringe over about 5 min. The reaction was then left to stir at room temperature and was monitored by TLC. Once all of the starting material had disappeared (ca. 3 h) H_2O (approx. 20 mL) was added, and the reaction mixture was extracted into dichloromethane three times. The organic phase was washed twice with brine. The combined aqueous phases were re-extracted into CH_2Cl_2 . All the CH_2Cl_2 fractions were dried with Na_2SO_4 for 30 min. The drying agent was removed by filtration through a sintered funnel and the solvent was evaporated under reduced pressure. (Note: Treatment of the combined aqueous phases with NaOH followed by CH_2Cl_2 extraction led to the recovery of the starting amine with an average yield of 50%.) The crude product was then purified on a column of neutral aluminium oxide (pentane/ethyl acetate/triethylamine, 50:50:1) (732 mg, 53%). ^1H NMR (75 MHz, CDCl_3): $\delta = 8.43$ (m, 2 H, Py), 7.77 (d, $J = 7.8 \text{ Hz}$, 2 H, Py), 7.47–7.56 (m, 2 H, Py), 7.04–7.10 (m, 2 H, Py), 3.98 (AB, $J = 12 \text{ Hz}$, $J = 60 \text{ Hz}$, 2 H, CH_2CO), 3.71 (AB, $J = 14.4 \text{ Hz}$, $J = 32.4 \text{ Hz}$, 2 H, CH_2), 3.37 (AB, $J = 16.5 \text{ Hz}$, $J = 44.7 \text{ Hz}$, 2 H, CH_2), 2.6 (br., 2 H, Cy), 2.15 (s, 3 H, Me), 1.70 (br., 2 H, Cy), 1.39 (s, 9 H, *t*Bu), 1.10–1.16 (m, 4 H, Cy) ppm.

The resulting oil (732 mg, 1.73 mmol) was dissolved in CH_2Cl_2 (3 mL) under an inert atmosphere. Trifluoroacetic acid (2.53 mL, 20 equiv.) was then added slowly at 0°C . The reaction mixture was stirred at 0°C for 30 min. The reaction was allowed to warm to room temperature and left to stir overnight. The volume of the resulting mixture was reduced to about 4/5 under reduced pressure. The solution was then added dropwise into diethyl ether (30 mL) to precipitate the product. The resulting yellow paste was triturated several times to remove all of the trifluoroacetic acid. The remaining ether was then evaporated and left under vacuum for 5 h. The reaction was quantitative (636 mg). ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$): $\delta = 8.65$ (br., 2 H, Py), 7.92 (br., 2 H, Py), 7.61 (br., 2 H, Py), 7.46 (br., 2 H, Py), 4.89 (br., 2 H, CH_2), 4.37 (br., 2 H, CH_2), 3.53

(m, 2 H, CH₂CO), 3.01 (br., 2 H, Cy), 2.42 (m, 2 H, Cy), 1.90 (m, 2 H, Cy), 1.38 (m, 4 H, Cy) ppm.

***N*-Carboxymethyl-*N'*-methyl-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine:** **L¹** was synthesized using the same procedure from BPHMEN. Yield for the two steps: 50%. ¹³C NMR (75 MHz, MeOD): δ = 172.8 (CO₂H), 157.8 (Py), 149.5 (Py), 147.9 (Py), 138.7 (Py), 137.7 (Py), 125.0 (Py), 124.4 (Py), 65.5 (CH₂Py), 58.8 (CH₂Py), 57.6 (CH₂CO), 54.2 (CH₂), 49.3 (CH₂), 40.1 (Me) ppm.

***N,N'*-Dicarboxymethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine:** **L²** was synthesized using the same procedure from *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine with 2.2 equiv. of *tert*-butyl 2-bromoacetate. Yield for the two steps: 41%. ¹³C NMR (75 MHz, [D₆]acetone): δ = 172.1 (CO₂H), 152.3 (Py), 145.1 (Py), 142.8 (Py), 126.1 (Py), 125.3 (Py), 56.1 (CH₂Py or CH₂CO₂H), 54.2 (CH₂Py or CH₂CO₂H), 51.1 (CH₂) ppm.

***N,N'*-Dicarboxymethyl-(1*R*,2*R*)-*N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine:** **L⁴** was synthesized using the same procedure from *N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine with 2.2 equiv. of *tert*-butyl 2-bromoacetate. Yield for the two steps: 41%. ¹³C NMR (75 MHz, [D₆]acetone): δ = 171.0 (CO₂H), 152.2 (Py), 145.5 (Py), 142.2 (Py), 125.6 (Py), 125.2 (Py), 65.2 (Cy), 62.1 (CH₂CO), 51.4 (CH₂Py), 24.2 (Cy) ppm.

Synthesis of Metal Complexes

[Fe^{II}(BPMCn)](Fe^{II}Cl₄) and [Fe^{II}(BPMEN)](Fe^{II}Cl₄): [Fe^{II}-(BPMCn)](Fe^{II}Cl₄) and [Fe^{II}(BPMEN)](Fe^{II}Cl₄) were synthesized according to a literature procedure.^[13,32] ESI-MS (acetone): *m/z* (%) = 162.8 (100) [Fe^{II}Cl₃]⁺.

[Fe^{II}(L³)(C₃H₆O)](Fe^{II}Cl₄) (General Procedure): In a glove box, **L³** (102.9 mg, 0.28 mmol) was dissolved in acetone (approx. 10 mL). Fe^{II}Cl₂ (55.9 mg, 0.28 mmol) was added, and the mixture was left to stir for 30 min. The complex precipitated out within 5 min. More solid appeared on addition of diethyl ether. The complex presented as a yellow solid (60%). ¹H NMR (300 MHz, [D₆]acetone): δ = 153.1, 149.9, 121.0, 105.6, 93.1, 86.1, 67.6, 60.5, 59.1, 56.8, 53.4, 51.1, 49.4, 48.3, 47.4, 46.6, 44.1, 38.6, 36.9, 29.4, 27.2, 23.6, 22.7, 21.3, 15.0, 14.5, 13.8, 9.89, 6.42, 5.25, 2.20, 1.13, -0.11, -1.54, -3.11, -3.69, -4.80, -7.88, -12.5, -15.1, -19.8 ppm. IR (KBr): ν̄ = 3442 (ν_{OH}), 2926 (ν_{CH}), 1638 (ν_{C=O_{as}}), 1443 (ν_{C=O_s}) cm⁻¹. ESI-MS (acetone): *m/z* (%) = 423.4 (100) [L - H + Fe^{II}]⁺, 459.2 (24) [L + Cl + Fe^{II}], 481.3 (83) [L - H + Cl + Na + Fe^{II}]. Because of its sensitivity to oxygen, the Fe^{II}Cl₄ counterion was transformed to the more stable dimer Cl₃Fe^{II}OHFe^{II}Cl₃ during sample preparation for elemental analysis. [Fe^{II}(L³)(C₃H₆O)](Cl₃Fe^{II}OHFe^{II}Cl₃)₂·1H₂O: C₂₄H₄₀Cl₁₂Fe₅N₄O₇ (1201.27): calcd. C 24.35, H 3.16, N 4.73; found C 24.87, H 3.58, N 4.41.

[Fe^{II}(L¹)(C₃H₆O)](Fe^{II}Cl₄): The same procedure was used as described above; yield 74%. ¹H NMR (300 MHz, [D₆]acetone): δ = 161.5, 152.8, 129.6, 105.4, 97.5, 94.5, 88.1, 77.3, 57.1, 56.1, 53.5, 52.6, 51.8, 50.0, 48.6, 43.7, 42.8, 39.7, 31.9, 29.5, 27.7, 16.4, 9.27, 5.46, 5.26, 5.01, 2.99, 0.56, -1.14, -2.52, -4.23, -17.4 ppm. IR (KBr): ν̄ = 3400 (ν_{OH}), 1620 (ν_{C=O_{as}}), 1609 (ν_{C=N}), 1445 (ν_{C=O_s}) cm⁻¹. ESI-MS (acetone): *m/z* (%) = 369.3 (100) [L - H + Fe^{II}]⁺. [Fe^{II}(L¹)(C₃H₆O)](Cl₃Fe^{II}OHFe^{II}Cl₃)·2H₂O: C₂₀H₃₂Cl₆Fe₃N₄O₆ (804.76): calcd. C 29.85, H 4.01, Cl 26.43, Fe 20.82, N 6.96; found C 29.22, H 3.38, Cl 28.39, Fe 19.62, N 7.95.

[Fe^{II}(L⁴)(Cl)]₂(Fe^{II}Cl₄): The same procedure was used as described above; yield 59%. ¹H NMR (300 MHz, [D₆]acetone): δ = 54.8, 53.2, 51.6 and 42.3 (CH₂, H_m and H_{m'}), 21.5, 18.9, 17.0, 13.6, 13.2, 10.7, 10.3 and 8.14 (CH₂), -3.53, -3.43, -8.08, -17.2 (CH₂ and H_p) ppm. IR (KBr): ν̄ = 3392 (ν_{OH}), 1647 (ν_{C=O_{as}}), 1607 (ν_{C=N}), 1444

(ν_{C=O_s}) cm⁻¹. ESI-MS (acetone): *m/z* = 467.4 (100) [L - H + Fe^{II}]⁺, 933.4 (83) [2(L - H) - H + 2Fe^{II}]⁺, 955.4 (34) [2(L - 2H) + Na + 2Fe^{II}]⁺. [Fe^{II}(L⁴)(Cl)]₂(Fe^{II}Cl₄): C₄₄H₅₆Cl₆Fe₃N₈O (1093.24): calcd. C 43.85, H 4.68, N 9.30; found C 43.62, H 4.97, N 9.15.

[Fe^{II}(L⁴)(C₃H₆O)](ClO₄)₂: In a glove box, **L⁴** (105.3 mg, 0.26 mmol) was dissolved in acetone (approx. 10 mL). Fe^{II}(ClO₄)₂ (65.1 mg, 0.26 mmol) was added, and the mixture was stirred for 30 min. Addition of diethyl ether (5 mL) to the yellow-green solution led to the precipitation of the complex. The product was washed with diethyl ether and dried under vacuum to afford a yellowish solid (43%). ¹H NMR (300 MHz, [D₆]acetone): δ = 127.9 (H_o), 97.9 and 88.7 (CH₂), 60.3, 57.7, 49.4 and 45.2 (H_m, H_{m'} and CH₂), 14.8 (H_p), -4.63, -8.20 and -14.7 (CH₂) ppm. IR (KBr): ν̄ = 3400 (ν_{OH}), 1640 (ν_{C=O_{as}}), 1608 (ν_{C=N}), 1436 (ν_{C=O_s}), 1144, 1090 and 1111 (ν_{ClO}) cm⁻¹. ESI-MS (acetone): *m/z* (%) = 234.2 (64) [L + Fe^{II}]²⁺/2, 467.3 (100) [L - H + Fe^{II}]⁺, 566.8 (7) [L + ClO₄ + Fe^{II}]⁺. [Fe^{II}(L⁴)(C₃H₆O)](ClO₄)₂·(H₂O): C₂₅H₃₆Cl₂FeN₄O₁₄ (743.33): calcd. C 40.40, H 4.84, Fe 7.50, N 7.54; found C 40.60, H 4.93, Fe 6.50, N 7.49.

[Fe^{II}(L²)(ClO₄)₂]: The same procedure was used as described above; yield 51%. ¹H NMR (300 MHz, [D₆]acetone): δ = 125.9 (H_o), 98.3, 89.8 and 67.9 (CH₂), 57.4, 49.1 and 45.3 (H_m, H_{m'} and CH₂), 13.0 (H_p), -29.7 (H_p or CH₂) ppm. IR (KBr): ν̄ = 3436 (ν_{OH}), 1622 (ν_{C=O_{as}}), 1611 (ν_{C=N}), 1447 (ν_{C=O_s}), 1121 and 1108 (ν_{ClO}) cm⁻¹. ESI-MS (acetone): *m/z* (%) = 448.2 (100) [L - H + Cl + Fe^{II}]⁺, 413.3 (46) [L - H + Fe^{II}]⁺. [Fe^{II}(L²)(ClO₄)₂·C₁₈H₂₂Cl₂FeN₄O₁₂ (613.14): calcd. C 35.26, H 3.62, Cl 11.56, Fe 9.11, N 9.14; found C 35.63, H 3.93, Cl 10.40, Fe 9.44, N 8.93.

[Fe^{III}(L⁴)(Cl)](Fe^{III}Cl₄): Under air, **L⁴** (63 mg, 0.15 mmol) was dissolved in acetone (approx. 6 mL). Fe^{III}Cl₃·6H₂O (41 mg, 0.15 mmol) dissolved in acetone (approx. 2 mL) was added dropwise to afford an orange solution. After 2 h of stirring, the complex was precipitated by the addition of diethyl ether (approx. 10 mL). The product was washed with diethyl ether and dried under vacuum to give a yellow solid (44%). ¹H NMR (300 MHz, MeOD): δ = 76.7, 58.9, 26.7 and -18.6 ppm. IR (KBr): ν̄ = 3412 (ν_{OH}), 2936 (ν_{CH}), 1643 (ν_{C=O_{as}}), 1445 (ν_{C=O_s}) cm⁻¹. ESI-MS (MeOH): *m/z* (%) = 466.3 (100) [L - 2H + Fe^{III}]⁺, 502.2 (5) [L - H + Cl + Fe^{III}]⁺. [Fe^{III}(L⁴)(Cl)](Fe^{III}Cl₄): C₂₁H₃₀Cl₅Fe₂N₄O₄ (691.45): calcd. C 36.48, H 4.37, Fe 16.15, Cl 25.64, N 8.10; found C 36.89, H 4.13, Fe 16.45, Cl 26.02, N 8.04.

Reaction Conditions for Catalysis Experiments: A H₂O₂ solution in CH₃CN (150 μL, 2.0 M, diluted from a 50% H₂O₂ solution) was delivered by syringe pump over 30 min at room temperature in air (or added all at once) to a vigorously stirred CH₃CN solution (850 μL) that contained catalyst (1 μmol), substrate (200 μmol), and of AgCF₃SO₃ (4.5 μmol). The final concentrations were 1 mM iron catalyst, 300 mM H₂O₂, and 200 mM substrate. The solution was stirred for another 30 min after the H₂O₂ addition. These experiments were carried out at room temperature with a variable amount of acetic acid (100 equiv. of CH₃COOH or a 1:2 mixture CH₃CN/CH₃COOH) or with HClO₄ (1 mM). A benzophenone solution in CH₂Cl₂ (20 μL, 1 M) was added as an internal reference to the samples before GC analysis. The products were identified by comparison of their GC retention times and GC-MS with those of authentic compounds and ¹H NMR spectroscopy. For NMR spectroscopic characterization, the solution was washed with saturated NaHCO₃ solution, and the organic layer was dried with Na₂SO₄ then evaporated under reduced pressure before analysis. All experiments were run at least in duplicate, and the reported data are the average of these reactions. See Supporting Information for product identification for (*R*)-carvone oxidation.

Supporting Information (see footnote on the first page of this article): Complex characterization (ESI-MS, NMR spectra in the presence of O₂ or triflate), characterization of the products of (*R*)-carvone oxidation.

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Titanium–Imido Complexes with Pendant Groups – Synthesis, Characterization, and Evaluation of Their Role as Precatalysts for Ethylene Polymerization

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Keywords: Titanium / Imido ligands / N ligands / Coordination chemistry / Polymerization

The synthesis of several anilines (Ar^{PG}NH₂) substituted in the *ortho* position with pendant groups (PGs, terminated by potentially coordinative arene, thienyl, furanyl, or pyridyl functionalities) was accomplished by a two- to five-step synthesis in good yields. The Ar^{PG}NH₂ proligands were used for the preparation of titanium complexes starting from Ti(NMe₂)₄ in the presence of excess Me₃SiCl. Complexes of the general formula [Ti(NAr^{PG})Cl₂(NHMe₂)_x] (x = 1, 2), which are supported by a terminal imido functionality, were obtained in 60–95 % yield. The nature of the pendant group influences the coordination mode of the ligand. Although only monodentate imido linkages have been observed with

ligands where PG is arene, thiophene, and furan, ligands with substituted pyridine sidearms lead to chelating imido–donor functionalities. The potential hemilabile behavior of some imido–donor ligands, which results from the reversible coordination of the side arm, was studied by variable-temperature ¹H NMR spectroscopy. These compounds were evaluated as precatalysts for ethylene polymerization with various aluminum cocatalysts. Ultrahigh molecular-weight (UHMW) polyethylenes were obtained. All compounds were fully characterized by spectroscopic methods (¹H and ¹³C NMR), and elemental analysis and some were also characterized by single-crystal X-ray diffraction.

Introduction

Being isolobal with [C₅H₅][−] (Cp),^[1] the dianionic, π-donor terminal imido functional group [NR]^{2−} (R = alkyl or aryl) has emerged as an alternative spectator ligand to Cp ligands (e.g. in alkene metathesis and olefin polymerization).^[2–4] Imido complexes have also found application in materials chemistry (organometallic chemical vapor deposition^[5] and polyoxometalates)^[6] and have been implicated in a number of stoichiometric or catalytic transformations that involve the M=NR linkage itself, such as ammoxidation of propene,^[7] metathesis reactions,^[8] C–H activation,^[9] reactions with unsaturated C=C^[10] or C–X bonds,^[11] alkyne hydroamination,^[12,13] carboamination reaction,^[14] and strained-heterocycle opening.^[9d,15]

Several groups have probed the interactions of early-metal systems with pendant arenes, thienyl, or ether groups on Cp ligands and reported an enhancement of the catalytic activities in some examples for olefin oligo- or polymeriza-

tion, which is due to the hemilabile coordination of the pendant fragment at some stage in the catalytic cycle.^[16,17] In a somewhat related system, Magna et al. reported aryloxide–titanium complexes with pendant groups, which exhibit interesting catalytic activity for the selective dimerization of ethylene.^[18]

Although we^[19] and others^[4f,20] have shown that early-transition-metal complexes can incorporate functionalities at the periphery of the imido functionality, few complexes are known that incorporate a chelating imido–donor, i.e. with an imido group attached to the same metal center through the N atom of the imido functionality and a second donor atom.^[19,20a,20d,20e,20f] To the best of our knowledge, no hemilabile behavior has been demonstrated in such ligand systems (Figure 1).

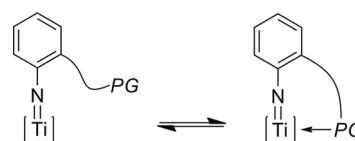


Figure 1. Titanium–imido systems with hemilabile or coordinated pendant groups.

We have previously prepared such imido–titanium complexes with a very short side arm (the distance between the imido N atom and the donor), which lead to bridging imido

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the author.

bimetallic complexes (Figure 2).^[19,21] The synthesis of aniline proligands substituted in the *ortho* position with pendant groups of longer and varying side-arm lengths and donor functionalities (with potentially coordinative S, O, N, and C atoms) was targeted with the goal of fostering chelation. Synthetic methods to obtain these proligands (Figure 3) and the preparation of the resulting titanium–imido

compounds are described in this paper. Preliminary reactivity studies towards ethylene polymerization are also reported.

Results and Discussion

1. Synthesis of the Imido Proligands

Unfortunately, there was no general method for the synthesis of the aniline proligands that were substituted in the *ortho* position with pendant groups of varying side-arm lengths and donor functionalities. Consequently, we developed three different methods (*A*, *B*, and *C*) that depended on the length of the linker between the aniline and the pendant group and the nature of the donor atoms of the pendant group. These three methods used are illustrated in Schemes 1, 2, and 3 and are fully detailed in the Supporting Information. They are based on the use of commercially-available precursors, afford the desired substituted anilines in two to five steps in reasonably good overall yields, and are summarized below.

Starting from 2-cyanoaniline, anilines with one (PG = thienyl, furanyl) or two carbon atoms (PG = phenyl, 2-picolinyl) in the linker between the aniline ring and the pendant group were synthesized according to the first route (Method *A*, Scheme 1). Importantly, this method afforded two types of proligand: anilines with an unsaturated methyldene on the linker were obtained in two steps through a

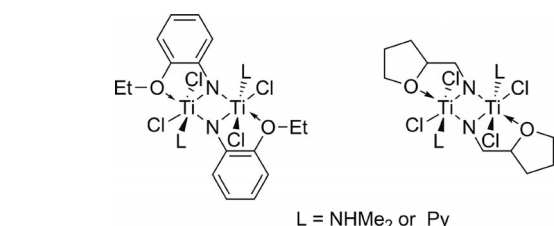


Figure 2. Previously reported titanium complexes with chelating, bridging imido–donor ligands (from ref.^[19]).

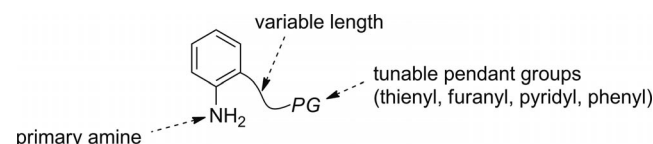
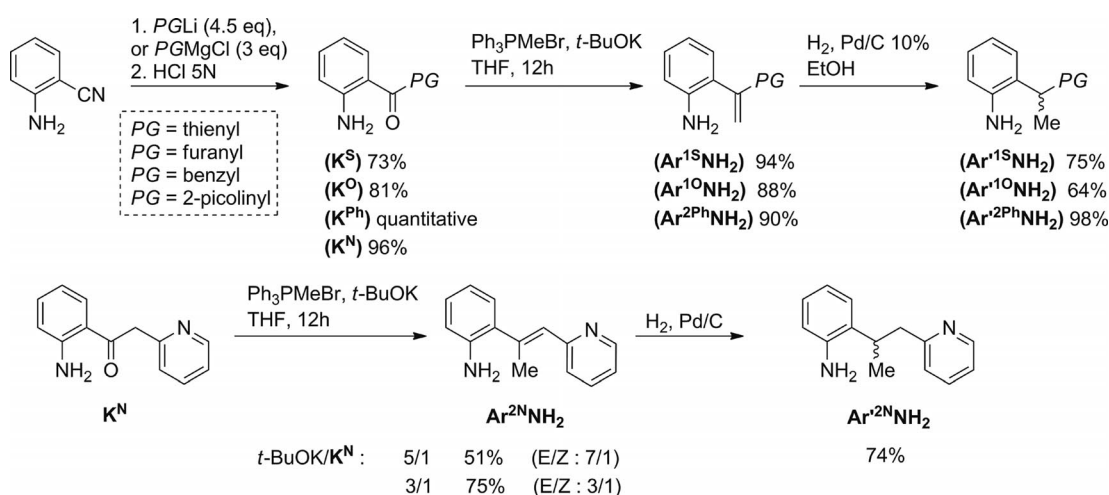
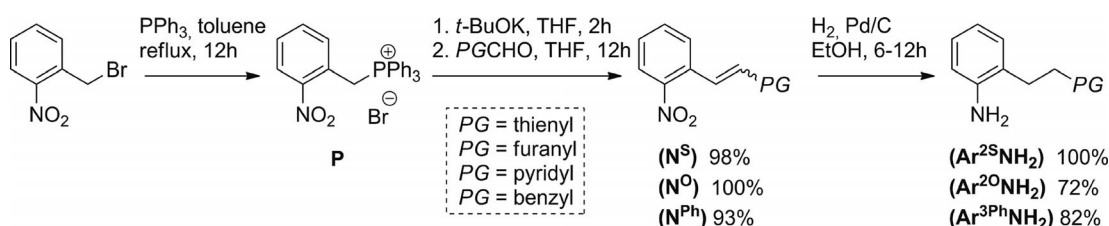


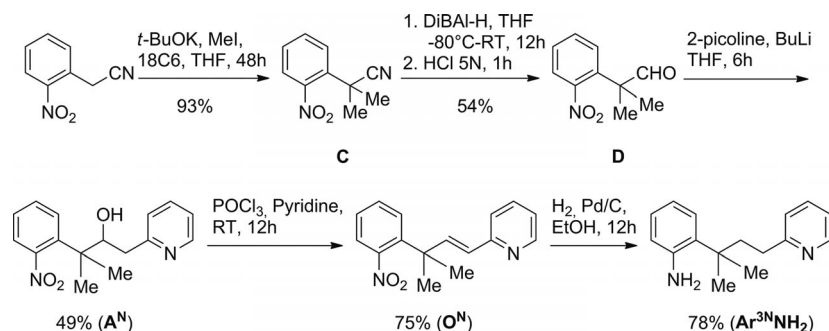
Figure 3. Targeted *ortho*-substituted aniline proligands with a pendant group.



Scheme 1. Method *A* for the synthesis of substituted anilines with one- and two-carbon spacers.



Scheme 2. Method *B* for the synthesis of substituted anilines with two- and three-carbon spacers.



Scheme 3. Method C for the synthesis of substituted anilines with three-carbon spacers.

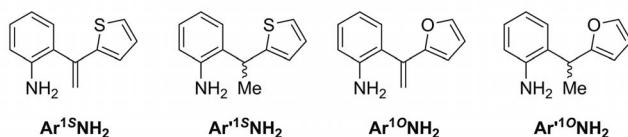
Wittig reaction, and a third reduction step produced anilines with a saturated linker.

The second route (Method B, Scheme 2) consists of a three-step synthesis starting from 2-nitrobenzyl bromide, which afforded anilines with two (PG = thienyl, furanyl, pyridyl) or three carbon atoms (PG = phenyl) in the linker between the aniline ring and the pendant group.

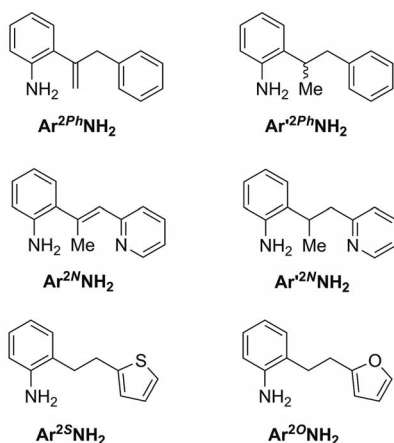
The last route (Method C, Scheme 3) produced anilines with a more sterically encumbered three-carbon spacer with two methyl groups at the α -position in order to force the coordination of the PG to the metal center. This method was only used for the synthesis of anilines with PG = pyridyl.

The substituted anilines are named Ar^nPGNH_2 (Figure 4) to take into account the number of carbon atoms (n) in the

- one-carbon chain spacer



- two-carbon chain spacer



- three-carbon chain spacer

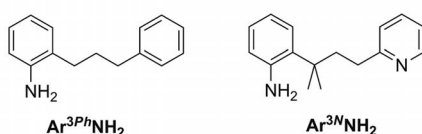


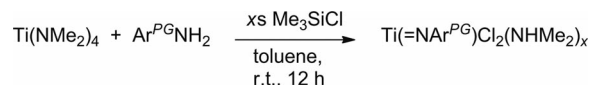
Figure 4. Substituted anilines prepared in this study.

linker chain between the *ortho* position of the aniline and the pendant group, and the nature of the PG (PG = S for thienyl, O for furanyl, N for pyridyl, Ph for phenyl).

2. Synthesis of the Titanium–Imido Complexes

a) Imido Complexes with PG = Thienyl, Furanyl, and Phenyl

The imido–titanium complexes were prepared according to our general procedure for easy access to various titanium– and vanadium–imido compounds of the type $[\text{M}(=\text{NR})\text{Cl}_2(\text{NHMe}_2)_2]$.^[19,22–25] In a one-pot synthesis, a toluene solution of $\text{Ti}(\text{NMe}_2)_4$ was treated with 1 equiv. of Ar^nPGNH_2 followed by the addition of 6 equiv. of Me_3SiCl (Scheme 4). After suitable workup, the imido complexes were obtained in yields from 59–95% as orange or red solids (Figure 5). Elemental analysis and ^1H and ^{13}C NMR spectra are in agreement with compounds of the general formula $[\text{Ti}(=\text{NAr}^n\text{PG})\text{Cl}_2(\text{NHMe}_2)_2]$, i.e. with two dimethylamino ligands coordinated to the metal center.



Scheme 4. General procedure for the synthesis of the titanium–imido complexes.

Single crystals of three of these complexes, O^1 , S^1 , and S^2 , suitable for X-ray diffraction studies were obtained from room temp. toluene or cold toluene/pentane solutions. Thermal ellipsoid plots are presented in Figures 6, 7, and 8, and selected metric parameters are given in Table 1. Two independent molecules are present in the molecular structure of O^1 , but as the geometric parameters are not significantly different, only one of these molecules (molecule A) is discussed.

In the solid state, the molecular structures of the three bisdimethylamino adducts (S^1 , O^1 , and S^2) are best described as a distorted trigonal bipyramid for S^1 with axial dimethylamine ligands ($\tau = 0.58$) or a distorted square pyramid for O^1 and S^2 [$\tau = 0.36$ (O^1), and 0.37 (S^2)].^[26] The $\text{N}_{\text{imido}}\text{--Ti--Cl}$ angles are in the range $107\text{--}115^\circ$, and the $\text{N}_{\text{imido}}\text{--Ti--N}_{\text{NHMe}_2}$ angles are in the range $94\text{--}100^\circ$. The distances and angles associated with the titanium center and the ligands are comparable to those found in other

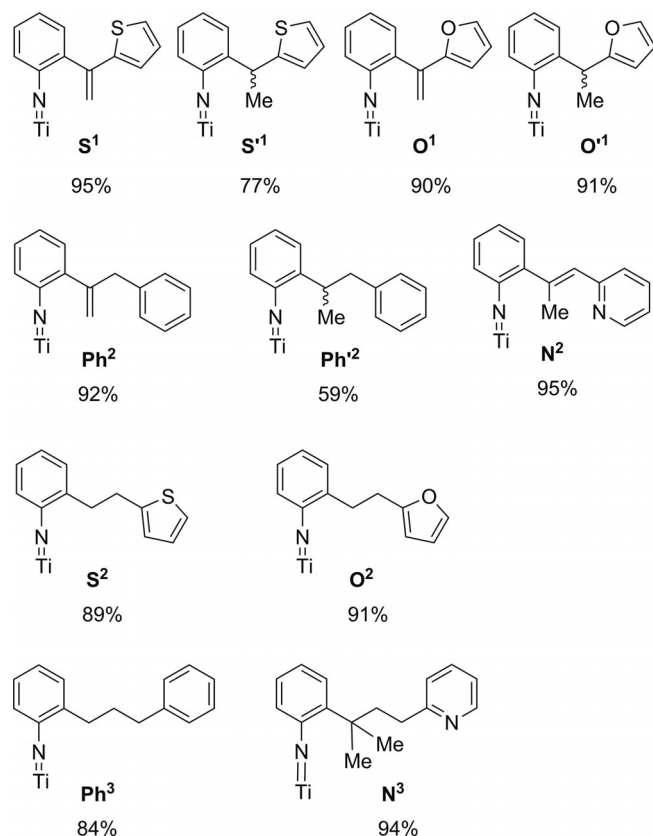


Figure 5. $[\text{Ti}(\text{=NAr}^{\text{PG}})\text{Cl}_2(\text{NHMe}_2)_2]$ with corresponding yields and labels.

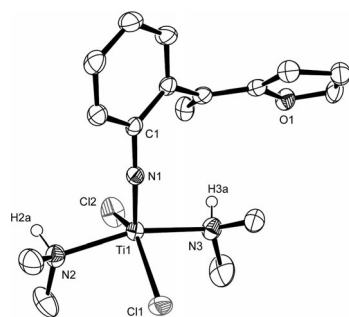


Figure 6. Thermal ellipsoid plot of **O¹** (molecule A) with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

$[\text{M}(\text{=NR})\text{Cl}_2(\text{NHMe}_2)_2]$ complexes ($\text{M} = \text{Ti}$,^[24,25,27] V^[22,23]). The complexes exhibit a short Ti–N_{imido} distance of 1.6979(16) for **O¹**, 1.700(2) for **S¹**, and 1.701(3) Å for **S²**, and the imido linkage is almost linear [Ti–N_{imido}–C_{ipso} 175.72(14), 174.6(2), and 166.9(2)° in **O¹**, **S¹**, and **S²**, respectively]. This is consistent with the lone pair on nitrogen being donated to an acceptor orbital on titanium, and the imido Ti–N bond can be considered as a triple bond.

The crystal structure determinations also unambiguously show noninteracting functional thienyl (**S¹**, **S²**), and furanyl (**O¹**) groups, with normal metric parameters, which are listed in Table 1. Both chlorine atoms occupy equatorial

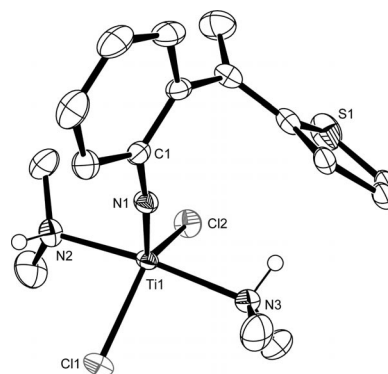


Figure 7. Thermal ellipsoid plot of **S¹** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

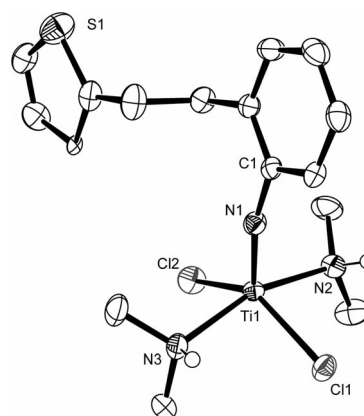


Figure 8. Thermal ellipsoid plot of **S²** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Table 1. Comparison of average interatomic distances [Å] and angles [°] in $[\text{Ti}(\text{=NAr}^{\text{PG}})\text{Cl}_2(\text{NHMe}_2)_2]$.

	O¹ [a]	S¹	S²
Ti–N _{imido}	1.6979(16)	1.700(2)	1.701(3)
N _{imido} –C _{ipso}	1.390(2)	1.389(4)	1.389(4)
Ti–Cl	2.3387(6)	2.3387(10)	2.3652(9)
	2.3441(6)	2.3251(10)	2.3375(9)
Ti–N _{NHMe2}	2.184(16)	2.202(3)	2.214(3)
	2.2088(16)	2.204(3)	2.188(3)
H _{NHMe2} ...Cl	2.403	2.482	2.529
Ti–N _{imido} –C _{ipso}	175.72(14)	174.6(2)	166.9(2)
Cl–Ti–Cl	138.17(3)	131.60(4)	140.39(4)
N _{NHMe2} –Ti–N _{NHMe2}	160.21(7)	170.57(10)	162.55(10)
N _{imido} –Ti–N _{NHMe2}	100.20(7)	94.45(11)	100.64(11)
	99.57(7)	94.97(11)	95.62(11)
N–H...Cl	158.4	159.8	148.3
Ti...D ^{PG} [b]	5.453	4.511	7.132 [c]
τ	0.36	0.58	0.37

[a] Geometric parameters are given for independent molecule A.

[b] D^{PG} is the donor atom in the PG. [c] A shorter (4.566 Å) intermolecular Ti...S distance is found.

sites in the trigonal bipyramid or square pyramid with Cl1–Ti–Cl2 angles of 138.17(3) (**O¹**), 131.60(16) (**S¹**), and

140.39(4)° (S²) and mean Ti–Cl bond lengths of 2.34 (O¹), 2.34 (S¹), and 2.35 Å (S²). The two *trans* dimethylamino ligands have mean Ti–N_{NHMe₂} bond lengths of ca. 2.20 Å for the three compounds. The supramolecular structure is characterized by Me₂N–H···Cl intermolecular hydrogen bonds (NH···Cl 2.403–2.529 Å, N–H···Cl 159.8–148.3°), which is a feature that is common to many related compounds.^[22,24,27]

Heating solid O¹ at 60 °C under dynamic vacuum (ca. 5 × 10^{−2} mbar) resulted in no sign of PG donor atom coordination and left unchanged solids with some degree of decomposition (evidenced by the formation of free aniline ligands and NH₂Me₂Cl). The ammonium salt NH₂Me₂Cl was also detected in substantial amounts after solid O² had been left under dynamic vacuum (ca. 9 × 10^{−4} mbar) for 12 h at room temp. This suggests that, in the solid state, decomposition of these complexes occurs before the coordination of the O or S atom. However, the compounds are thermally stable in solution: heating a C₆D₆ solution of O¹ to 80 °C resulted in no sign of decomposition, PG donor atom coordination, or NHMe₂ elimination. Furthermore, a variable-temperature ¹H NMR study of O² in [D₈]toluene showed that the proton in the 2-position from the furanyl O atom (*α* from O) is almost unchanged when lowering the temperature. At low temperature, the only proton that is notably low-field shifted (from 6.35 ppm at 295 K to 6.85 ppm at 195 K, see Supporting Information) is the H atom in the 3-position (*β*' from O). This behavior (no line broadening) suggests the presence of a preferred average orientation of the furanyl H or C atoms in the 3-position instead of a dynamic exchange that involves reversible coordination of the oxygen atom.

b) Imido Complexes with PG = Pyridyl

The reaction of the pyridyl-containing PG Ar^{2N}NH₂ with Ti(NMe₂)₄ in the presence of Me₃SiCl under similar condi-

tions as described above yields an orange solid in 95% yield. NMR spectroscopy and an X-ray diffraction study clearly show the formation of a bisdimethylamino adduct: [Ti(=NAr^{2N})Cl₂(NHMe₂)₂] (N²).

Figure 9 shows the molecular structure of N², and selected metric parameters are given in Table 2. The structure of N² resembles that of other five-coordinate [Ti(=NAr^{PG})Cl₂(NHMe₂)₂] complexes described here with comparable metric parameters [Ti–N_{imido} 1.7129(8) Å, Ti–N_{imido}–Cl 179.11(8)°, Cl–Ti–Cl 131.857(15)°, mean Ti–Cl 2.351 Å, mean Ti–N_{amine} 2.217 Å]. The main feature in the pentacoordinate titanium center is again the absence of coordination of the PG pyridine nitrogen atom (see below, Ti···N_{Py} 4.931 Å). The molecular structure is characterized by an intramolecular hydrogen bond between the pyridine nitrogen atom and the hydrogen atom of a NHMe₂ ligand (N2) [NH···N_{Py} 2.408 Å, N–H···N_{Py} 145.8°].

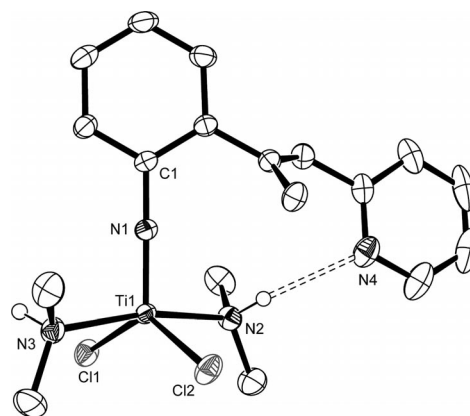


Figure 9. Thermal ellipsoid plot of N² with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Table 2. Comparison of average interatomic distances [Å] and angles [°] in [Ti(=NAr^{PG})Cl₂(NHMe₂)_x] complexes containing pyridyl PGs.

	N ²	N ^{'2}	N ^{''2}	N ^{'''2}	N ³	N ^{'3}
Ti–N _{imido}	1.7129(8)	1.694(3)	1.708(3)	1.7011(15)	1.7107(13)	1.7006(3)
N _{imido} –C _{ipso}	1.3868(12)	1.385(5)	1.375(4)	1.387(2)	1.391(2)	1.389(2)
Ti–Cl	2.3607(4), 2.3347(4)	2.3437(12), 2.3455(12)	2.4029(11), 2.4190(11), 2.4696(10), 2.7771(11)	2.3407(5), 2.3334(6)	2.3465(5), 2.3298(5)	2.3660(5), 2.3349(5)
Ti–N _{NHMe₂}	2.2232(9), 2.2104(9)	2.194(3)	–	2.2100(15), 2.1991(15)	2.2230(14), 2.1924(13)	2.1973(14)
Ti–N _{Py}	–	2.222(3)	2.314(3)	–	–	2.2400(14)
Ti···N _{Py}	4.931	–	–	4.387	4.569	–
H _{NHMe₂} ···Cl	2.411	–	–	2.485	–	2.444
Ti–N _{imido} –C _{ipso}	179.11(8)	172.3(3)	172.5(2)	174.86(13)	164.48(12)	167.69(12)
Cl–Ti–Cl	131.857(15)	142.68(5)	84.83(3), 79.32(3), 80.76(3)	128.12(2)	135.42(2)	138.77(2)
N _{NHMe₂} –Ti–N _{NHMe₂}	168.74(3)	–	–	173.55(6)	164.76(5)	–
N _{NHMe₂} –Ti–N _{Py}	–	159.14(12)	–	–	–	157.70(6)
N _{imido} –Ti–N _{NHMe₂}	95.31(4), 95.80(4)	98.15(14)	–	94.96(6), 91.35(7)	99.62(6), 95.32(6)	99.46(6)
N _{imido} –Ti–N _{Py}	–	102.55(14)	97.19(11)	–	–	102.68(6)
N–H···Cl	166.0	–	–	162.9	–	155.5
τ	0.61	0.27	–	0.76	0.49	0.32

The noncoordination of the strong donor in the pendant pyridine in N^2 is significant, and might be explained by (i) the weaker donating properties of the N atom due to extended delocalization through the C=C double bond and/or (ii) the rigidity of the unsaturated linker.

In order to test the influence of the length of the side arm on the potential coordination of the pendant pyridine group, we treated the analogous saturated prolignand $Ar'^{2N}NH_2$ with $Ti(NMe_2)_4$ in the presence of Me_3SiCl (Scheme 5). Under identical experimental conditions we observed (by ^1H NMR spectroscopy of an aliquot of the solution) the formation of two compounds: a major species N'^2 and a minor species N''^2 . Integration of the ^1H NMR spectrum indicates the presence of only one $NHMe_2$ ligand per imido in N'^2 , which is in agreement with a compound of formula $[Ti(=NAr'^{2N})Cl_2(NHMe_2)]_1$, whereas signals assigned to dimethylammonium are present in the spectrum of N''^2 . Complex N''^2 was isolated in a very low yield as yellow crystals suitable for an X-ray diffraction study.

The molecular structure of N''^2 is presented in Figure 10, and selected metric parameters are given in Table 2. Complex N''^2 is formulated as the ionic complex $[Ti(=NAr'^{2N})$

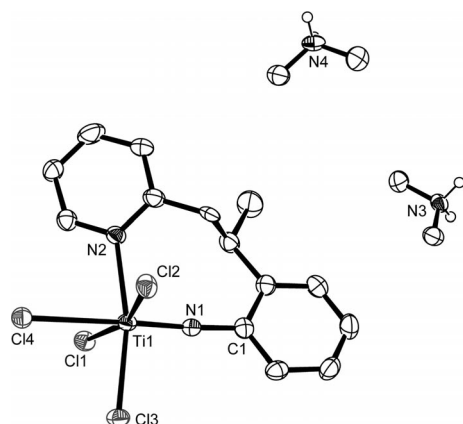


Figure 10. Thermal ellipsoid plot of N''^2 with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

$Cl_4][NH_2Me_2]_2$. The chelating imido–pyridine ligand forms an eight-membered ring. The octahedrally coordinated titanium center is surrounded by four chlorine atoms, the nitrogen atom of a linear imido linkage $[Ti-N_{imido} 1.708(3) \text{ \AA}, Ti-N_{imido}-C1 172.5(2)^\circ]$, and the N atom of the pendant pyridine group in the *cis* position with respect to the N_{imido} atom $[Ti-N_{Py} 2.314(3) \text{ \AA}, N_{imido}-Ti-N_{Py} 97.19(11)^\circ]$. The Ti–Cl bond length *trans* to the N_{imido} atom is severely elongated $[2.7771(11) \text{ \AA}]$ due to the *trans* influence of the imido ligand.

X-ray quality crystals of neutral N'^2 were also obtained, which allowed us to determine its molecular structure by X-ray diffraction (Figure 11). The most prominent feature of the molecular structure of N'^2 is the coordination of the nitrogen atom of the pendant pyridine group to the titanium center, which forms an eight-membered ring. The pyridine substituent is located *trans* to the remaining dimethylamino ligand $[Ti-N_{NHMe_2} 2.194(3) \text{ \AA}, Ti-N_{Py} 2.222(3) \text{ \AA}]$ within a square pyramidal complex ($\tau = 0.27$). The geometric parameters associated with the titanium center and the ligands are comparable to those found in related $[Ti(=NAr)Cl_2(NHMe_2)_2]$ complexes presented here (see Table 2). The imido functionality exhibits a short Ti– N_{imido}

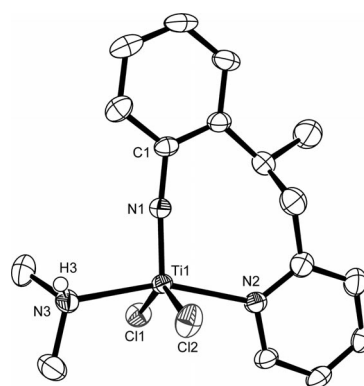
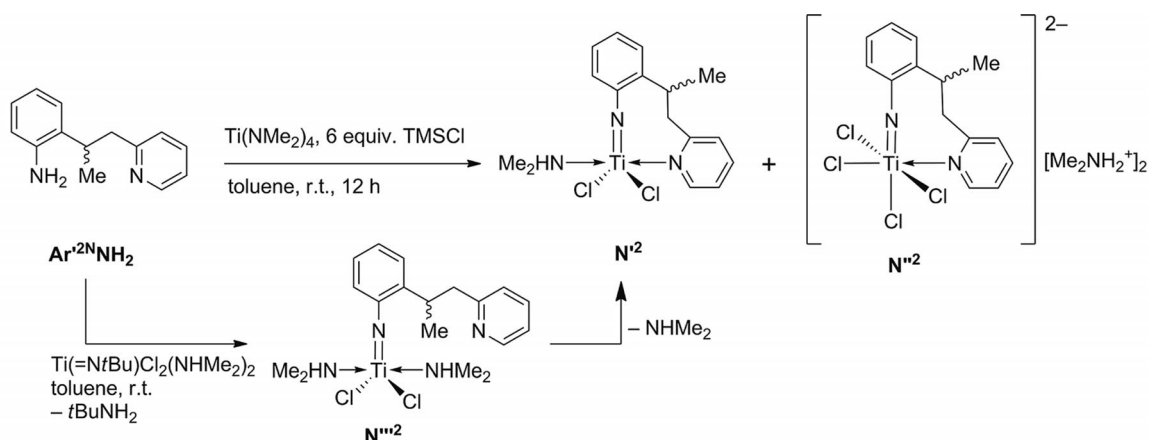


Figure 11. Thermal ellipsoid plot of N'^2 with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C and toluene solvate molecule omitted. H atoms bonded to N drawn as spheres of arbitrary radius.



Scheme 5. Synthesis of chelating imido–pyridine complexes from $Ar'^{2N}NH_2$.

distance of 1.694(3) Å and an almost linear imido linkage [Ti–N_{imido}–C_{ipso} 172.3(3)°]. The respective *trans*-located chlorine atoms occupy basal sites in the square pyramid with a Cl1–Ti–Cl2 angle of 142.68(5)° and mean Ti–Cl bond lengths of 2.34 Å.

Formation of the ionic N² might result from the reaction with in situ generated Me₂NH₂Cl [i.e. from a reaction between liberated NHMe₂ and Me₃SiCl,^[28] Equation (1)]. The factors that govern the formation of such an ammonium salt are still under scrutiny. Nevertheless, in seeking an alternative synthetic strategy to N² free of ionic N², the transimination reaction of [Ti(=N*t*Bu)Cl₂(NHMe₂)₂] with an equimolar amount of Ar³NH₂ was considered (Scheme 5). This mild exchange reaction afforded a high yield of pure N².^[29] Interestingly, small amounts of the intermediate bis(dimethylamino) adduct (N²) were crystallized from the pentane washings from this reaction. As N² is very similar to N², it will not be discussed (Figure 12 and Table 2), but the isolation of both complexes with and without coordination of the N atom of the pyridine strongly support the potential hemilabile character of the pyridine PG in these ligands.

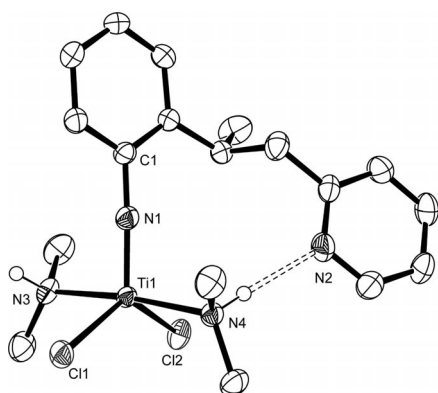


Figure 12. Thermal ellipsoid plot of N² with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Further proof of the intramolecular coordination of such pyridine PGs comes from our studies with Ar³NH₂, which possesses a longer, three-carbon linker (Scheme 6).

Treatment of a toluene solution of Ti(NMe₂)₄ with Ar³NH₂ in the presence of 6 equiv. of Me₃SiCl at room

temp. for 12 h afforded orange N³. The formation of the bis-NHMe₂ adduct was further confirmed by the ¹H NMR spectrum of N³ and X-ray structure determination. A thermal ellipsoid plot is presented in Figure 13, and selected metric parameters are given in Table 2. The structure is similar to the other five-coordinate bis(dimethylamino) adducts presented here and is not detailed further.

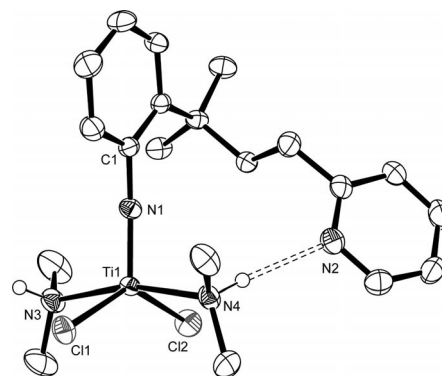
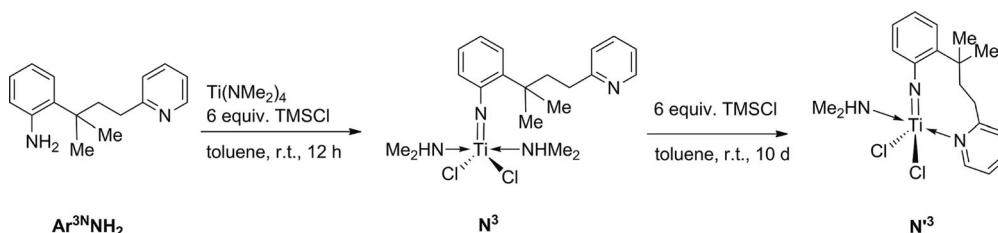
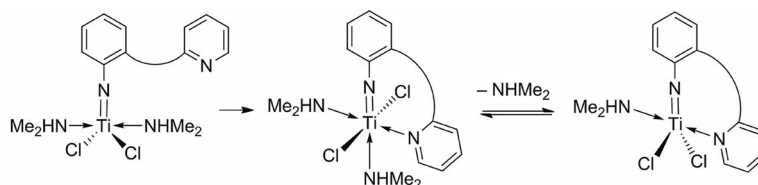


Figure 13. Thermal ellipsoid plot of N³ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

However, with longer reaction time, we noted a slow evolution of the NMR spectrum of the above reaction mixture [Ti(NMe₂)₄, Ar³NH₂, Me₃SiCl]. After 10 d of reaction in the presence of Me₃SiCl, a new complex, N³, was obtained as the unique species (Scheme 6). We later found it more convenient and reproducible to prepare N³ from isolated N³ and Me₃SiCl in toluene. The exact role of the excess Me₃SiCl in this transformation is presently unknown. Me₃SiCl might help the decooordination of the dimethylamine through silylation of the coordinated NHMe₂ (see above). Furthermore, in the absence of Me₃SiCl, repeated dissolution of N³ in toluene followed by vacuum treatment (repeated five times) led to dimethylamine elimination with concomitant formation of N³ (although complete transformation was not achieved, as about 10% of N³ was still present after five repetitions of this treatment). This suggests that vacuum treatment also plays an important role in displacing the equilibrium of NHMe₂ decooordination. Hence, the chelate complex N³ seems more difficult to obtain than the parent N², which we attribute to the length of the donor side arm: the eight-membered metallacycle in N² is probably more favorable than the nine-membered ring in N³.



Scheme 6. Synthesis of monodentate and chelating imido-pyridine complexes from Ar³NH₂.



Scheme 7. From monodentate to chelating imido-pyridine complexes.

A thermal ellipsoid plot of the solid-state structure of **N**³ is presented in Figure 14, and selected metric parameters are given in Table 2. The molecular structure of **N**³ clearly indicates the coordination of the nitrogen atom of the pendant pyridine group to the metal center, which forms a nine-membered ring. The pyridine substituent is *trans* to the remaining dimethylamino ligand. The geometry of the metal center is a distorted trigonal bipyramid ($\tau = 0.77$). The distances and angles associated with the titanium center and the ligands are comparable to those found in related $[\text{Ti}(=\text{NAr})\text{Cl}_2(\text{NHMe}_2)_2]$ complexes presented here (Table 2). The complex exhibits a short Ti–N_{imido} distance of 1.7006(3) Å and an almost linear imido linkage [Ti–N_{imido}–C_{ipso} 167.69(12)°]. The chlorine atoms occupy equatorial sites in the trigonal bipyramid with a Cl1–Ti–Cl2 angle of 138.77(2)° and mean Ti–Cl bond lengths of 2.35 Å. The *trans* dimethylamino and pyridine ligands have similar Ti–N bond lengths [Ti–N_{NHMe2} 2.1973(14) Å, Ti–N_{Py} 2.2400(14) Å]. Molecules of **N**³ are also associated by a network of Me₂N–H···Cl hydrogen bonds.

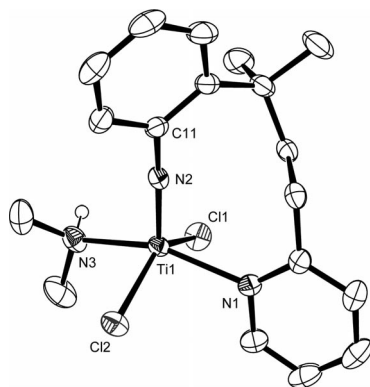


Figure 14. Thermal ellipsoid plot of **N**³ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

A variable-temperature ¹H NMR study was conducted on a [D₈]toluene solution of **N**³ (Supporting Information). At high temperatures (318–358 K), the broadening of several signals is observed, in particular those assigned to pyridine and aryl *ortho*-H. This fluxional behavior indicates a dynamic equilibrium between two species. At lower temperatures, different behavior is evidenced with broadening and splitting of the signals of NHMe₂ (both NH and Me), the methyl groups on the sidearm, and the methylene protons (attached to the pyridyl substituent) of the sidearm. The 2D ¹H–¹⁵N NMR and NOESY experiments, show a

correlation between the NH proton (¹H δ = 7.37 ppm) of one NHMe₂ (¹⁵N δ = –339 ppm) with the nitrogen atom of the pyridine (¹⁵N δ = –78 ppm) at 183 K. This behavior results from the presence of only one compound at low temperature, which has a hydrogen bond between the N atom of the pyridine and the NH of one dimethylamine ligand, as observed in the solid-state structure of **N**³.

The fact that we have not been able to establish hemilability in complexes supported by ligands with a pyridine PG most probably arises from the stability of pentacoordinate bis(dimethylamine) complexes (possibly enhanced by H bonding with pyridine N donors), as well as facile and irreversible NHMe₂ displacement in hypothetical octahedral bis(dimethylamine) intermediates through coordination of the pyridine PG (and elimination of the NHMe₂ *trans* to the imido function), which leads to pentacoordinate mono-NHMe₂ chelate complexes (Scheme 7).

3. Preliminary Catalytic Ethylene Polymerization Studies

Several precatalysts have been evaluated in the polymerization reaction of ethylene with various cocatalysts [methylaluminumoxane (MAO) and triethylaluminum (TEA)] and under different conditions. The results are summarized in Table 3, with reference to $[\text{Ti}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)\text{Cl}_2(\text{NHMe}_2)_2]$ as a precatalyst.^[19]

Whatever the precatalyst, low to moderate activities were observed (Table 3, Entries 1–12). No significant influence on the activity is observed whether the pendant group is a thiophenyl, a phenyl, a furanyl, or a pyridyl group. An increase of activity is observed with **S**¹ and **Ph**² when activated with MAO compared to TEA. Decreasing the temperature from 60 to 25 °C led to a slight decrease in activity for **N**² (Entries 9 and 10). Optimization of the titanium concentration led to an increase in activity of up to 24000 g/(mol_{Ti} h bar) (Entries 6, 7, and 11). However, no clear benefit to the polymerization activity could be evidenced by the presence of the PG compared to $[\text{Ti}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)\text{Cl}_2(\text{NHMe}_2)_2]$ (Entry 12). Furthermore, the activities of these precatalysts remain largely inferior to the some of the most productive imido–titanium precatalysts.^[2c,4g,30] One explanation for the relatively poor activity of our systems is the presence of donor ligands in the precatalysts that could interact with the aluminum cocatalyst.

Size exclusion chromatography could not be carried out on the polymer samples as gels were obtained. Accordingly, we conclude that the polymers were UHMW polyethylenes with *M*_w above 10⁶ g mol^{–1}. The presence of an additional side arm might therefore favor propagation over termination.

Table 3. Ethylene polymerization with different titanium–imido precatalysts.^[a]

Entry	Precatalyst (mmol)	Cocatalyst	Al/Ti	Polymer yield [g]	Activity [g/(mol _{Ti} h bar)] ^[b]
1	S ¹ (0.15)	MAO	200	5.6	1866
2	S ¹ (0.15)	TEA	3	0.7	233
3	Ph ² (0.15)	MAO	200	6.3	2100
4	Ph ² (0.15)	TEA	3	0.5	167
5	N ² (0.15)	MAO	200	8.7	2900
6	O ² (0.0125)	MAO	500	5.6	22400
7	Ph ³ (0.0125)	MAO	500	6.1	24400
8	N ³ (0.15)	MAO	200	9.3	3100
9	N ² (0.15)	MAO	200	9.5	3167
10 ^[c]	N ² (0.15)	MAO	200	6.1	2033
11	N ² (0.0125)	MAO	500	6.0	24000
12	N ² (0.0125)	TEA	3	0.26	104
13	[Ti(=NAr)Cl ₂ (NHMe ₂) ₂] ^[d]	MAO	500	7.6	30400

[a] Conditions: toluene (25 mL), 60 °C, ethylene (20 bar), 1 h. [b] Calculated from isolated polymer. [c] *T* = 25 °C instead of 60 °C. [d] With Ar = 2,6-C₆H₃ (synthesis according to ref.^[19]).

Conclusions

New imido prolignands that possess a potentially coordinating functional PG have been synthesized. The corresponding imido complexes were prepared by reaction with Ti(NMe₂)₄ in the presence of Me₃SiCl or by transamination from [Ti(NⁱBu)Cl₂(NHMe₂)₂]. The O-, S-, and Ph-based ligands afforded five-coordinate complexes [Ti(NAr^{PG})Cl₂(NHMe₂)₂] with no sign of PG coordination, whereas ligands that bear a pyridyl substituent, which is a better coordinating group, associated with a longer and more flexible side arm led to the formation of chelated imido–pyridine complexes [Ti(NAr^{PG})Cl₂(NHMe₂)₁]. However, the hemilabile behavior of these ligands could not be firmly established. When associated with various aluminum activators, some of these complexes are precatalysts for ethylene polymerization, which produced UHMW polyethylenes. Contrary to that reported occasionally in the literature, the presence and/or the nature of the PG seems to favor propagation over termination. Another detrimental consequence of these PG-functionalized imido compounds could be direct interaction with the cocatalyst. Further studies are necessary to fully understand these catalytic systems and probe the effects of the various PGs.

Experimental Section

General Methods and Instrumentation: All manipulations were carried out using standard Schlenk or dry box techniques under an atmosphere of argon. Solvents were dried with appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded with Bruker ARX250, DPX300, Avance300, and Avance500 spectrometers and referenced internally to residual protiosolvent (¹H) resonances and are reported relative to tetramethylsilane. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). IR spectra were recorded with a Perkin–Elmer Spectrum GX FT-IR spectrometer. Samples were prepared under an argon atmosphere in a glove box as nujol mulls between NaCl plates. Gel permeation chromatography was conducted with a Waters Alliance GPCV 2000 chromatograph equipped with three columns (two Styragel HT6E and one Styragel HT2). Samples (1 mg mL^{−1}) were eluted

with 1,2,4-trichlorobenzene with a flow rate of 1 mL min^{−1} at 150 °C. Ti(NMe₂)₄ was purchased from Aldrich. [Ti(=N-2,6-*i*Pr₂-C₆H₃)Cl₂(NHMe₂)₂] was prepared according to our published procedure.^[19] MAO (10 wt.-% toluene solution) and TEA were purchased from Chemtura.

Crystal Structure Determination: The structures of nine compounds were determined. Crystal data collection and processing parameters are given in Tables 4 and 5. The selected crystals, which were sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N₂. For all the structures, data were collected at low temperature (*T* = 180 K) either with a Stoe Imaging Plate Diffraction System, an Oxford Diffraction Kappa CCD Excalibur diffractometer, or a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo-*K*_α radiation (*λ* = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well measured reflections. Crystal decay was monitored during data collection by measuring 200 reflections by image and no significant fluctuation of the intensities was observed. Structures were solved by direct methods using the program SIR92^[31] and subsequent difference Fourier maps, models were refined by least-squares procedures on a *F*² with SHELXL-97^[32] integrated in WINGX version 1.64,^[33] and empirical absorption corrections were applied to the data.^[34] For **N**² and **N**³, it was not possible to solve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON^[35] resulted in a smooth refinement. As a few low-order reflections were missing from the data set, the electron count is underestimated. Thus, the values given for *D*(calc), *F*(000), and the molecular weight are only valid for the ordered part of the structure. Details of the structure solution and refinements are given in the Supporting Information (CIF files), together with a full list of atomic coordinates, bond lengths and angles, and displacement parameters for all structures.

CCDC-836637 (for **O**¹), -836638 (for **S**¹), -836639 (for **N**²), -836640 (for **N**²), -836641 (for **N**²), -836642 (for **N**³), -836643 (for **N**³), -836644 (for **S**²), and -836645 (for **N**²) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Prolignands: A full description of the synthesis of the prolignands is given in the Supporting Information.

Table 4. Crystallographic data, data collection, and refinement parameters for **O**¹, **S**¹, **S**², and **N**².

	O ¹	S ¹	S ²	N ²
Chemical formula	C ₁₆ H ₂₃ Cl ₂ N ₃ OTi	C ₁₆ H ₂₃ Cl ₂ N ₃ STi	C ₁₆ H ₂₅ Cl ₂ N ₃ STi	C ₁₈ H ₂₆ Cl ₂ N ₄ Ti
Formula weight	392.14	408.21	410.25	417.23
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	17.7630(6)	8.5177(18)	13.5942(3)	17.576(3)
<i>b</i> [Å]	14.8830(3)	27.216(5)	7.2519(2)	10.2796(15)
<i>c</i> [Å]	16.2330(5)	8.943(2)	20.4286(5)	12.3180(19)
α [°]	90	90	90	90
β [°]	115.862(4)	101.761(6)	93.011(2)	103.577(9)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	3861.7(2)	2029.8(7)	2011.15(9)	2163.3(6)
<i>Z</i>	8	4	4	4
<i>D</i> _{calcd.} [g cm ⁻³]	1.349	1.336	1.355	1.281
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.726	0.789	0.797	0.65
<i>F</i> (000)	1632	848	856	872
θ range [°]	3.08 to 26.37	2.55 to 25.68	3.36 to 26.37	2.61 to 38.69
Measured reflections	40093	18475	17088	55082
Unique reflections/ <i>R</i> _{int}	7886/0.0574	3855/0.0316	4088/0.0361	12212/0.0309
Parameters/restraints	435/6	206/3	212/0	231/0
Final <i>R</i> indices	<i>R</i> 1 = 0.0312,	<i>R</i> 1 = 0.0463,	<i>R</i> 1 = 0.0459,	<i>R</i> 1 = 0.0383,
[<i>I</i> > σ 2(<i>I</i>)]	<i>wR</i> 2 = 0.058	<i>wR</i> 2 = 0.1251	<i>wR</i> 2 = 0.1300	<i>wR</i> 2 = 0.0874
Final <i>R</i> indices	<i>R</i> 1 = 0.061,	<i>R</i> 1 = 0.0585,	<i>R</i> 1 = 0.0560,	<i>R</i> 1 = 0.0739,
(all data)	<i>wR</i> 2 = 0.0624	<i>wR</i> 2 = 0.1346	<i>wR</i> 2 = 0.1377	<i>wR</i> 2 = 0.1019
Goodness of fit	0.876	1.032	1.039	1.004
$\Delta\rho_{\text{max}}$ – $\Delta\rho_{\text{min}}$	0.293 and –0.28	1.904 and –0.795	1.057 and –0.802	0.592 and –0.286

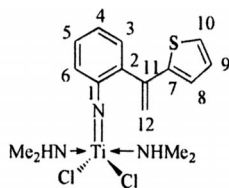
Table 5. Crystallographic data, data collection, and refinement parameters for **N**^{'2}, **N**^{''2}, **N**³, and **N**^{'3}.

	N ^{'2}	N ^{''2}	N ^{'''2}	N ³	N ^{'3}
Chemical formula	C ₁₆ H ₂₁ Cl ₂ N ₃ Ti, C ₇ H ₈	C ₁₈ H ₃₀ Cl ₄ N ₄ Ti	C ₁₈ H ₂₈ Cl ₂ N ₄ Ti	C ₂₀ H ₃₂ Cl ₂ N ₄ Ti	C ₁₈ H ₂₅ Cl ₂ N ₃ Ti
Formula weight	466.29	492.16	419.24	447.30	402.21
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$
<i>a</i> [Å]	7.5496(7)	7.9478(6)	29.7027(18)	10.02920(10)	8.5768(5)
<i>b</i> [Å]	10.7460(10)	12.1653(11)	16.5297(10)	10.81580(10)	10.2656(6)
<i>c</i> [Å]	28.686(3)	16.5930(11)	9.1432(7)	21.4911(2)	13.8592(7)
α [°]	90	76.999(7)	90	90	81.360(2)
β [°]	94.007(6)	81.157(6)	106.421(2)	90	74.808(2)
γ [°]	90	88.214(7)	90	90	86.146(2)
<i>V</i> [Å ³]	2321.6(4)	1544.6(2)	4306.0(5)	2331.22(4)	1163.74(11)
<i>Z</i>	4	2	8	4	2
<i>D</i> _{calcd.} [g cm ⁻³]	1.334	1.058	1.293	1.274	1.148
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.613	0.631	0.654	0.608	0.601
<i>F</i> (000)	976	512	1760	944	420
θ range [°]	1.42 to 26.37	3.35 to 24.71	2.46 to 27.86	3.36 to 26.37	1.54 to 26.37
Measured reflections	21076	17091	19825	48330	20142
Unique reflections/ <i>R</i> _{int}	4743/ <i>R</i> (int) = 0.0483	5269/0.0605	5111/0.0387	4767/0.0413	4746/0.0243
Parameters/restraints	266/0	249/0	231/0	250/0	221/0
Final <i>R</i> indices	<i>R</i> 1 = 0.0603,	<i>R</i> 1 = 0.0374,	<i>R</i> 1 = 0.0339,	<i>R</i> 1 = 0.0226,	<i>R</i> 1 = 0.0327,
[<i>I</i> > σ 2(<i>I</i>)]	<i>wR</i> 2 = 0.1356	<i>wR</i> 2 = 0.0919	<i>wR</i> 2 = 0.0772	<i>wR</i> 2 = 0.0568	<i>wR</i> 2 = 0.0881
Final <i>R</i> indices	<i>R</i> 1 = 0.1039,	<i>R</i> 1 = 0.0729,	<i>R</i> 1 = 0.0584,	<i>R</i> 1 = 0.0248,	<i>R</i> 1 = 0.0425,
(all data)	<i>wR</i> 2 = 0.1530	<i>wR</i> 2 = 0.0961	<i>wR</i> 2 = 0.0872	<i>wR</i> 2 = 0.0584	<i>wR</i> 2 = 0.0923
Goodness of fit	1.045	0.842	1.014	1.065	1.076
$\Delta\rho_{\text{max}}$ – $\Delta\rho_{\text{min}}$	1.098 and –0.400	0.284 and –0.234	0.281 and –0.220	0.235 and –0.131	0.280 and –0.202

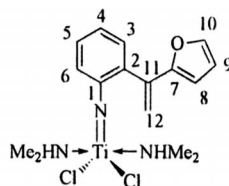
Syntheses of Titanium–Imido Complexes

General Procedure:^[19] To a toluene solution (2 mL) of Ti-(NMe₂)₄ (300 mg, 1.34 mmol) was slowly added the aniline ArNH₂ (1–1.1 equiv.) at room temperature. After slow addition of trimeth-

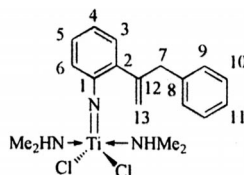
ylsilyl chloride (TMSCl, 1.1 mL), the solution was stirred overnight at room temperature. The volatiles were removed under reduced pressure, the residue was washed with pentane (3 × 6 mL), and dried under vacuum to afford the pure material.

Synthesis of **S**¹

This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\text{Ar}^{1\text{S}}\text{NH}_2$ (100 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). **S**¹ (175 mg, 0.43 mmol, 95%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at -35°C . ^1H NMR (250 MHz, C_6D_6): δ = 7.05–7.15 (m, 2 H, $\text{H}^3 + \text{H}^5$), 7.02 (dt, J = 1.5, 7.7 Hz, 1 H, H^{10}), 6.81 (dd, J = 0.7, 5.1 Hz, 1 H, H^9), 6.70–6.78 (m, 2 H, $\text{H}^4 + \text{H}^8$), 6.64 (dd, J = 3.7, 5.1 Hz, 1 H, H^6), 5.94 (s, 1 H, $\text{H}^{12\text{a}}$), 5.31 (s, 1 H, $\text{H}^{12\text{b}}$), 2.60 (m, 2 H, H_{NH}), 2.26 (d, J = 6.1 Hz, 12 H, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.5 MHz, C_6D_6): δ = 144.20 (C^1), 143.91 (C^{11}), 141.49 (C^7), 134.73 (C^2), 129.53 (C^3), 128.07 (C^5), 126.91 (C^9), 126.18 (C^8), 125.83 (C^{10}), 124.67 (C^4), 122.21 (C^6), 114.59 (C^{12}), 40.51 (C_{Me}) ppm. $\text{C}_{16}\text{H}_{23}\text{Cl}_2\text{N}_3\text{STi}$ (408.21): calcd. C 47.08, H 5.68, N 10.29; found C 46.81, H 5.61, N 10.03.

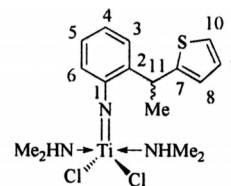
Synthesis of **O**¹

This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\text{Ar}^{1\text{O}}\text{NH}_2$ (270 mg, 1.46 mmol), and TMSCl (1.0 mL, 7.88 mmol). **O**¹ (470 mg, 1.20 mmol, 90%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at -35°C . ^1H NMR (250 MHz, C_6D_6): δ = 6.97–7.15 (m, 4 H, $\text{H}^3 + \text{H}^4 + \text{H}^5 + \text{H}^{10}$), 6.73 (dt, J = 1.0, 7.4 Hz, 1 H, H^6), 6.16 (d, J = 1.0 Hz, 1 H, $\text{H}^{12\text{a}}$), 6.09 (dd, J = 1.8, 3.1 Hz, 1 H, H^9), 5.93 (d, J = 3.1 Hz, 1 H, H^8), 5.38 (d, J = 1.0 Hz, 1 H, $\text{H}^{12\text{b}}$), 2.80 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, H_{NMe_2}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.5 MHz, C_6D_6): δ = 158.30 (C^1), 155.54 (C^7), 142.28 (C^{10}), 137.20 (C^{11}), 132.72 (C^2), 129.60 (C^3), 128.01 (C^5), 125.99 (C^4), 122.15 (C^6), 113.51 (C^{12}), 110.94 (C^9), 108.34 (C^8), 40.17 (C_{Me}) ppm. $\text{C}_{16}\text{H}_{23}\text{Cl}_2\text{N}_3\text{OTi}$ (392.15): calcd. C 49.00, H 5.91, N 10.72; found C 48.89, H 5.95, N 10.58.

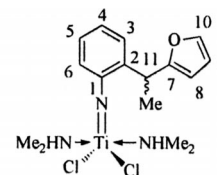
Synthesis of **Ph**²

This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (200 mg, 0.89 mmol), toluene (2 mL), $\text{Ar}^{2\text{Ph}}\text{NH}_2$ (208 mg, 1.00 mmol), and TMSCl (0.7 mL, 5.5 mmol). **Ph**²

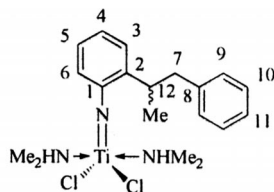
(340 mg, 0.82 mmol, 92%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 7.46–7.52 (m, 2 H, H^{10}), 7.36 (dd, J = 1.1, 8.2 Hz, 1 H, H^{11}), 7.14–7.24 (m, 2 H, H^9), 7.04–7.11 (m, 1 H, H^3), 6.96–7.04 (m, 2 H, $\text{H}^4 + \text{H}^5$), 6.69 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 5.15–5.25 (m, 2 H, H^{13}), 4.35 (s, 2 H, H^7), 2.77 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.5 MHz, C_6D_6): δ = 158.21 (C^1), 150.50 (C^{12}), 140.25 (C^8), 134.24 (C^2), 129.77 (C^9), 129.10 (C^5), 128.31 (C^{10}), 128.20 (C^3), 127.50 (C^{11}), 126.09 (C^4), 122.61 (C^{13}), 115.29 (C^6), 43.83 (C^7), 40.47 (C_{Me}) ppm. $\text{C}_{19}\text{H}_{27}\text{Cl}_2\text{N}_3\text{Ti}$ (416.21): calcd. C 54.83, H 6.54, N 10.10; found C 54.77, H 6.58, N 9.97.

Synthesis of **S**¹

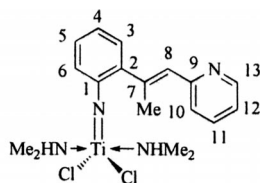
This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\text{Ar}^{1\text{S}}\text{NH}_2$ (100 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). **S**¹ (140 mg, 0.34 mmol, 77%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 6.70 (dd, J = 1.4, 7.9 Hz, 1 H, H^3), 7.13 (dd, J = 1.4, 7.7 Hz, 1 H, H^4), 6.92–6.99 (m, 2 H, $\text{H}^5 + \text{H}^{10}$), 6.81 (dd, J = 1.2, 5.1 Hz, 1 H, H^9), 6.76 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 6.70 (dd, J = 3.4, 5.1 Hz, 1 H, H^8), 5.73 (q, J = 7.2 Hz, 1 H, H^{11}), 2.69 (m, 2 H, H_{NH}), 2.23 (t, J = 6.4 Hz, 12 H, $\text{H}_{\text{Me(NH)}}$), 1.68 (d, J = 7.2 Hz, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.5 MHz, C_6D_6): δ = 158.84 (C^1), 152.86 (C^7), 138.57 (C^2), 127.65 (C^{10}), 126.71 (C^3), 126.30 (C^5), 126.22 (C^6), 124.08 (C^4), 123.27 (C^9), 122.99 (C^8), 40.64 ($\text{C}_{\text{Me(NH)}}$), 40.11 ($\text{C}_{\text{Me(NH)}}$), 34.81 (C^{11}), 23.27 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3239 (ν_{NH}) cm^{-1} . $\text{C}_{16}\text{H}_{25}\text{Cl}_2\text{N}_3\text{STi}$ (410.23): calcd. C 46.84, H 6.14, N 10.24, found C 46.92, H 6.43, N 10.14.

Synthesis of **O**¹

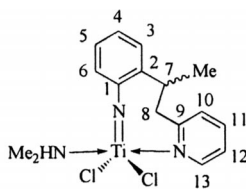
This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\text{Ar}^{1\text{O}}\text{NH}_2$ (94 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). **O**¹ (160 mg, 0.41 mmol, 91%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 7.24 (dd, J = 1.0, 7.9 Hz, 1 H, H^{10}), 7.09–7.12 (m, 1 H, H^3), 7.04 (dd, J = 1.1, 7.7 Hz, 1 H, H^5), 6.94 (dt, J = 1.4, 7.7 Hz, 1 H, H^4), 6.73 (dt, J = 1.1, 7.6 Hz, 1 H, H^6), 6.05–6.15 (m, 2 H, $\text{H}^8 + \text{H}^9$), 5.53 (q, J = 7.1 Hz, 1 H, H^{11}), 2.79 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, $\text{H}_{\text{Me(NH)}}$), 1.77 (d, J = 7.1 Hz, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (62.5 MHz, C_6D_6): δ = 160.32 (C^1), 158.84 (C^7), 141.05 (C^{10}), 136.91 (C^2), 126.80 (C^3), 126.63 (C^5), 126.51 (C^4), 123.08 (C^6), 109.90 (C^9), 105.14 (C^8), 40.48 ($\text{C}_{\text{Me(NH)}}$), 40.27 ($\text{C}_{\text{Me(NH)}}$), 33.40 (C^{11}), 20.30 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3280, 3251 (ν_{NH}) cm^{-1} . $\text{C}_{16}\text{H}_{25}\text{Cl}_2\text{N}_3\text{OTi}$ (394.16): calcd. C 48.75, H 6.39, N 10.66; found C 48.63, H 6.62, N 10.83.

Synthesis of Ph^{12} 

This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\text{Ar}^{2\text{Ph}}\text{NH}_2$ (300 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). Ph^{12} (330 mg, 0.79 mmol, 59%) was obtained as an orange solid. ^1H NMR (300 MHz, C_6D_6): δ = 7.28–7.34 (m, 2 H, H^{10}), 7.18–7.24 (m, 1 H, H^{11}), 7.02–7.15 (m, 3 H, $\text{H}^5 + \text{H}^9$), 6.95–7.00 (m, 1 H, H^3), 6.91 (dt, J = 1.6, 7.5 Hz, 1 H, H^4), 6.80 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 4.49 (m, 1 H, H^{12}), 2.87 (m, 2 H, H^7), 2.61 (m, 2 H, H_{NH}), 2.23 (t, J = 5.9 Hz, 12 H, $\text{H}_{\text{Me}(\text{NH})}$), 1.29 (d, J = 7.0 Hz, 3 H, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 159.16 (C^1), 141.57 (C^8), 129.20 (C^2), 127.86 (C^{10}), 127.06 (C^9), 125.90 (C^3), 125.85 (C^5), 125.58 (C^4), 123.06 (C^6), 44.90 (C^7), 40.72 ($\text{C}_{\text{Me}(\text{NH})}$), 39.97 ($\text{C}_{\text{Me}(\text{NH})}$), 34.33 (C^{12}), 22.13 (C_{Me}) (C^{11} signal not observed; probably obscured by C_6D_6 signals) ppm. $\text{C}_{19}\text{H}_{29}\text{Cl}_2\text{N}_3\text{Ti}$ (418.23): calcd. C 54.56, H 6.99, N 10.05; found C 54.59, H 6.76, N 9.95.

Synthesis of N^2 

This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\text{Ar}^{2\text{N}}\text{NH}_2$ (280 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). N^2 (515 mg, 1.28 mmol, 95%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at -35°C . ^1H NMR (300 MHz, C_6D_6): δ = 8.36–8.44 (m, 1 H, H^{13}), 7.15–7.22 (m, 2 H, $\text{H}^{10} + \text{H}^{12}$), 6.95–7.10 (m, 3 H, $\text{H}^3 + \text{H}^4 + \text{H}^5$), 6.90–6.95 (m, 1 H, H^8), 6.77 (dt, J = 1.5, 7.4 Hz, 1 H, H^6), 6.59–6.67 (m, 1 H, H^{11}), 3.68–3.84 (m, 2 H, H_{NH}), 2.60 (d, J = 1.4 Hz, 3 H, H_{Me}), 2.40 (d, J = 6.1 Hz, 12 H, $\text{H}_{\text{Me}(\text{NH})}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 158.12 (C^9), 157.60 (C^1), 149.24 (C^{13}), 142.69 (C^7), 138.74 (C^2), 135.78 (C^{11}), 129.34 (C^8), 127.46 (C^4), 127.16 (C^3), 125.62 (C^5), 124.02 (C^{10}), 122.10 (C^6), 120.85 (C^{12}), 40.44 ($\text{C}_{\text{Me}(\text{NH})}$), 20.64 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3228 (ν_{NH}) cm^{-1} . $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{N}_4\text{Ti}$ (417.20): calcd. C 51.82, H 6.28, N 13.43; found C 51.65, H 6.58, N 13.39.

Synthesis of N^{12} 

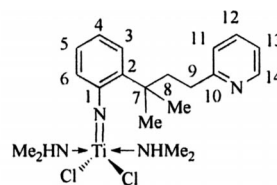
Method 1 (general procedure): This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (300 mg,

1.34 mmol), toluene (2 mL), $\text{Ar}^{2\text{N}}\text{NH}_2$ (280 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). A grey solid was obtained, which was shown by NMR to contain a mixture of N^{12} and N^{11} (4:1) (515 mg). The complexes were separated by selective crystallization (toluene, -35°C). Yield for N^{12} : 385 mg (77%).

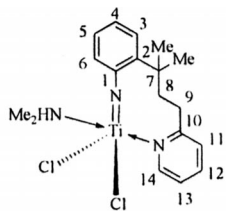
Method 2: $\text{Ar}^{2\text{N}}\text{NH}_2$ (227 mg, 1.07 mmol) was added at room temperature to a toluene solution (6 mL) of $[\text{Ti}(\text{N}t\text{Bu})\text{Cl}_2(\text{NHMe}_2)_2]$ (300 mg, 1.07 mmol). After stirring overnight, the volatiles were removed under reduced pressure, the residue was washed with pentane/toluene (9:1) (3×2 mL), and concentrated under vacuum to afford N^{12} (390 mg, 1.05 mmol, 98%) as a tan solid. ^1H NMR (400 MHz, C_6D_6): δ = 8.65–8.70 (m, 1 H, H^{13}), 7.01–7.10 (m, 2 H, $\text{H}^3 + \text{H}^5$), 6.89 (t, J = 7.4 Hz, 1 H, H^4), 6.77 (t, J = 7.4 Hz, 1 H, H^{11}), 6.71 (d, J = 7.6 Hz, 1 H, H^6), 6.43 (d, J = 7.6 Hz, 1 H, H^{10}), 6.40 (t, J = 6.4 Hz, 1 H, H^{12}), 4.10 (d, J = 13.3 Hz, 1 H, H^8), 3.83–3.92 (m, 1 H, H^7), 3.06–3.18 (m, 1 H, H_{NH}), 2.53 (t, J = 6.0 Hz, 6 H, $\text{H}_{\text{Me}(\text{NH})}$), 2.13 (dd, J = 8.2, 13.3 Hz, 1 H, H^9), 0.98 (d, J = 6.9 Hz, 3 H, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ = 162.38 (C^9), 161.12 (C^1), 149.74 (C^{13}), 143.74 (C^2), 138.81 (C^{11}), 125.80 (C^3), 125.30 (C^{10}), 124.03 (C^5), 121.72 (C^4), 120.85 (C^{12}), 118.92 (C^6), 48.15 (C^8), 41.33 ($\text{C}_{\text{Me}(\text{NH})}$), 41.05 ($\text{C}_{\text{Me}(\text{NH})}$), 37.48 (C^7), 16.15 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3217 (ν_{NH}) cm^{-1} . $\text{C}_{16}\text{H}_{21}\text{Cl}_2\text{N}_3\text{Ti}$ (374.13): calcd. C 51.36, H 5.66, N 11.23; found C 51.40, H 5.91, N 11.46.

Synthesis of N^{12} : N^{12} was obtained as a minor product in the synthesis of complex N^{12} (see Method 1, above). Crystals suitable for an X-ray diffraction study were obtained from recrystallization of a mixture of N^{12} and N^{11} from $\text{C}_6\text{D}_6/\text{CDCl}_3$ (9:1) at -35°C .

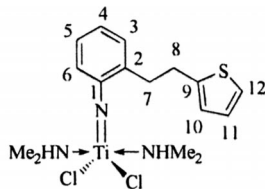
Synthesis of Complex $\text{N}^{11/12}$: $\text{N}^{11/12}$ was obtained in low amount as an intermediate in the synthesis of N^2 (see Method 2, above). Crystals suitable for X-ray diffraction were obtained from recrystallization from a mixture of toluene/pentane (-35°C).

Synthesis of N^3 

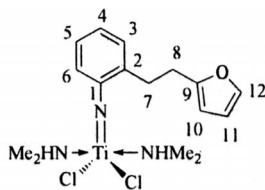
This compound was prepared using the general procedure starting from $\text{Ti}(\text{NMe}_2)_4$ (300 mg, 1.34 mmol), toluene (6 mL), $\text{Ar}^{3\text{N}}\text{NH}_2$ (320 mg, 1.34 mmol), and TMSCl (1.0 mL, 7.9 mmol). N^3 (560 mg, 1.26 mmol, 94%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at -35°C . ^1H NMR (300 MHz, C_6D_6): δ = 8.11 (d, J = 4.3 Hz, 1 H, H^{14}), 7.84 (d, J = 7.8 Hz, 1 H, H^3), 6.98–7.16 (m, 3 H, $\text{H}^4 + \text{H}^5 + \text{H}^{13}$), 6.76 (m, 1 H, H^{11}), 6.69 (d, J = 7.8 Hz, 1 H, H^6), 6.57 (dd, J = 5.3, 6.7 Hz, 1 H, H^{12}), 4.66–4.85 (m, 2 H, H_{NH}), 2.88–3.00 (m, 2 H, H^9), 2.52 (d, J = 6.0 Hz, $\text{H}_{\text{Me}(\text{NH})}$), 2.40–2.48 (m, 2 H, H^8), 1.61 (s, 6 H, H_{Me}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 163.49 (C^{10}), 159.85 (C^1), 148.82 (C^{14}), 136.98 (C^2), 136.27 (C^{13}), 132.99 (C^3), 126.75 (C^5), 126.26 (C^4), 123.11 (C^{11}), 122.63 (C^6), 120.54 (C^{12}), 42.25 (C^9), 40.36 ($\text{C}_{\text{Me}(\text{NH})}$), 38.46 (C^7), 35.03 (C^8), 29.09 (C_{Me}) ppm. ^{15}N NMR (50.71 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): δ = 298 K -75.5 (N_{Py}), -343.0 (NHMe_2); 183 K -77.6 (N_{Py}), -339 ($\text{NH}\cdots\text{N}_{\text{Py}}$), -342 (NHMe_2) ppm. IR: $\tilde{\nu}$ = 3285 (ν_{NH}) cm^{-1} . $\text{C}_{20}\text{H}_{32}\text{Cl}_2\text{N}_4\text{Ti}$ (447.27): calcd. C 53.71, H 7.21, N 12.53; found C 53.69, H 7.39, N 12.34.

Synthesis of N³

A of toluene solution (6 mL) of N³ (205 mg, 0.46 mmol) and TMSCl (0.7 mL, 5.5 mmol) was left for 10 d at room temp. Removing the volatiles under vacuum and washing with pentane afforded N³ (160 mg, 0.40 mmol, 87%) as a yellow solid. Recrystallization from toluene/pentane at −35 °C gave crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, C₆D₆): δ = 8.37–8.40 (m, 1 H, H¹⁴), 7.17–7.24 (m, 2 H, H³ + H⁵), 7.01–7.08 (m, 1 H, H⁴), 6.84–6.89 (m, 1 H, H⁶), 6.77 (dt, *J* = 1.6, 7.8 Hz, 1 H, H¹²), 6.47 (d, *J* = 7.8 Hz, 1 H, H¹¹), 6.34–6.39 (m, 1 H, H¹³), 3.18–3.28 (m, 1 H, H_{NH}), 2.54 (d, *J* = 6.1 Hz, 6 H, H_{MeNH}), 1.37 (s, 6 H, H_{Me}) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ = 162.87 (C¹⁰), 159.85 (C¹), 149.31 (C¹⁴), 138.99 (C¹²), 138.15 (C²), 128.73 (C³), 127.63 (C⁵), 126.23 (C⁴), 125.19 (C¹¹), 122.91 (C⁶), 120.42 (C¹³), 44.95 (C_{Me-NH}), 40.64 (C⁷), 39.44 (C⁸ + C⁹), 35.95 (C_{Me}) ppm. IR: ν̃ = 3226 (ν_{NH}) cm^{−1}. C₁₈H₂₅Cl₂N₃Ti (402.18): calcd. C 53.75, H 6.27, N 10.45; found C 53.70, H 6.22, N 10.39.

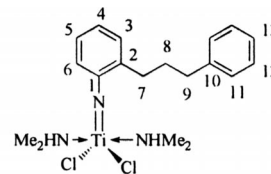
Synthesis of S²

This compound was prepared using the general procedure starting from Ti(NMe₂)₄ (300 mg, 1.34 mmol), toluene (2 mL), Ar^{2S}NH₂ (272 mg, 1.34 mmol), and TMSCl (1 mL, 8.03 mmol). S² (490 mg, 1.20 mmol, 89%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at −35 °C. ¹H NMR (300 MHz, C₆D₆): δ = 7.28 (dd, *J* = 1.0, 7.7 Hz, 1 H, H³), 7.10–7.19 (m, 1 H, H⁴), 6.96 (dt, *J* = 1.5, 7.7 Hz, 1 H, H⁶), 6.87–6.92 (m, 1 H, H¹²), 6.78–6.86 (m, 2 H, H⁵ + H¹¹), 6.73 (dt, *J* = 1.2, 7.5 Hz, 1 H, H¹⁰), 3.36–3.45 (m, 2 H, H⁸), 3.24–3.33 (m, 2 H, H⁷), 2.66–2.82 (m, 2 H, H_{NH}), 2.25 (d, *J* = 6.1 Hz, 12 H, H_{Me}) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 159.83 (C¹), 144.87 (C⁹), 133.77 (C²), 129.00 (C¹²), 126.97 (C³), 126.80 (C⁵), 126.45 (C⁶), 125.06 (C⁴), 123.07 (C¹¹), 122.91 (C¹⁰), 40.39 (C_{Me}), 34.09 (C⁷), 31.49 (C⁸) ppm. IR: ν̃ = 3288, 3253 (ν_{NH}) cm^{−1}. C₁₆H₂₅Cl₂N₃STi (410.23): calcd. C 46.84, H 6.14, N 10.24; found C 46.63, H 6.25, N 10.21.

Synthesis of O²

This compound was prepared using the general procedure starting from Ti(NMe₂)₄ (300 mg, 1.34 mmol), toluene (2 mL), Ar^{2O}NH₂ (250 mg, 1.34 mmol), and TMSCl (1 mL, 8.03 mmol). O² (480 mg,

1.22 mmol, 91%) was obtained as an orange solid. ¹H NMR (300 MHz, C₆D₆): δ = 7.28 (dd, *J* = 0.9, 7.7 Hz, 1 H, H³), 7.16–7.20 (m, 1 H, H¹²), 6.96 (dt, *J* = 1.4, 7.7 Hz, 1 H, H⁵), 6.89–6.93 (m, 1 H, H⁴), 6.73 (dt, *J* = 1.2, 7.5 Hz, 1 H, H⁶), 6.40 (dd, *J* = 0.7, 3.1 Hz, 1 H, H¹⁰), 6.19 (dd, *J* = 1.9, 3.0 Hz, 1 H, H¹¹), 3.40–3.47 (m, 2 H, H⁸), 3.15–3.22 (m, 2 H, H⁷), 2.69–2.82 (m, 2 H, H_{NH}), 2.24 (d, *J* = 6.2 Hz, 12 H, H_{Me}) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 159.82 (C¹), 156.22 (C⁹), 140.85 (C¹²), 134.05 (C²), 128.77 (C³), 126.76 (C⁵), 126.38 (C⁶), 122.92 (C⁴), 110.45 (C¹¹), 105.73 (C¹⁰), 40.34 (C_{Me}), 30.77 (C⁷), 29.62 (C⁸) ppm. IR: ν̃ = 3262, 3227 (ν_{NH}) cm^{−1}. C₁₆H₂₅Cl₂N₃OTi (394.16): calcd. C 48.75, H 6.39, N 10.66; found C 48.65, H 6.48, N 10.68.

Synthesis of Ph³

This compound was prepared using the general procedure starting from Ti(NMe₂)₄ (300 mg, 1.34 mmol), toluene (2 mL), Ar^{3Ph}NH₂ (283 mg, 1.34 mmol), and TMSCl (1 mL, 8.0 mmol). Ph³ (470 mg, 1.13 mmol, 84%) was obtained as an orange solid. ¹H NMR (400 MHz, C₆D₆): δ = 7.30–7.34 (m, 2 H, H¹²), 7.16–7.28 (m, 3 H, H³ + H¹¹), 7.04–7.10 (m, 1 H, H⁴), 6.94–7.00 (m, 2 H, H⁵ + H¹³), 6.79 (dt, *J* = 1.3, 7.5 Hz, 1 H, H⁶), 3.07–3.13 (m, 2 H, H⁹), 2.89–3.96 (m, 2 H, H⁷), 2.66–2.76 (m, 2 H, H_{NH}), 2.24 (d, *J* = 6.1 Hz, 12 H, H_{Me}), 2.05–2.15 (m, 2 H, H⁸) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ = 159.94 (C¹), 142.94 (C¹⁰), 135.51 (C²), 128.80 (C¹²), 128.65 (C¹³), 128.45 (C¹¹), 126.53 (C³), 126.04 (C⁵), 125.78 (C⁴), 122.88 (C⁶), 40.34 (C_{Me}), 36.27 (C⁹), 33.51 (C⁷), 30.71 (C⁸) ppm. IR: ν̃ = 3262 (ν_{NH}) cm^{−1}. C₁₉H₂₉Cl₂N₃Ti (418.23): calcd. C 54.56, H 6.99, N 10.05; found C 54.31, H 7.16, N 10.08.

Ethylene Polymerization Studies: All catalytic reactions were carried out in a 110 mL stainless steel autoclave equipped with a mechanical stirrer. A toluene solution of the complex was introduced under an ethylene atmosphere, and the cocatalyst was added. The reactor was sealed and fed with ethylene up to 10 bar. The reactor was heated to the desired temperature with stirring and the pressure adjusted to 20 bar. After 1 h at constant pressure, the reactor was cooled to room temperature and depressurized. The catalyst and the cocatalyst were quenched by addition of 10% HCl in MeOH. The polymer formed was collected by filtration, washed with methanol, and dried in vacuo at 60 °C.

Supporting Information (see footnote on the first page of this article): VT NMR experiments and synthetic details for all compounds prepared in this article.

Acknowledgments

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Cyclic Phosphonium Bis(fluoroaryl)boranes – Trends in Lewis Acidities and Application in Diels–Alder Catalysis

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Keywords: Boron / Homogeneous catalysis / Lewis acids / Perfluoroarenes / Phosphorus

The rigid cyclic Lewis acids [(C₆F₅)B(CH₂)(C₆F₄)P(*t*Bu)₂]⁺ (**[1]**⁺), [(C₆F₅)B(CH₂)(C₆F₃H)P(*t*Bu)₂]⁺ (**[2]**⁺), and [(C₆H₅)B(CH₂)(C₆F₄)P(*t*Bu)₂]⁺ (**[3]**⁺), possess Gutmann acceptor numbers of AN = 87.3, 85.7, and 85.7, respectively, which are among the highest for organoboranes. Starting from (**1**)OTf, adducts [(**1**)Do][OTf] (Do = OPEt₃, pyridine, H₂O) have been prepared and fully characterized. In all three cases, X-ray crystallography revealed significantly shorter B–O/N bond

lengths than those in the corresponding adducts (C₆F₅)₃B·Do. Both the free Lewis acid [**1**][Al(O(*t*BuF))₄] and its triflate adduct (**1**)OTf have successfully been employed as catalysts for the [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene. Moreover, we have shown that chiral phosphonium boranes are accessible by replacement of one *t*Bu group in [**1**]⁺ by a Me substituent {cf. [**4**]⁺ = [(C₆F₅)B(CH₂)(C₆F₄)P(Me)(*t*Bu)]⁺}.

Introduction

Lewis acidic arylboranes find applications as homogeneous (co)catalysts^[1–6] and anion sensors.^[7–10] The use of perfluorinated aryl substituents or the incorporation of a positive charge into the molecular framework are tools to optimize the Lewis acid strength for any given task.^[11–20] The reinforcing effect of a positive charge on the adduct bond of an anionic Lewis base is merely of an electrostatic nature and therefore distance-dependent. Thus, in order to guarantee a stabilizing effect that is invariable in time, a rigid molecular framework is required so that the distance between the boron atom and the cationic center always remains the same.

Following this concept, we have recently prepared cyclic phosphonium boranes [**A**][WCA] (Figure 1). Because of their high Lewis acidity, the free boranes are only existent in combination with the extremely weakly coordinating anion [WCA][–] = [Al(O(*t*BuF))₄][–].^[21,22] In this paper, we report on the quantitative trend in the Lewis acidities of these compounds as a function of the degree of fluorination at the exocyclic phenyl substituent (i.e., R¹ = C₆F₅, C₆H₅) or the phenylene bridge (i.e., R² = F, H). Moreover, we compare the performance of the free acid [**A**][WCA] (R¹ = C₆F₅, R² = F, R³ = *t*Bu) and its corresponding triflate adduct (**A**)OTf^[21] as Diels–Alder catalysts, and we explore whether chiral Lewis acids can be generated by variation of the substituent R³ at the phosphorus atom.

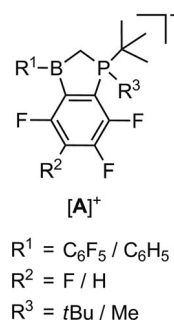
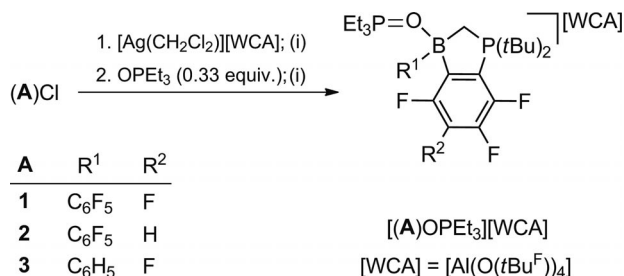


Figure 1. General structural motif of the cationic phosphonium boranes investigated in this work.

Results and Discussion

Assessment of the Lewis Acidities of [**A**]⁺-Type Compounds by NMR Spectroscopic Methods

For Lewis acidity determinations by the Gutmann–Beckett method^[23–25] we used a protocol similar to that described by Stephan et al.^[15a] (Scheme 1): First, the free



Scheme 1. Preparation of cationic phosphonium boranes [**A**][WCA] (**A** = **1**, **2**, **3**) from their corresponding chloro adducts (**A**)Cl and subsequent addition of OPEt₃ for Lewis acidity determination by the Gutmann–Beckett method. (i) CD₂Cl₂, room temp., 2 min.

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Lewis acids $[1]^+$, $[2]^+$, and $[3]^+$ were liberated from their corresponding chloro adducts $(1)Cl$,^[21] $(2)Cl$, and $(3)Cl$ ^[21] by addition of $[Ag(CH_2Cl_2)][WCA]$.^[26] A substoichiometric amount of $OPeEt_3$ was added, and the $^{31}P\{^1H\}$ NMR spectrum was recorded in CD_2Cl_2 to determine the Gutmann acceptor number (AN; Table 1).

Table 1. $^{31}P\{^1H\}$ NMR chemical shift values of $OPeEt_3$ in the Lewis acid–base adducts $[(1)OPeEt_3][WCA]$, $[(2)OPeEt_3][WCA]$, and $[(3)OPeEt_3][WCA]$. Gutmann acceptor numbers (AN) of the Lewis acids $[1][WCA]$, $[2][WCA]$, and $[3][WCA]$.

Boron-containing Lewis acid	$\delta(^{31}P\{^1H\})$ [ppm] ^[a]	AN ^[b]
None	50.5	21.0 ^[c]
$(C_6F_5)_3B$	77.1 ^[d]	80.0
$[1][WCA]$	80.4	87.3
$[2][WCA]$	79.7	85.7
$[3][WCA]$	79.7	85.7

[a] CD_2Cl_2 , 27 °C. [b] $AN = [\delta(^{31}P\{^1H\})_{\text{sample}} - 41.0] \times [100 / (86.14 - 41.0)]$.^[24] [c] $AN(CH_2Cl_2)$ according to our own measurement; literature value: $AN(CH_2Cl_2) = 20.4$.^[23] [d] Our own measurement; literature value: $\delta(^{31}P\{^1H\})$, CD_2Cl_2 = 78.1.^[15b]

All three phosphonium borane derivatives possess a higher acceptor number ($AN = 87.3$, 85.7 , 85.7 , respectively) than the neutral molecule $(C_6F_5)_3B$ ($AN = 80.0$) and even the phosphonium borane $[(C_6F_5)_2B-(p-C_6F_4)-P(H)(tBu)_2]^+$ ($AN = 80.2$).^[15a] The less exhaustively fluorinated species $[2]^+$ and $[3]^+$ are slightly weaker Lewis acids than $[1]^+$ ($\Delta(AN) = 1.6$). Somewhat surprisingly, replacement of *one* F atom on the phenylene bridge (cf. $[2]^+$) appears to have a similar effect on the acceptor number than substitution of all *five* F atoms for H atoms on the exocyclic phenyl ring in $[3]^+$ (this result has been reproduced twice).

The $^{31}P\{^1H\}$ NMR chemical shift value of $OPeEt_3$ in its Lewis acid–base adducts is influenced by the position of the association/dissociation equilibrium. In order to obtain data of a sample consisting exclusively of an adduct, we prepared $[(1)OPeEt_3][OTf]$ from the triflate $(1)OTf$ ^[21] (Scheme 2) and measured its $^{31}P\{^1H\}$ NMR spectrum in the solid state (see the Supporting Information for a plot of the spectrum). The chemical shift values of 86.1 ppm (BCH_2P) and 79.9 ppm ($OPeEt_3$) deviate by a maximum of 1.1 ppm from those obtained for $[(1)OPeEt_3][OTf]$ {85.2 ppm (BCH_2P), 80.9 ppm ($OPeEt_3$)} and $[(1)OPeEt_3][WCA]$ {85.0 ppm (BCH_2P), 80.4 ppm ($OPeEt_3$)} in CD_2Cl_2 solution. Since the $OPeEt_3$ phosphorus atom of $[(1)OPeEt_3][OTf]$ is *less* shielded in solution than in the solid state, we

conclude that the solution equilibrium contains essentially no uncoordinated $OPeEt_3$.

$[(1)OPeEt_3][OTf]$ crystallizes with two crystallographically independent molecules in the asymmetric unit $\{[(1)OPeEt_3][OTf], [(1)OPeEt_3][OTf]^A\}$, of which only $[(1)OPeEt_3][OTf]$ is discussed further (Figure 2).

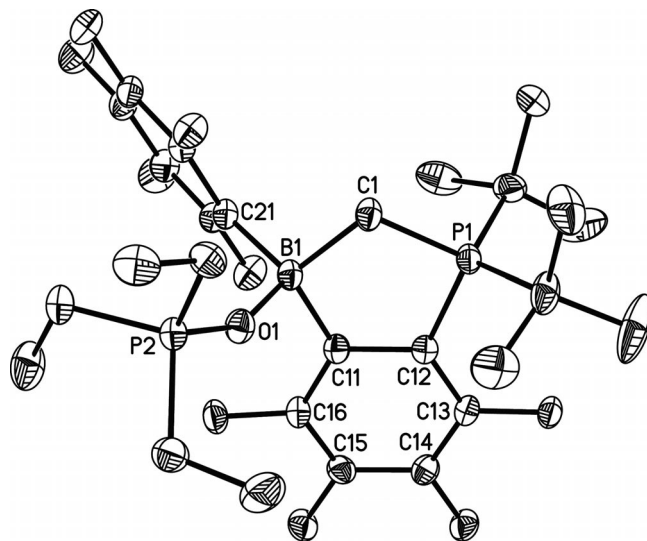
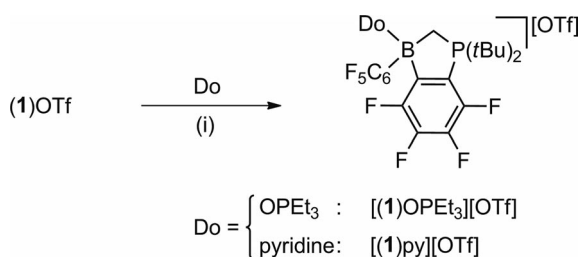


Figure 2. Molecular structure and numbering scheme of the cation of compound $[(1)OPeEt_3][OTf]$. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)–P(2) 1.526(3), B(1)–O(1) 1.523(5), B(1)–C(1) 1.656(6), B(1)–C(11) 1.623(6), B(1)–C(21) 1.643(6), P(1)–C(1) 1.803(4), P(1)–C(12) 1.809(4); B(1)–O(1)–P(2) 152.7(3), B(1)–C(1)–P(1) 107.5(3), C(1)–B(1)–C(11) 106.2(3), C(1)–P(1)–C(12) 98.6(2); C(1)–B(1)–C(11)–C(12) 1.2(5), C(1)–P(1)–C(12)–C(11) 5.3(3).

The X-ray crystal structure analysis confirms that the triflate ion has been replaced by the neutral $OPeEt_3$ molecule, thereby maintaining the tetracoordinate state of the boron atom. This substitution reaction does not lead to any significant changes in key structural parameters of the borane fragment. The B(1)–O(1) bond length amounts to 1.523(5) Å, which is shorter by 0.066(5) Å than that of the starting compound $(1)OTf$ [1.589(3) Å]^[21] and still slightly shorter than that of $(C_6F_5)_3B \cdot OPeEt_3$ [1.533(3) Å].^[25] A more significant difference is found in the O–P bond lengths of $[(1)OPeEt_3][OTf]$ [1.526(3) Å] compared to $(C_6F_5)_3B \cdot OPeEt_3$ [1.497(2) Å]^[25] (cf. also $OPCy_3$: O–P = 1.490(2) Å; Cy = cyclohexyl).^[27] We are aware of the fact that bond lengths in the solid state do not necessarily correlate with bond strengths. However, in the present case, the differences in the Gutmann acceptor numbers of $[1]^+$ vs. $(C_6F_5)_3B$ are nicely reflected by the trends in the B–O and O–P bond lengths of their corresponding $OPeEt_3$ adducts.

As a second independent measure of Lewis acidities, the Childs NMR spectroscopic method,^[28] with crotonaldehyde instead of $OPeEt_3$, is often employed.^[15a] Since crotonaldehyde is not stable over time in the presence of strong Lewis acids, we prepared the pyridine adduct $[(1)py][OTf]$ instead and took its $^{13}C\{^1H\}$ NMR chemical shift values as a diagnostic tool.



Scheme 2. Substitution of the triflate ligand in $(1)OTf$ by uncharged donors Do. (i) CH_2Cl_2 , room temp., 12 h.

The compound readily precipitates from a concentrated CH_2Cl_2 solution of **(1)OTf** upon addition of 1 equiv. of pyridine (Scheme 2); crystals of $[(1)\text{py}][\text{OTf}]$ suitable for X-ray diffraction were grown by slow concentration of a dilute CH_2Cl_2 solution.

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $[(1)\text{py}][\text{OTf}]$ is characterized by a resonance at 0.7 ppm. In Table 2, the pyridine ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shift values of $[(1)\text{py}][\text{OTf}]$ are compared with those of free pyridine, other selected borane–pyridine adducts, and pyridinium salts. Pyridine protonation results in the shielding of the C-2,6 nuclei and the deshielding of C-4 and C-3,5. Qualitatively similar effects are observed upon borane–pyridine coordination. A closer inspection of the data reveals a continuous upfield shift of the C-2,6 resonances with an overall $\Delta(\delta)$ of -3.6 ppm along the sequence $\text{py} \rightarrow \text{Ph}_3\text{B}\cdot\text{py} \rightarrow (\text{C}_6\text{F}_5)_3\text{B}\cdot\text{py} \rightarrow [(1)\text{py}][\text{OTf}]$, while the C-4 signal and the C-3,5 resonances are shifted to lower field by $\Delta(\delta) = 8.0$ and 4.0 ppm, respectively. We note analogous trends also for the chemical shift values of 4-H and 3,5-H (the 2,6-H resonances are less meaningful, because they are closer to the borane frameworks and therefore influenced by magnetic anisotropy effects). Even though these measurements do not provide quantitative acceptor numbers, they nevertheless support our previously established order of Lewis acidities, that is, $[1]^+ > (\text{C}_6\text{F}_5)_3\text{B} > \text{Ph}_3\text{B}$.

Table 2. Compilation of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shift values of free and coordinated pyridine.

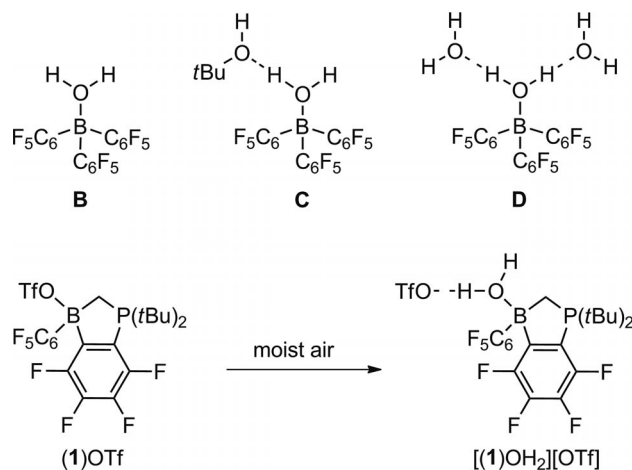
	$\delta(^1\text{H})^{[a]}$			$\delta(^{13}\text{C}\{^1\text{H}\})^{[a]}$		
	2,6-H	4-H	3,5-H	C-2,6	C-4	C-3,5
Pyridine	8.58	7.67	7.27	150.2	136.1	124.0
$\text{Ph}_3\text{B}\cdot\text{py}$	8.57	8.06	7.56	148.3	141.0	125.6
$(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{py}$	8.61	8.21	7.71	147.2	143.2	126.2
$[(1)\text{py}][\text{OTf}]$	8.57	8.30	7.92	146.6	144.1	128.0
$[\text{H}\cdot\text{py}][\text{OTs}]^{[b]}$	8.93	8.43	7.94	142.3	146.3	127.6
$[\text{H}\cdot\text{py}][\text{Cl}]$	8.90	8.51	8.02	141.2	146.1	127.5

[a] CD_2Cl_2 , 27 °C. [b] OTs = *p*-toluenesulfonate.

The most revealing structural parameter of $[(1)\text{py}][\text{OTf}]$ (see the Supporting Information for details of its solid-state structure) is the B–N bond length [1.599(4) Å], which is shorter by 0.029(4) Å than the B–N bond in $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{py}$ [1.628(2) Å].^[29]

In this context, we also became interested in the molecular structure of the water adduct $[(1)\text{OH}_2]^+$, which we wanted to compare with the structures of the $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OH}_2$ complexes **B**, **C**, and **D** (Scheme 3). The main emphasis lay on B–O bond length variations as an approximate measure of the degree of O–H bond polarization, which should in turn be influenced by the Lewis acidity of the boron center.

Both the chloroborate **(1)Cl**^[21] and the acetoxyporate **(1)OAc**^[21] are water-stable, and the solids can be handled and stored in air for extended periods of time. In contrast, **(1)OTf** readily hydrolyzes under similar conditions. Consequently, $[(1)\text{OH}_2][\text{OTf}]$ formed in essentially quantitative yield upon stirring an Et_2O solution of **(1)OTf** in air for 48 h (Scheme 3). The NMR spectroscopic data of the compound are unexceptional $\{\delta(^{11}\text{B}\{^1\text{H}\}) = 1.9$ ppm;



Scheme 3. Top: water adducts of $(\text{C}_6\text{F}_5)_3\text{B}$ known in the literature; bottom: hydrolysis of **(1)OTf**.

$\delta(^{31}\text{P}\{^1\text{H}\}) = 86.9$ ppm}; in the ^1H NMR spectrum, the OH_2 protons give rise to an extremely broad signal at approximately 5 ppm {cf. the resonance of water in CD_2Cl_2 appears at $\delta(^1\text{H}) = 1.52$ ppm}.^[30]

Single crystals of $[(1)\text{OH}_2][\text{OTf}]$ were grown from CH_2Cl_2 . X-ray crystal structure analysis revealed a water molecule coordinated to the boron atom (Figure 3). Both OH_2 atoms were located in the difference Fourier map and were freely refined. In the solid state, the ion pair $[(1)\text{OH}_2]^+[\text{OTf}]^-$ exists as a centrosymmetric dimer, which is

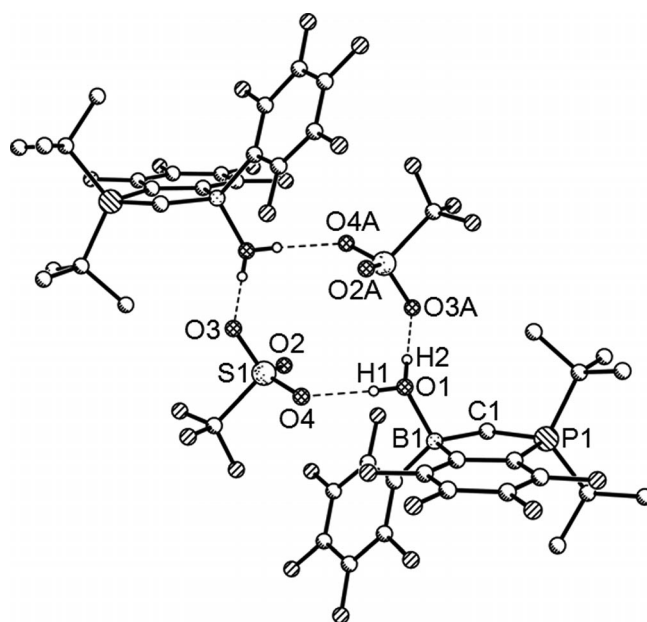


Figure 3. Dimeric structure of $[(1)\text{OH}_2][\text{OTf}]$ in the solid state. Except on the H_2O molecule, H atoms have been omitted for clarity. Selected bond lengths [Å], atom...atom distances [Å], and bond angles [°]: O(1)–H(1) 0.80(2), O(1)–H(2) 0.98(3), B(1)–O(1) 1.553(2), B(1)–C(1) 1.642(2), P(1)–C(1) 1.794(1), H(1)...O(4) 1.84(2), H(2)...O(3A) 1.67(3), O(1)...O(4) 2.647(2), O(1)...O(3A) 2.640(1), O(1)–H(1)...O(4) 177(2), O(1)–H(2)...O(3A) 171(3), B(1)–C(1)–P(1) 108.3(1). Symmetry transformation used to generate equivalent atoms: A = $-x + 1, -y + 1, -z$.

held together by four HO–H $\cdots$ OTf hydrogen bonds. Bonding of the triflate anion to [1]⁺ benefits to a greater degree from Coulomb attraction than water coordination. Nevertheless, the B–O bond of (1)OTf [1.589(3) Å] is elongated by 0.036(3) Å relative to that of [(1)OH₂][OTf] [1.553(2) Å]. The (C₆F₅)₃B·OH₂ adducts **B**, **C**, and **D** possess B–O bond lengths of 1.608(3),^[31] 1.583(3),^[31] and 1.577(1) Å,^[32] respectively. Thus, an increasing number of hydrogen bonds about the water molecule, which should in turn increase the average O–H polarity, results in a gradual decrease of the B–O bond lengths. Of all species **B**, **C**, and **D**, compound **D**, which also establishes two hydrogen bonds per water molecule, is most closely related to [(1)OH₂][OTf]. We observe a further significant shortening of the B–O bond from 1.577(1) Å in **D** to 1.553(2) Å in [(1)OH₂][OTf]. This result conforms to the higher Lewis acidity of [1]⁺ compared to that of (C₆F₅)₃B.

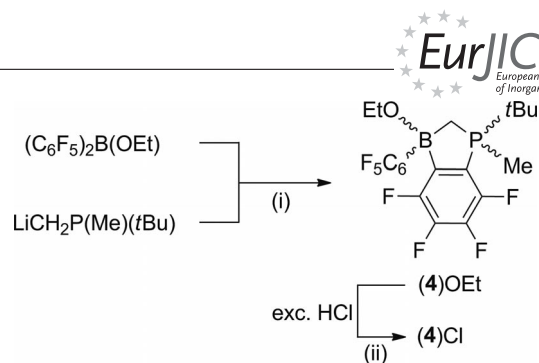
Stereoselectivity of Nucleophilic Substitution Reactions at the Boron Centers of [A]⁺-Type Compounds

So far, we have gathered spectroscopic and crystallographic evidence for a higher Lewis acidity of [A]⁺-type cations relative to the neutral Lewis acid (C₆F₅)₃B. Using a prototypical substitution reaction at boron, we next studied whether the free cationic Lewis acid [A]⁺ is present in the association/dissociation equilibrium with its donor (Do) adduct (A)Do to a sufficiently high degree to influence the outcome of the reaction.

The boron atom in (A)Do is a chiral center. Introduction of a second chiral center into the molecule will therefore generate (A)Do in a specific diastereomeric ratio. If Do is quantitatively substituted by another Lewis base Do', two different scenarios can be envisioned: (1) The diastereomeric ratio is strictly reversed in (A)Do', which would be indicative of an S_N2 reaction mechanism. (2) The diastereomeric ratio changes as a result of a competing S_N1 pathway (possibly assisted by intermediate OEt₂ coordination). The extent of this change, in turn, correlates with the proportion of the free Lewis acid [A]⁺ {or [A(OEt₂)]⁺} in the reaction mixture.

Replacement of one *t*Bu group in [1]⁺ by a Me substituent offers a convenient way to introduce a second chiral center into the molecule. We therefore treated (C₆F₅)₂B(OEt)^[33] with LiCH₂P(Me)(*t*Bu) at –78 °C in toluene and obtained (4)OEt in a 1:3 diastereomeric ratio according to NMR spectroscopy [Scheme 4; LiCH₂P(Me)(*t*Bu) (cf. the Supporting Information) was prepared in a fashion similar to LiCH₂P(*t*Bu)₂^[34]]. The ¹¹B{¹H} and ³¹P{¹H} NMR chemical shift values of both diastereomers of (4)OEt are virtually the same, but the *t*Bu proton resonances are well separated and appear as doublets at δ = 0.66 ppm (major diastereomer; C₆D₆) and δ = 0.53 ppm (minor diastereomer; C₆D₆).

(4)OEt is a fairly inert compound and therefore has to be activated by transformation into the chloro derivative (4)Cl with the help of HCl in Et₂O. This latter reaction is



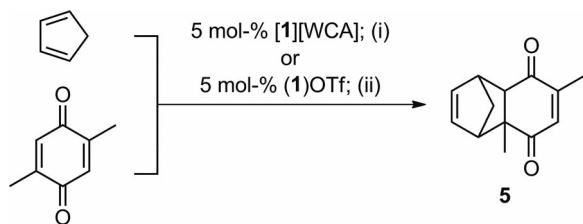
Scheme 4. Synthesis of (4)OEt and its transformation into the chloro derivative (4)Cl: (i) toluene, –78 °C → room temp., 12 h; (4)OEt is obtained as a mixture of two diastereomers in a 1:3 ratio. (ii) Et₂O, room temp., 18 h.

not only crucial for the entire chemistry of [A]⁺-type compounds, but it is also clean and quantitative and therefore qualifies as a test reaction for the stereospecificity of nucleophilic transformations at the boron atom. As expected, upon addition of 4 equiv. of HCl in Et₂O to the diastereomeric mixture of (4)OEt in Et₂O (Scheme 4), the exclusive formation of two diastereomers of the chloro adduct (4)Cl was observed (for an X-ray crystal structure analysis of the diastereomer in which the Cl atom and the Me substituent are located on the same side of the five-membered heterocycle, see the Supporting Information). The experiment was repeated five times; however, the diastereomeric ratio of (4)Cl turned out to be poorly reproducible and changed upon standing and workup. We therefore isolated a pure sample of the major diastereomer of (4)OEt by column chromatography and protolyzed it with HCl in Et₂O as described above. Again, ¹H NMR spectroscopy revealed a dynamic behavior with no obvious dependence on solvent polarity or temperature. Since the stereomeric information at boron is lost upon going from (4)OEt to (4)Cl, we conclude that the phosphonium borane [4]⁺ {presumably in the form of a weak adduct [4(OEt₂)]⁺} is present in a significant amount in the reaction mixture.

Assessment of the Catalytic Activity of [1]⁺ in a Diels–Alder Reaction

During the last decade, the potential of (cationic) boranes for the catalysis of, for example, [4+2] and [3+2] cycloaddition reactions has been recognized, and even enantioselective transformations have been developed.^[35] We therefore decided to undertake an exploratory investigation of the catalytic activity of [1]⁺ in the well-studied [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene^[36] (Scheme 5).

Both the free Lewis acid [1][WCA] and the triflate adduct (1)OTf were employed. Since [1][WCA] is extremely sensitive to any kind of nucleophile, a solution of this compound in CH₂Cl₂ was freshly prepared as described above. Even though the catalyst solution was separated from the AgCl precipitate prior to use, the presence of residual [Ag]⁺ traces cannot be fully excluded. Thus, we first performed blind tests of the catalytic activity of [Ag(CH₂Cl₂)][WCA] in



Scheme 5. Application of [1][WCA] and (1)OTf as catalysts for the reaction of cyclopentadiene (CpH) with 2,5-dimethyl-1,4-benzoquinone: (i) 1.2 equiv. CpH, CH₂Cl₂, room temp., 2.5 h. (ii) 1.4 equiv. CpH, CH₂Cl₂, room temp., 24 h.

CH₂Cl₂ solution. Addition of the salt (5 mol-%) to the diene/dienophile mixture at room temp. caused an immediate color change from yellow to dark brown. After 2.5 h, the cycloaddition product **5**^[36] was already detectable in the ¹H NMR spectrum. In addition to that, broad and ill-defined signals appeared in the alkyl region of the spectrum, and a silver mirror gradually formed on the walls of the reaction vessel. It is known that cyclopentadiene tends to polymerize in the presence of Lewis acids,^[37] which, in our case, is most likely a major side reaction.

Table 3 summarizes all catalysis results obtained with [1][WCA] and (1)OTf (CH₂Cl₂, room temp.). The transformations were monitored by ¹H NMR spectroscopy (C₆D₆); conversion rates were determined by signal integration. In the uncatalyzed background reaction, the first product resonances^[36] appeared after approximately 5 h (entry 1). About 20 h later, the conversion to **5** had reached 27%, the yellow color of the solution persisted, and no side products were detectable. Similarly moderate yields were obtained in the presence of the precatalyst (1)Cl (entry 2). The use of 2 mol-% of [1][WCA] gave **5** in 81% spectroscopic yield after only 2.5 h (entry 3). Prolonged stirring did not induce further significant changes. An increase in the catalyst loading to 5 mol-% had only a small effect on the obtained yield of **5** (87% after 2.5 h; entry 4), thereby indicating that the equilibrium concentration has been reached at this stage.

Table 3. Investigation of the Diels–Alder reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene (CpH) in the presence of different catalysts.^[a]

Entry	Catalyst	α (Catalyst) [mol-%]	Dienophile/ CpH ratio	Yield ^[b] [%] after			
				2.5 h	5 h	10 h	24 h
1	None	0	1 1	0	3	11	27
2	(1)Cl	5	1 1	0	4	[c]	19
3	[1][WCA]	2	1 1	81	83	[c]	78
4		5	1 1	87	85	[c]	76
5		5	1 1.2 ^[d]	95 ^[e]	87	[c]	76
6	(1)OTf	5	1 1	55	58	[c]	81
7		5	1 1.4 ^[f]	49	53	76	91 ^[g]
8		10	1 1.4 ^[f]	55	63	90	96 ^[g]

[a] Reaction conditions: 2,5-dimethyl-1,4-benzoquinone (0.15 mmol), CpH (0.15 mmol), CH₂Cl₂, room temp. [b] Reaction monitored by ¹H NMR spectroscopy. [c] Yield not determined. [d] 1 equiv. of CpH was present at the beginning of the reaction; further CpH was added after 1 h (0.2 equiv.). [e] Workup after 2.5 h; isolated yield: 87%. [f] 1 equiv. of CpH was present at the beginning of the reaction; further CpH was added after 4 h (0.2 equiv.) and 6 h (0.2 equiv.). [g] Workup after 24 h; isolated yield: 80%.

Interestingly, we observed a slow decrease in the product concentration (76% after 24 h) with a concomitant increase in the amount of the 2,5-dimethyl-1,4-benzoquinone starting material. Parallel to that, signs of cyclopentadiene polymerization were visible in the NMR spectrum. Thus, extended reaction times result in lower yields of **5**, because cyclopentadiene is continuously removed from the dynamic equilibrium, which favors the back reaction. To validate this interpretation, we repeated the reaction with 5 mol-% catalyst loading, but this time added another 0.2 equiv. of cyclopentadiene 1 h after the beginning of the reaction. In that way, a further improved spectroscopic yield of 95% (2.5 h) was achieved, which, again, decreased over time. In a second run under the same conditions, the reaction was quenched after 2.5 h by admission of air and provided **5** in 87% isolated yield after chromatographic workup.

In a next step, (1)OTf was tried as the catalyst, because now any [Ag]⁺ contaminants can be excluded and this storable compound is easier to handle than [1][WCA]. (1)OTf also catalyzes the reaction of 2,5-dimethyl-1,4-benzoquinone with cyclopentadiene, albeit at a slower rate: With 5 mol-% of the catalyst, the conversion to **5** was 55% complete after 2.5 h (entry 6). After 24 h, the reaction mixture contained 81% of the target compound; cyclopentadiene polymerization was still negligible. An increase in the amount of added cyclopentadiene improved the spectroscopic yield of **5** to 91% (24 h; entry 7). Finally, the use of 10 mol-% of the catalyst together with 1.4 equiv. of cyclopentadiene resulted in virtually quantitative yield (entry 8).

Conclusions

According to the Gutmann–Beckett NMR spectroscopic method, the rigid cyclic phosphonium boranes [(C₆F₅)₃B(CH₂)(C₆F₄)P(*t*Bu)₂]⁺ ([1]⁺), [(C₆F₅)B(CH₂)(C₆F₃H)P(*t*Bu)₂]⁺ ([2]⁺), and [(C₆H₅)B(CH₂)(C₆F₄)P(*t*Bu)₂]⁺ ([3]⁺) possess acceptor numbers of AN = 87.3, 85.7, and 85.7, respectively, and are therefore stronger Lewis acids than the popular neutral borane (C₆F₅)₃B (AN = 80.0). This conclusion is supported further by the results of X-ray crystal structure analyses of adducts [(1)Do]⁺ and (C₆F₅)₃B·Do (Do = OPET₃, pyridine, H₂O), which consistently reveal significantly shorter B–O/N bond lengths in the former case.

Starting from diastereomerically pure (4)OEt {[4]⁺ = [(C₆F₅)B(CH₂)(C₆F₄)P(Me)(*t*Bu)]⁺}, the protolytic transformation (4)OEt → (4)Cl proceeds with the complete loss of stereomeric information at the chiral boron center, thereby indicating that a significant amount of the free Lewis acid [4]⁺ is present in the reaction mixture.

In line with that, (1)OTf, which possesses an even better leaving group than chloride, can be used to catalyze the [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene. With respect to the unmasked Lewis acid [1][Al(O(*t*Bu)^F)₄], (1)OTf leads to a slower conversion rate, but, nevertheless, to quantitative yields of the cycloaddition product with no detectable concomitant polymerization of cyclopentadiene.

On the basis on the experience gathered with **[4]⁺**, we are currently developing enantiomerically pure chiral derivatives, which offer promising perspectives for enantioselective Lewis acid catalysis.

Experimental Section

General Considerations: Unless stated otherwise, all manipulations were carried out under a nitrogen atmosphere by using Schlenk-tube techniques or in an argon-filled glovebox. Solvents were dried by distillation from Na (pentane, hexane), Na/benzophenone (Et₂O, benzene, toluene), or CaH₂ (CH₂Cl₂, pyridine). *i*PrOH was treated with a small amount of Na, distilled, and degassed through several freeze-pump-thaw cycles. NMR spectroscopic data were collected with a Bruker Avance 300 or Avance 400 spectrometer. Chemical shift values (¹H/¹³C{¹H}) are reported in parts per million (ppm) relative to Me₄Si and were referenced to (residual) solvent signals (C₆D₆: 7.15/128.0; CD₂Cl₂: 5.32/53.8; CDCl₃: 7.26/77.2; [D₈]THF: 3.58/67.2). Heteronuclear chemical shift values were referenced to external F₃B·OEt₂ (¹B{¹H}), FCCl₃ (¹⁹F{¹H}), and 85% H₃PO₄ (³¹P{¹H}). Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, n.r. = multiplet expected in the ¹H NMR spectrum but not resolved, n.o. = signal not observed. The compounds [Ag(CH₂Cl₂)]([WCA]),^[26] (C₆F₅)₂B(OEt),^[38] (C₆F₅)₂BH·SMe₂,^[39] LiCH₂P(*t*Bu)₂,^[34] (1)Cl,^[21] (1)OTf,^[21] (2)OEt,^[21] (3)Cl,^[21] [1][WCA],^[21] and [3][WCA]^[21] were synthesized according to literature procedures. A convenient optimized synthesis of the known compound (C₆F₅)₂B(O*i*Pr)^[40] and its transformation into (1)O*i*Pr are described in the Supporting Information. Me₂P(*t*Bu) has been mentioned in the literature;^[41] however, the isolation of the free phosphane has not been described yet. We therefore provide details of the synthesis, isolation, and NMR spectroscopic characterization of Me₂P(*t*Bu) and LiCH₂P(Me)(*t*Bu) in the Supporting Information. 2,5-Dimethyl-1,4-benzoquinone (Aldrich) was sublimed prior to use. OPET₃ was purchased from Aldrich and used as received.

(2)Cl: HCl in Et₂O (0.91 M; 0.88 mL, 0.80 mmol) was added at room temp. by syringe to a stirred solution of (2)OEt (0.10 g, 0.20 mmol) in Et₂O (7 mL), whereupon a colorless precipitate immediately formed. After stirring the resulting suspension for 48 h, all volatiles were removed in vacuo to obtain (2)Cl in analytically pure form. Single crystals suitable for X-ray crystallography were obtained by slow concentration of a CH₂Cl₂ solution of (2)Cl at room temp. Yield: 0.095 g (0.19 mmol, 95%). ¹H NMR (400.1 MHz, C₆D₆): δ = 6.58 (m, 1 H, Ar-H), 1.90 (dd, ²J_{H,H} = 16.3, ²J_{P,H} = 11.6 Hz, 1 H, BCH₂P), 1.33 (dd, ²J_{H,H} = 16.3, ²J_{P,H} = 8.7 Hz, 1 H, BCH₂P), 0.73 [d, ³J_{P,H} = 15.8 Hz, 9 H, C(CH₃)₃], 0.45 [d, ³J_{P,H} = 15.5 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, C₆D₆): δ = -2.3 (*h*_{1/2} = 120 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 111.2 (m, Ar-CH), 34.7 [m, C(CH₃)₃], 34.3 [m, C(CH₃)₃], 27.1 [m, C(CH₃)₃], 26.1 [m, C(CH₃)₃], 15.2 (m, BCH₂P) ppm. ¹⁹F{¹H} NMR (282.3 MHz, C₆D₆): δ = -98.2 (m, 1 F), -130.9 (m, 1 F), -131.7 (br., 2 F, C₆F₅), -134.9 (m, 1 F), -159.3 (t, ³J_{F,F} = 21 Hz, 1 F, C₆F₅), -164.7 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 86.0 (m) ppm. MS (ESI⁺): *m/z* (%) = 467 (100) [2]⁺. C₂₁H₂₁BClF₈P (502.61): calcd. C 50.18, H 4.21; found C 50.37, H 4.43.

[(1)OPET₃][OTf]: A solution of (1)OTf (0.15 g, 0.24 mmol) and OPET₃ (0.032 g, 0.24 mmol) in CH₂Cl₂ (5 mL) was stirred at room temp. for 12 h, then concentrated under reduced pressure to a volume of 0.3 mL and layered with pentane (0.2 mL). Crystallization of [(1)OPET₃][OTf] started after 30 min and continued for another

1 d. Single crystals suitable for X-ray diffraction were isolated by decantation. For further characterization, the colorless crystalline material was washed with hexane (4 × 0.5 mL), ground, and dried in vacuo over a period of 6 h. Yield: 0.12 g (0.16 mmol, 67%). ¹H NMR (300.0 MHz, CD₂Cl₂): δ = 2.03 (dq, ²J_{P,H} = 11.8, ³J_{H,H} = 7.7 Hz, 6 H, PCH₂CH₃), 1.61 (m, 2 H, BCH₂P), 1.48 [d, ³J_{P,H} = 16.3 Hz, 9 H, C(CH₃)₃], 1.24 [d, ³J_{P,H} = 16.2 Hz, 9 H, C(CH₃)₃], 1.06 (dt, ³J_{P,H} = 18.7, ³J_{H,H} = 7.7 Hz, 9 H, PCH₂CH₃) ppm. ¹¹B{¹H} NMR (96.3 MHz, CD₂Cl₂): δ = 2.3 (*h*_{1/2} = 250 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 36.1 [d, ¹J_{P,C} = 32 Hz, C(CH₃)₃], 35.9 [d, ¹J_{P,C} = 35 Hz, C(CH₃)₃], 27.8 [m, C(CH₃)₃], 27.1 [m, C(CH₃)₃], 18.1 (d, ¹J_{P,C} = 65 Hz, PCH₂CH₃), 13.9 (m, BCH₂P), 5.6 (d, ²J_{P,C} = 5 Hz, PCH₂CH₃) ppm. ¹⁹F{¹H} NMR (282.3 MHz, CD₂Cl₂): δ = -79.0 (s, 3 F, OSO₂CF₃), -120.7 (m, 1 F), -127.4 (m, 1 F), -133.1 (m, 2 F, C₆F₅), -144.9 (m, 1 F), -150.9 (m, 1 F), -155.7 (tt, ³J_{F,F} = 20, ⁴J_{F,F} = 2 Hz, 1 F, C₆F₅), -162.2 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 85.2 (m, 1 P, BCH₂P), 80.9 (s, 1 P, OPET₃) ppm. MS (ESI⁺): *m/z* (%) = 485 (6) [1]⁺, 619 (100) [(1)-OPET₃]⁺. MS (ESI⁻): *m/z* (%) = 149 (100) [OSO₂CF₃]⁻. C₂₈H₃₅BF₁₂O₄P₂S (768.37): calcd. C 43.77, H 4.59, S 4.17; found C 43.59, H 4.61, S 4.30.

[(1)py][OTf]: A solution of pyridine in CH₂Cl₂ (0.52 M; 0.10 mL, 0.052 mmol) was added at room temp. by syringe to a stirred solution of (1)OTf (0.030 g, 0.047 mmol) in CH₂Cl₂ (1 mL). The reaction mixture was stirred for 12 h, whereupon a colorless solid precipitated. The solvent and excess pyridine were removed in vacuo to obtain analytically pure [(1)py][OTf]. Yield: 0.033 g (0.046 mmol, 98%). Single crystals suitable for X-ray crystallography were grown by slow concentration of a CH₂Cl₂ solution of [(1)py][OTf] at room temp. ¹H NMR (300.0 MHz, CD₂Cl₂): δ = 8.57 (d, ³J_{H,H} = 6.1 Hz, 2 H, pyH-2,6), 8.30 (tt, ³J_{H,H} = 7.7, ⁴J_{H,H} = 1.3 Hz, 1 H, pyH-4), 7.92 (m, 2 H, pyH-3,5), 2.33–2.10 (m, 2 H, BCH₂P), 1.42 [d, ³J_{P,H} = 16.1 Hz, 9 H, C(CH₃)₃], 1.37 [d, ³J_{P,H} = 15.9 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, CD₂Cl₂): δ = 0.7 (*h*_{1/2} = 130 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 146.6 (pyC-2,6), 144.1 (pyC-4), 128.0 (pyC-3,5), 36.9 [d, ¹J_{P,C} = 31 Hz, C(CH₃)₃], 36.4 [d, ¹J_{P,C} = 32 Hz, C(CH₃)₃], 27.7 [m, C(CH₃)₃], 27.5 [m, C(CH₃)₃], 13.7 (m, BCH₂P) ppm. ¹⁹F{¹H} NMR (282.3 MHz, CD₂Cl₂): δ = -78.9 (s, 3 F, OSO₂CF₃), -120.6 (m, 1 F), -126.8 (m, 1 F), -131.7 (m, 2 F, C₆F₅), -143.5 (m, 1 F), -149.8 (m, 1 F), -154.6 (tt, ³J_{F,F} = 20, ⁴J_{F,F} = 3 Hz, 1 F, C₆F₅), -162.1 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 87.5 (m) ppm. MS (ESI⁺): *m/z* (%) = 485 (100) [1]⁺, 564 (9) [(1)py]⁺. MS (ESI⁻): *m/z* (%) = 149 (100) [OSO₂CF₃]⁻. C₂₇H₂₅BF₁₂NO₃PS (713.32): calcd. C 45.46, H 3.53, N 1.96, S 4.50; found C 44.52, H 3.66, N 1.78, S 4.61. *Note:* The deviation from the calculated value for carbon is due to boron carbide formation during combustion.

[(1)OH₂][OTf]: A solution of (1)OTf (0.12 g, 0.19 mmol) in Et₂O (10 mL) was stirred in air at room temp. for 48 h. The solvent was removed in vacuo yielding [(1)OH₂][OTf] in analytically pure form. Yield: 0.12 g (0.18 mmol, 95%). Slow concentration of a CH₂Cl₂ solution of [(1)OH₂][OTf] at room temp. gave X-ray quality crystals. ¹H NMR (300.0 MHz, CD₂Cl₂): δ = 4.90 (br., *h*_{1/2} = 300 Hz, H₂O), 1.89 (dd, ²J_{H,H} = 16.5, ²J_{P,H} = 13.3 Hz, 1 H, BCH₂P), 1.52 (dd, ²J_{H,H} = 16.5, ²J_{P,H} = 8.5 Hz, 1 H, BCH₂P), 1.47 [d, ³J_{P,H} = 16.4 Hz, 9 H, C(CH₃)₃], 1.26 [d, ³J_{P,H} = 16.0 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, CD₂Cl₂): δ = 1.9 (*h*_{1/2} = 380 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): δ = n.o. (FC, BC_{Ar}, PC_{Ar}, BCH₂P), 36.2 [d, ¹J_{P,C} = 31 Hz, C(CH₃)₃], 35.8 [d, ¹J_{P,C} = 33 Hz, C(CH₃)₃], 27.7 [m, C(CH₃)₃], 27.1 [m, C(CH₃)₃] ppm. ¹⁹F{¹H} NMR (282.3 MHz, CD₂Cl₂): δ = -79.3 (s, 3 F, OSO₂CF₃),

–122.5 (m, 1 F), –127.6 (m, 1 F), –133.7 (m, 2 F, C₆F₅), –145.5 (m, 1 F), –152.0 (m, 1 F), –157.3 (t, ³J_{F,F} = 20 Hz, 1 F, C₆F₅), –163.9 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 86.9 (m) ppm. MS (ESI⁺): *m/z* (%) = 485 (100) [1]⁺. MS (ESI[–]): *m/z* (%) = 149 (100) [OSO₂CF₃][–]. C₂₂H₂₂BF₁₂O₄PS (652.24): calcd. C 40.51, H 3.40, S 4.92; found C 40.56, H 3.61, S 5.44.

Synthesis of (4)OEt: A suspension of LiCH₂P(Me)(*t*Bu) (0.075 g, 0.60 mmol) in toluene (10 mL) was cooled to –78 °C. A solution of (C₆F₅)₂B(OEt) (0.23 g, 0.60 mmol) in toluene (3 mL) was added quickly by syringe. The resulting slurry was gradually warmed to room temp., stirred overnight, and quenched with deionized H₂O (1 mL). The mixture was dried with Na₂SO₄, filtered, and the insoluble material was extracted with toluene (3 × 3 mL). The combined organic phases were concentrated to dryness in vacuo, the oily residue was redissolved in benzene (8 mL) and freeze-dried in vacuo to remove trace amounts of toluene. The colorless solid (4)OEt was obtained as a 1:3 mixture of two diastereomers (¹H NMR spectroscopic control). Yield: 0.25 g (0.51 mmol, 85%). The major diastereomer was isolated by column chromatography (silica gel, hexane/EtOAc, 1.5:1). Yield: 0.13 g (0.27 mmol, 45%).

Major Diastereomer: ¹H NMR (300.0 MHz, C₆D₆): δ = 3.94 (m, 1 H, OCH₂CH₃), 3.30 (m, 1 H, OCH₂CH₃), 1.35 (t, ³J_{H,H} = 6.9 Hz, 3 H, OCH₂CH₃), 1.27 (m, 1 H, BCH₂P), 0.70 (d, ²J_{P,H} = 12.8 Hz, 3 H, PCH₃), 0.66 [d, ³J_{P,H} = 16.9 Hz, 9 H, C(CH₃)₃], 0.54 (m, 1 H, BCH₂P) ppm. ¹¹B{¹H} NMR (96.3 MHz, C₆D₆): δ = 2.1 (*h*_{1/2} = 15 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 60.0 (OCH₂CH₃), 30.5 [d, ¹J_{P,C} = 44 Hz, C(CH₃)₃], 24.7 [m, C(CH₃)₃], 18.6 (OCH₂CH₃), 15.5 (m, BCH₂P), 6.5 (d, ¹J_{P,C} = 46 Hz, PCH₃) ppm. ¹⁹F{¹H} NMR (282.3 MHz, C₆D₆): δ = –126.8 (m, 1 F), –130.2 (m, 1 F), –136.5 (m, 2 F, C₆F₅), –145.8 (m, 1 F), –155.5 (m, 1 F), –160.3 (t, ³J_{F,F} = 21 Hz, 1 F, C₆F₅), –164.6 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 64.8 (m) ppm.

Minor Diastereomer: ¹H NMR (300.0 MHz, C₆D₆): δ = 3.73 (m, 1 H, OCH₂CH₃), 3.20 (m, 1 H, OCH₂CH₃), 1.28 (t, ³J_{H,H} = 6.9 Hz, 3 H, OCH₂CH₃), 1.07 (d, ²J_{P,H} = 13.4 Hz, 3 H, PCH₃), 1.01 (m, 1 H, BCH₂P), 0.58 (m, 1 H, BCH₂P), 0.53 [d, ³J_{P,H} = 16.8 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, C₆D₆): δ = 1.2 (*h*_{1/2} = 20 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 59.9 (OCH₂CH₃), 29.8 [d, ¹J_{P,C} = 44 Hz, C(CH₃)₃], 24.0 [m, C(CH₃)₃], 18.7 (OCH₂CH₃), 15.5 (m, BCH₂P), 6.2 (d, ¹J_{P,C} = 46 Hz, PCH₃) ppm. ¹⁹F{¹H} NMR (282.3 MHz, C₆D₆): δ = –127.6 (m, 1 F), –127.8 (m, 1 F), –135.7 (m, 2 F, C₆F₅), –146.5 (m, 1 F), –156.1 (m, 1 F), –160.4 (t, ³J_{F,F} = 21 Hz, 1 F, C₆F₅), –164.7 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 66.3 (m) ppm. MS (ESI⁺): *m/z* (%) = 443 (100) [4]⁺. MS (ESI[–]): *m/z* (%) = 487 (100) [M – H][–]. C₂₀H₁₉BF₉OP (488.13): calcd. C 49.21, H 3.92; found C 49.54, H 3.99.

Synthesis of (4)Cl: A solution of HCl in Et₂O (0.91 M; 2.4 mL, 2.18 mmol) was added quickly by syringe at room temp. to a stirred solution of (4)OEt (1:3 mixture of two diastereomers; 0.27 g, 0.55 mmol) in Et₂O (8 mL), whereupon a colorless precipitate immediately formed. The resulting suspension was stirred for 18 h to drive the reaction to completion. All volatiles were driven off under reduced pressure, and (4)Cl was obtained as a colorless solid in analytically pure form. Yield: 0.25 g (0.52 mmol, 95%). *Note:* NMR spectroscopic measurements (CDCl₃) on samples after workup revealed strong variations in the diastereomeric ratio (range = 1:3 to 1:12; the major diastereomer was always the same). Using the 1:12 mixture, X-ray quality crystals of one diastereomer were grown by slow concentration of a dilute Et₂O/CH₂Cl₂ solution (3:1) at room temp.

Major Diastereomer: ¹H NMR (300.0 MHz, CDCl₃): δ = 2.07 (d, ²J_{P,H} = 13.1 Hz, 3 H, PCH₃), 1.94–1.71 (m, 2 H, BCH₂P), 1.26 [d, ³J_{P,H} = 17.1 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, CDCl₃): δ = –2.1 (*h*_{1/2} = 120 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 31.0 [d, ¹J_{P,C} = 45 Hz, C(CH₃)₃], 24.5 [m, C(CH₃)₃], 16.8 (m, BCH₂P), 7.1 (d, ¹J_{P,C} = 46 Hz, PCH₃) ppm. ¹⁹F{¹H} NMR (282.3 MHz, CDCl₃): δ = –126.0 (m, 1 F), –129.5 (m, 1 F), –132.4 (m, 2 F, C₆F₅), –143.9 (m, 1 F), –154.0 (m, 1 F), –158.3 (tt, ³J_{F,F} = 20, ⁴J_{F,F} = 2 Hz, 1 F, C₆F₅), –164.0 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = 67.4 (m) ppm.

Minor Diastereomer: ¹H NMR (300.0 MHz, CDCl₃): δ = 1.92 (d, ²J_{P,H} = 12.9 Hz, 3 H, PCH₃), 1.94–1.71 (m, 2 H, BCH₂P), 1.42 [d, ³J_{P,H} = 17.3 Hz, 9 H, C(CH₃)₃] ppm. ¹¹B{¹H} NMR (96.3 MHz, CDCl₃): δ = –2.1 (*h*_{1/2} = 120 Hz) ppm. ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 31.4 [d, ¹J_{P,C} = 44 Hz, C(CH₃)₃], 25.3 [m, C(CH₃)₃], 16.8 (m, BCH₂P), 7.3 (d, ¹J_{P,C} = 46 Hz, PCH₃) ppm. ¹⁹F{¹H} NMR (282.3 MHz, CDCl₃): δ = –127.2 (m, 1 F), –129.3 (m, 1 F), –133.0 (m, 2 F, C₆F₅), –143.7 (m, 1 F), –154.0 (m, 1 F), –158.7 (tt, ³J_{F,F} = 20, ⁴J_{F,F} = 2 Hz, 1 F, C₆F₅), –164.2 (m, 2 F, C₆F₅) ppm. ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = 68.1 (m) ppm. MS (ESI⁺): *m/z* (%) = 443 (100) [4]⁺. C₁₈H₁₄BClF₉P (478.52): calcd. C 45.18, H 2.95; found C 45.15, H 3.01.

Gutmann–Beckett Measurements for Lewis Acidity Determination:

The Lewis acidities of compounds [1][WCA], [2][WCA], and [3][WCA] were determined by an NMR spectroscopic method as follows: (1) OPEt₃ was placed in an NMR tube. (2) In a different flask, CD₂Cl₂ was added to a mixture of [Ag(CH₂Cl₂)] [WCA] and the chloro adduct of the respective Lewis acid. (3) The resulting suspension was stirred for 2 min at room temp., filtered, and the clear yellow filtrate was transferred to the NMR tube. (4) The NMR tube was flame-sealed, and the ³¹P{¹H} NMR spectrum was recorded at 27 °C. In a similar fashion, a sample of (C₆F₅)₃B as the Lewis acid was investigated to ensure maximum comparability of the data. *Note:* The same NMR spectrometer was used for all measurements.

[(1)OPEt₃][WCA]: (1)Cl (0.058 g, 0.111 mmol), [Ag(CH₂Cl₂)] [WCA] (0.129 g, 0.111 mmol), and OPEt₃ (0.005 g, 0.037 mmol) in CD₂Cl₂ (0.7 mL). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 85.0 (m, 1 P, BCH₂P), 80.4 (s, 1 P, OPEt₃) ppm.

[(2)OPEt₃][WCA]: (2)Cl (0.048 g, 0.096 mmol), [Ag(CH₂Cl₂)] [WCA] (0.111 g, 0.096 mmol), and OPEt₃ (0.004 g, 0.032 mmol) in CD₂Cl₂ (0.6 mL). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 84.1 (m, 1 P, BCH₂P), 79.7 (s, 1 P, OPEt₃) ppm.

[(3)OPEt₃][WCA]: (3)Cl (0.048 g, 0.111 mmol), [Ag(CH₂Cl₂)] [WCA] (0.129 g, 0.111 mmol), and OPEt₃ (0.005 g, 0.037 mmol) in CD₂Cl₂ (0.7 mL). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 84.3 (m, 1 P, BCH₂P), 79.7 (s, 1 P, OPEt₃) ppm.

(C₆F₅)₃B·OPEt₃: (C₆F₅)₃B (0.057 g, 0.111 mmol) and OPEt₃ (0.005 g, 0.037 mmol) in CD₂Cl₂ (0.7 mL). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 77.1 (s) ppm.

Lewis Acid Catalyzed Diels–Alder Reaction of 2,5-Dimethyl-1,4-benzoquinone and Cyclopentadiene (CpH)

Catalysis with [1][WCA] (5 mol-%): (1)Cl (0.004 g, 7.5 μmol) and [Ag(CH₂Cl₂)] [WCA] (0.009 g, 7.5 μmol) were suspended in CH₂Cl₂ (1 mL) at room temp. The mixture was stirred for 2 min and filtered. 2,5-Dimethyl-1,4-benzoquinone (0.020 g, 0.15 mmol) was dissolved in a stock solution of freshly distilled CpH in CH₂Cl₂ (0.073 M; 2.1 mL, 0.15 mmol), and the catalyst solution was added

quickly by syringe. The color of the resulting mixture immediately changed from bright yellow to red. After 1 h, more of the CpH stock solution (0.073 M in CH_2Cl_2 ; 0.41 mL, 0.03 mmol) was added, the mixture was stirred for another 1.5 h and then opened to air. The solvent was removed in vacuo, and the crude product was purified by column chromatography (hexane/EtOAc, 19:1). Diels–Alder product **5** was obtained as a pale yellow solid. Yield: 0.026 g (0.13 mmol, 87%). The ^1H NMR chemical shift values of **5** were in agreement with the literature values.^[36]

Catalysis with (1)OTf (5 mol-%): A stock solution of freshly distilled CpH in CH_2Cl_2 (0.073 M; 2.1 mL, 0.15 mmol) was added at room temp. by syringe to a solid mixture of 2,5-dimethyl-1,4-benzoquinone (0.020 g, 0.15 mmol) and (1)OTf (0.005 g, 7.5 μmol). More of the CpH stock solution (0.073 M in CH_2Cl_2 ; 0.41 mL, 0.03 mmol) was added after 4 h and a further 0.2 equiv. after 6 h, whereupon the color of the mixture gradually changed from bright yellow to dark green. Stirring was continued for 18 h before opening the reaction mixture to air. The workup procedure was the same as described above. Yield: 0.025 g (0.12 mmol, 80%).

X-ray Crystal Structure Analysis of (2)Cl, [(1)OPET₃][OTf], [(1)py][OTf], [(1)OH₂][OTf], (1)OiPr $\times$ C₆H₆, and (4)Cl

Data were collected with a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo- K_α radiation. Empirical absorption corrections were performed for all structures by using the MULABS^[42] option in PLATON.^[43] The structures were solved by direct methods with the program SHELXS^[44] and refined against F^2 with full-matrix least-squares techniques with the program SHELXL-97.^[45] The crystal of [(1)OPET₃][OTf] was twinned (emulating monoclinic symmetry) with a contribution of 9.4(1)% for the minor domain. The twin law was (1 0 0/1 -1 0/0 0 -1). In [(1)OH₂][OTf], the H atoms bonded to O were freely refined (see also Table 4).

Table 4. Crystal data and structure refinement details for [(1)OPET₃][OTf] and [(1)OH₂][OTf].

	[(1)OPET ₃][OTf]	[(1)OH ₂][OTf]
Formula	C ₂₈ H ₃₅ BF ₁₂ O ₄ P ₂ S	C ₂₂ H ₂₂ BF ₁₂ O ₄ PS
FW	768.37	652.24
Color, shape	colorless, block	colorless, plate
Temperature [°C]	−100(2)	−100(2)
Radiation	Mo- K_α	Mo- K_α
	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
<i>a</i> [Å]	11.4760(4)	20.2478(13)
<i>b</i> [Å]	14.7143(5)	16.5460(9)
<i>c</i> [Å]	21.5525(8)	18.0243(12)
α [°]	86.549(3)	90
β [°]	89.043(3)	119.441(5)
γ [°]	67.235(3)	90
<i>V</i> [Å ³]	3349.7(2)	5258.7(6)
<i>Z</i>	4	8
<i>D</i> _{calcd.} [g cm ^{−3}]	1.524	1.648
<i>F</i> (000)	1576	2640
μ [mm ^{−1}]	0.293	0.299
Crystal size [mm]	0.35 $\times$ 0.29 $\times$ 0.27	0.33 $\times$ 0.18 $\times$ 0.09
Reflections collected	41059	35094
Indep. reflections (<i>R</i> _{int})	11828 (0.0709)	6041 (0.0567)
Data/restraints/parameters	11828/0/866	6041/0/378
<i>GOOF</i> on <i>F</i> ²	1.054	1.055
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0626, 0.1661	0.0352, 0.0947
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0707, 0.1786	0.0406, 0.0976
Largest diff. peak and hole [e Å ^{−3}]	1.041/−0.553	0.325/−0.454

CCDC-841735 {(2)Cl}, -841736 {[(1)OPET₃][OTf]}, -841737 {[(1)py][OTf]}, -846304 {[(1)OH₂][OTf]}, -841738 {(1)OiPr $\times$ C₆H₆}, and -841739 {(4)Cl} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

³¹P{¹H} MAS NMR Spectroscopic Measurements: ³¹P{¹H} solid-state MAS NMR spectroscopic experiments were carried out with a Bruker Avance WB 600 spectrometer equipped with a 4 mm MAS DVT double resonance probe at Larmor frequencies of 600.1 and 150.9 MHz for ¹H and ³¹P, respectively. Single-pulse excitation spectra were recorded by using 10 kHz sample spinning, a 4 μs excitation pulse, and 100 kHz SPINAL64^[46] ¹H decoupling during the acquisition time of 50 ms (recycle delay: 5 s). The spectrum was acquired with 128 transients and was referenced to 85% H₃PO₄ indirectly by setting the central line of crystalline triethylphosphane sulfide to 58.4 ppm.

Supporting Information (see footnote on the first page of this article): Synthesis and analytical data of (C₆F₅)₂B(OiPr) and (1)OiPr; synthesis and NMR spectroscopic characterization of Me₂P(*t*Bu) and LiCH₂P(Me)(*t*Bu). Selected crystallographic data, plots of the molecular structures, and selected geometric parameters of [(1)py][OTf], (1)OiPr $\times$ C₆H₆, (2)Cl, and (4)Cl. ³¹P{¹H} NMR spectrum of [(1)OPET₃][OTf] in CD₂Cl₂ solution and ³¹P{¹H} MAS NMR spectrum in the solid state. NMR spectroscopic data of [2][WCA].

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Ba₆P₁₂N₁₇O₉Br₃ – A Column-Type Phosphate Structure Solved from Single-Nanocrystal Data Obtained by Automated Electron Diffraction Tomography

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Oxonitridophosphate Ba₆P₁₂N₁₇O₉Br₃ was synthesized by heating a multicomponent mixture of BaBr₂, BaS, phosphoryl triamide and thiophosphoryl triamide in an evacuated and sealed silica-glass ampoule to 750 °C. Ba₆P₁₂N₁₇O₉Br₃ was obtained as the main product as a nanocrystalline powder. The crystal structure was determined ab initio on the basis of electron diffraction data acquired from a single needle-shaped nanocrystal by automated diffraction tomography. Ba₆P₁₂N₁₇O₉Br₃ crystallizes in the hexagonal space group

P6₃/m (no. 176) with unit cell parameters $a = 14.654(19)$, $c = 8.255(9)$ Å and $Z = 2$. Its structure includes triangular, column-shaped anions of $\frac{1}{3}\{(P_{12}N_{17}O_9)^{9-}\}$, which are built from vertex-sharing P(O,N)₄ tetrahedra with 3-rings and three-coordinate nitrogen atoms. The 1D anions are separated by Ba²⁺ and Br⁻ ions, which are arranged in channels parallel to the phosphate anions along [001]. The Ba²⁺ ions are eight- and nine-coordinated by Br⁻ and O/N atoms, respectively.

Introduction

Oxonitridophosphates represent a silicate-analogous class of compounds as the valence electron concentration of SiO₂ equals that of P/O/N, i.e. valence electron count = 16/3. Consequently, for P/O/N compounds a structural chemistry as complex as that of silicates is expected. The tetrahedron-based structures of (oxo)silicates are classified as orthosilicates with isolated Q⁰-type [SiO₄]⁴⁻ tetrahedra, disilicates with Q¹-type tetrahedra, chain- and ring-type structures in different conformations with Q²-type tetrahedra, ribbon- and layer-type structures with Q³-type tetrahedra and 3D frameworks, in which Q⁴-type tetrahedra are all-side vertex-connected to build diverse topologies.^[1] Although there is a huge number of examples for each category of oxosilicates, such abundance has not been reported for oxonitridophosphates; however, due to the presence of nitrogen within the tetrahedron-based networks the structural variability should be even larger. N atoms may, more frequently than O atoms, interconnect three (N^[3]) or even four (N^[4]) tetrahedral centres and the corresponding bond lengths and angles are much more flexible.^[2] The presence of nitrogen atoms can lead to 3D frameworks with a signifi-

cantly higher degree of condensation than the maximum value possible in oxosilicates. The introduction of a more covalent bond character may improve properties such as chemical, thermal and mechanical stability, which is advantageous for the potential applications of oxonitridophosphate networks (e.g. new zeolites).^[3] At present, only a comparably small number of P/O/N compounds is known; however, the individual representatives are different, which makes further research exciting.

The potential of the structural versatility of oxonitridophosphate chemistry has not been properly exploited to date because most P/O/N compounds elude identification and structural characterization. Typical reaction products are either amorphous or contain very small crystals, which often consist of various phases with different unknown compositions and cell parameters. As single crystals usually occur in the micro- or nanosize, structure characterization by single-crystal X-ray diffraction is not possible and has been substituted by combinations of different analytical methods such as powder (P)XRD and solid-state NMR spectroscopy.^[4] Such an approach, however, cannot be used as a standard route for the structural investigation of oxonitridophosphate, because the assignment of different phases to contributions of PXRD or NMR signals is difficult and not always successful. High-resolution TEM can visualize single nanoparticles, but gathering 3D structural information by this technique is not straightforward when the cell parameters exceed 1 nm or when the high electron dose rate required results in fast deterioration and amorphization.^[5]

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Electron diffraction can deliver structural information from single nanocrystals with sub-Angstrom resolution and significantly milder illumination but is traditionally biased by data incompleteness and dynamic effects.^[6] However, the recently-developed automated diffraction tomography (ADT) method for electron diffraction data acquisition and analysis^[7–10] has proved to be a straightforward, fast and efficient method for structure solution of nanocrystalline materials, even if highly beam sensitive.^[11–13] In conventional electron diffraction data acquisition, the crystal is manually oriented along low-index crystallographic zones, which is a time-consuming process and requires experience. In contrast, during ADT acquisition, the crystal is tilted along an arbitrary axis by steady steps, which exploits the full range of the TEM goniometer. ADT is able to deliver electron diffraction data with a higher completeness (up to 100% for orthorhombic or more symmetric crystal families) and a significant reduction of dynamic effects as the diffraction is collected off-zone.

A recent example of oxonitridophosphate structure determination by ADT is $\text{SrP}_3\text{N}_5\text{O}$.^[14] There, the structural investigation was facilitated by the synthesis of a single-phase material. Nevertheless, the ADT approach is as efficient for multiphase systems, where bulk methods, such as PXRD, are limited by peak overlap.^[15,16] The procedure is relatively straightforward when the compound of interest forms small crystals with well-defined morphologies and compositions so that recognition and isolation by low-resolution TEM imaging and energy-dispersive X-ray (EDX) spectroscopy can be performed. As this is the case for many P/O/N compounds, a systematic investigation of oxonitridophosphates has become possible.

Here, we report the synthesis and structure determination of a new oxonitridophosphate, $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$, which has a rare column structure built of vertex-sharing $\text{P}(\text{O},\text{N})_4$ tetrahedra. Although $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ was the main synthetic product, its yield was limited by the presence of other phases.

Results and Discussion

Synthesis

$\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ was obtained by the reaction of a multi-component system of BaBr_2 , BaS , $\text{PO}(\text{NH}_2)_3$ and $\text{PS}(\text{NH}_2)_3$ in silica glass ampoules at 750 °C. Not all of the reaction parameters could be controlled independently in such a synthetic system (e.g. NH_3 partial pressure and amount of oxygen) so the optimal conditions for obtaining phase-pure products could not be determined. However, the procedure given in the Experimental Section yields $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ as the main product with at least two side phases. This can be concluded from the PXRD pattern as the strongest reflections can be assigned to the main reflections of $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ (Supporting Information, Figure S3) and the remaining reflections cannot be jointly indexed. $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ was obtained as a nanocrystalline powder with rod-shaped crystallites.

Crystal Structure Analysis

A rod-shaped crystal of around $500 \times 80 \times 80$ nm was selected for ADT. An ADT tilt series of $\pm 60^\circ$ was acquired in steady steps of 1° . The acquisition was coupled with precession of the electronic beam in order to improve reflection intensity integration.^[9,17] After the 3D diffraction space was reconstructed,^[8] a metrically hexagonal cell with parameters $a \approx 14.7$ Å and $c \approx 8.3$ Å was determined. The long direction of growth of the rod was parallel to c . On the basis of this cell, an intensity data set was integrated and treated according to the kinematical approximation.

The Laue symmetry was $6/m$ (internal residual $R_{\text{sym}} = 22\%$) but not $6/mmm$ ($R_{\text{sym}} = 32\%$). The extinction condition $00l$ with $l = 2n$ leads to space groups $P6_3$ (no. 173) and $P6_3/m$ (no. 176), and ab initio structure solution was achieved with the latter. The correct solution was the one with the best residual (R) and the best figure of merit. All atom positions were determined at the first run and correctly identified using the default parameters. The structure model is in good agreement with the atomic ratio Ba/P/Br of 28:58:14 obtained by EDX spectroscopy (from the same crystal from which ADT data were acquired).

Table 1. Crystallographic data of $\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$ (esd values in parentheses) and details of ADT data collection, structure solution and refinement.

Formula	$\text{Ba}_6\text{P}_{12}\text{N}_{17}\text{O}_9\text{Br}_3$
Formula mass [g mol^{-1}]	1817.49
Crystal system	hexagonal
Space group	$P6_3/m$ (no. 176)
Cell parameters [Å]	$a = 14.654(19)$
(from X-ray powder diffraction)	$c = 8.255(9)$
Cell volume [Å ³]	$V = 1535(3)$
Z	2
ρ_c [g cm^{-3}]	3.932
Crystal shape, colour	column, colourless
Crystal size [μm]	$0.50 \times 0.08 \times 0.08$
Data collection	
Diffractometer/radiation	Tecni F30 S-TWIN TEM, $\lambda = 0.01970$ Å
Temperature [K]	295(2)
Tilt range [°]	$-60/+60$
h, k, l	$-19 \leq h \leq 19, -18 \leq k \leq 19, -10 \leq l \leq 10$
Measured reflections	8520
Completeness [%]	99
Resolution [Å]	0.77
R_{sym}	0.22
Structure Solution and Refinement	
Structure solution method	direct methods ^[18]
Structure refinement method	least-squares refinement on F^2 ^[19]
Independent reflections	1343
Independent reflections ($> 4\sigma$)	1121
Refined parameters	35
Constraints/restraints	2/21
R indices [$F_o^2 \geq 2\sigma(F_o^2)$]	$R1 = 0.276$ $wR2 = 0.649$
R indices (all data)	$R1 = 0.290$ $wR2 = 0.642$
GoF	2.192
Weighting scheme	$w^{-1} = \sigma^2 F_o^2 + (0.2000P)^2$ with $P = (F_o^2 + 2F_c^2)/3$
Max./min. residual electron density [e Å^{-3}]	0.588/−0.516

Accurate lattice parameters were determined from the eleven strongest peaks in the PXRD pattern, which were unambiguously assigned to the phase and uniquely indexed. The refinement of the structure of Ba₆P₁₂N₁₇O₉Br₃ was exclusively performed based on the ADT data, which provide a reliable and stable result as shown by the refinement of SrP₃N₅O.^[14] The final residuals are high when compared with those of standard X-ray refinement but are in the normal range for structure refinement based on electron diffraction data. The P–(O,N) distances were restrained to be equal within a certain standard deviation, and overall displacement parameters were used for chemically equivalent, light atoms. Crystallographic data and further details concerning the structure refinement are summarized in Table 1. Table 2 shows the positional and displacement parameters for all atoms.

Table 2. Atomic coordinates, Wyckoff symbols and isotropic displacement parameters (U_{iso}) [Å²] for the atoms in Ba₆P₁₂N₁₇O₉Br₃ (space group $P6_3/m$, esd values in parentheses); c.n. = coordination number; occupancy of N(2)–N(5) and O(2)–O(5) is 5/6 and 1/6, respectively.

Atom ^[c.n.]	Wyckoff symbol	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}/U_{eq}
Ba(1) ^[10]	6 <i>h</i>	0.5791(4)	0.9657(4)	¼	0.0549(16)
Ba(2) ^[10]	6 <i>h</i>	0.9230(10)	0.1973(10)	¼	0.121(4)
Br(1)	6 <i>h</i>	0.1410(13)	0.1925(13)	¼	0.104(4)
P(1) ^[4]	12 <i>i</i>	0.7843(6)	0.3428(6)	0.4218(9)	0.045(2)
P(2) ^[4]	12 <i>i</i>	0.8569(7)	0.5453(7)	0.5649(10)	0.050(2)
N(1) ^[3]	4 <i>f</i>	2/3	1/3	0.420(3)	0.054(6)
N/O(2) ^[2]	12 <i>i</i>	0.8715(8)	0.4604(8)	0.4610(15)	0.055(3) ^[a]
N/O(3) ^[2]	12 <i>i</i>	0.7828(9)	0.2627(7)	0.5595(14)	
N/O(4) ^[2]	6 <i>h</i>	0.8053(14)	0.3065(14)	¼	
N/O(5) ^[2]	6 <i>h</i>	0.1091(15)	0.4586(16)	¼	
O(6) ^[1]	12 <i>i</i>	0.9355(12)	0.6616(11)	0.493(2)	0.079(5)

[a] The value applies to all atoms N/O(2) to N/O(5).

Structure Description and Discussion

Ba₆P₁₂N₁₇O₉Br₃ exhibits a structure characterized by isolated columnar anions. The columns themselves, however, are highly condensed so that the overall degree of condensation (ratio of tetrahedral centres and bridging atoms), $\kappa = 0.46$, is rather high. Classification into the conventional categories of tetrahedral networks (see introduction) is not possible for Ba₆P₁₂N₁₇O₉Br₃. A comparably complex 1D anion has been observed in Ce₂₉Si₁₄N₄₃O₇.^[20]

The structure of Ba₆P₁₂N₁₇O₉Br₃ can be derived from that of rare-earth metaborates RE(BO₂)₃ (RE = Tb–Lu)^[21] and isotopic oxonitridophosphate SrP₃N₅O,^[14] respectively. In these compounds, triangular columns, such as those in Ba₆P₁₂N₁₇O₉Br₃, form corrugated layers. Formally, the structure of Ba₆P₁₂N₁₇O₉Br₃ is obtained by cutting columns out of the layers, where the Br[−] ions act as “chemical scissors”. The triangular columns run along [001] with the Ba²⁺ and Br[−] ions located between them (Figure 1). The $\frac{1}{\infty}\{(P_{12}N_{17}O_9)^{9-}\}$ columns (Figure 2) are composed of Q⁴- and Q³-type P(O,N)₄ tetrahedra with a Q⁴/Q³ molar ratio of 1:1, which comprise terminally bound oxygen and three-

coordinate nitrogen atoms. The formal building block for the complex anion corresponds to the chlorophosphazene P₆N₇Cl₉^[22] (Figure 3), which is composed of three condensed 3-rings. The columns are generated by the formal substitution of all chlorine atoms by oxygen and nitrogen atoms and the infinite interconnection of the resulting P₆O₃N(O,N)₁₂ entities along [001]. These domed building units face concave/concave and convex/convex and are interconnected by six bridging O or N atoms. The linkage of these entities (on one side with three O/N atoms of their inner three tetrahedra and on the other side with three O/N atoms of their outer three tetrahedral) results in 4- and 6-rings, respectively (Figure 2). The O(6) atom does not interconnect the tetrahedra within a column and is terminally bound.

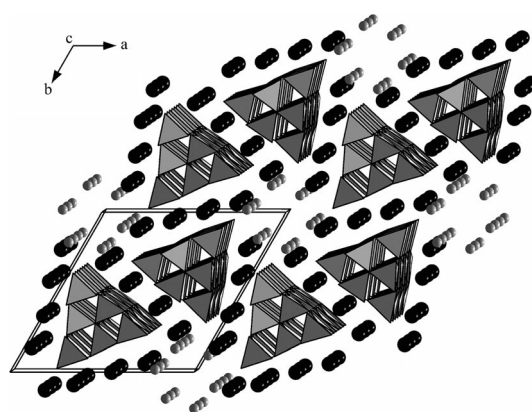


Figure 1. Crystal structure of Ba₆P₁₂N₁₇O₉Br₃ viewed along [001]. Triangular columns of $\frac{1}{\infty}\{(P_{12}N_{17}O_9)^{9-}\}$ are built from vertex-sharing P(O,N)₄ tetrahedra separated by Ba²⁺ ions (black) and Br[−] (gray) ions to form channels along [001].

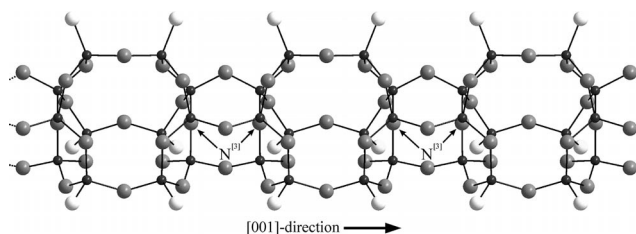


Figure 2. Structure of a single triangular column in Ba₆P₁₂N₁₇O₉Br₃ viewed along [100] (P black, O/N gray, O white); three-coordinate N(1) is indicated.

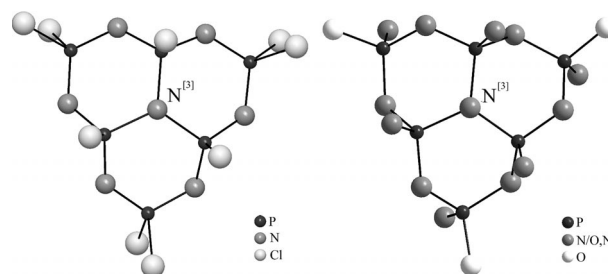


Figure 3. A single molecule of P₆N₇Cl₉ (left)^[22] and the corresponding formal building unit in Ba₆P₁₂N₁₇O₉Br₃ (right).

The range of bond lengths (158.3–165.8 pm) corresponds to that usually observed in oxonitridophosphates. The resulting angles range between 107.9 and 111.1°, which is close to the values of a regular tetrahedron (109.5°). The P–(O,N)–P angles between 120.1 and 141.8° are also typical for P/O/N networks. More information about bond lengths and angles is given in Table 3.

Table 3. Selected interatomic distances [pm] and angles [°] in Ba₆P₁₂N₁₇O₉Br₃ (esd values in parentheses).

Ba(1)–(O,N)	276.4(16)–320.3(12)	9 times
Ba(2)–(O,N)	288.0(31)–369.3(19)	8 times
Ba(1)–Br	348.0(24)	
Ba(2)–Br	316.0(22), 323.0(28)	
P–(O,N)	158.3(12)–165.8(10)	8 times
P–N(1) ^[3] –P	120.0(4), 120.0(5), 120.0(5)	
P–(O,N)–P	120.1(8)–141.8(5)	4 times
(O,N)–P–(O,N)	107.9(8)–111.1(9)	12 times

The formula $\left[\left(\text{P}_{12}^{[4]}\text{N}_{17}^{[3]}\text{O}_{15}^{[2]}\text{O}_6^{[1]}\right)^{4-}\right]$ of the 1D anion in Ba₆P₁₂N₁₇O₉Br₃ involves two- and threefold bridging as well as terminal O/N atoms. As the direct experimental differentiation between O and N is impossible owing to their similar scattering factors, their reasonable assignment was based on Pauling's rules and experience with other oxonitridic compounds, for which solid-state NMR and lattice energy calculations have been helpful for proper O/N assignment. N^[3] was assumed with full nitrogen occupancy as it links three tetrahedra. The terminally bound position was assigned to fully occupied O^[1]. For the twofold bridging positions, an N^[2] occupancy with a statistical admixture of 1/6 O^[2] was assumed. Other ordered or disordered models may also be possible, however, one has to stick to the atomic ratio N/O = 17:9 as long as the Br positions are fully occupied (as suggested by the refinement) and no hydrogen is present in the compound, which can be assumed by comparison with similar, hydrogen-free SrP₃N₅O (proved by elemental analysis).

The electrostatic plausibility for the structure model, also in respect of the atomic O/N ratio and their distribution, was verified with lattice energy calculations according to the Madelung part of lattice energy (MAPLE) concept.^[23] The calculations were carried out for two differently O/N-ordered structural models using the formal ionic charges of the atoms (Table S1). The total MAPLE value averaged over the two models (319181 kJ mol^{−1}) is close to the sum of the total MAPLE values of the hypothetical starting materials 3BaBr₂ + 9BaO + 9PON + 5P₃N₅ (323053 kJ mol^{−1}; Δ = 1.2%).

The columnar anions in Ba₆P₁₂N₁₇O₉Br₃ are separated by Ba²⁺ ions. Both crystallographically independent Ba²⁺ sites exhibit a coordination number of ten (Figure S1). Ba(1) is surrounded by nine O/N atoms and one Br[−] ion. The O/N atoms, including two terminal O atoms, are located at distances between 276.4 and 320.3 pm. The Ba(1)–Br distance is 348.0 pm. Ba(2) is surrounded by eight O/N atoms, four of which are terminal O atoms, and two Br[−] anions. The Ba(2)–(O,N) distances range from 288.0–369.3 pm (Figure S1), whereas the Ba(2)–Br distances have

values of 316.0 and 323.0 pm. All of the distances (Table 3) agree well with the sum of the respective ionic radii involved.^[24,25]

The Br[−] ions in Ba₆P₁₂N₁₇O₉Br₃ are arranged to form channels along [001] (Figure 1). Staggered stacks of Br[−] triangles with a separation of 412.8 pm are arranged according to the 6₃ screw axis (Figure S2). The Br–Br distance within the triangles is 438.1 pm.

Conclusions

The ADT method, now routinely operable, opens the chance to discover new compounds even from inhomogeneous and nanocrystalline samples. This chance should be grasped as the concept of oxonitridophosphates yields extraordinary compounds with open-framework structures, such as P₄N₄(NH)₄(NH₃),^[26] Li_xH_{12−x−y+z}[P₁₂O_yN_{24−y}]X_z (X = Cl, Br)^[27] and Ba₁₉P₃₆O_{6+x}N_{66−x}Cl_{8+x},^[4] and highly condensed layer structures, such as Sr₃P₆O₆N₈.^[28] The ADT structure determination of SrP₃N₅O^[14] has revealed a layer structure with a degree of condensation κ = 1/2, and Ba₆P₁₂N₁₇O₉Br₃ represents a further exceptional structure. To the best of our knowledge, such a highly condensed, 1D anion as that seen in Ba₆P₁₂N₁₇O₉Br₃ has not been observed in any tetrahedron-based class of compounds so far. Ba₆P₁₂N₁₇O₉Br₃ can be considered as a variant of SrP₃N₅O cut into snippets. The “chemical scissors” are Br[−] ions, which form columns from corrugated layers and stabilize the channels in Ba₆P₁₂N₁₇O₉Br₃. Starting from this channel arrangement, it would be interesting to see if further cations, e.g. Li⁺, can be incorporated. With an enlargement of the structure in the <100> directions and a simultaneous adaptation of the O/N ratio for charge equalization, this could lead to future lithium ion conductors.

One of our aims was the synthesis of phase-pure Ba₆P₁₂N₁₇O₉Br₃. Currently, at least two side phases are present in typical samples. These phases might be related to both SrP₃N₅O and Ba₆P₁₂N₁₇O₉Br₃. It can be imagined that structural cut-outs of (e.g. two or three) interlinked (double or triple) columns might be present as single-phase nanocrystals or nanodomains. Other intermediate compounds could exhibit crystal structures built up of finite pieces of a column (prism-like). As for SrP₃N₅O and Ba₆P₁₂N₁₇O₉Br₃, the systematic investigation of other oxonitridophosphate structures could benefit from single-crystal electron diffraction data collected by ADT.

Experimental Section

Synthesis: Phosphoryl triamide and thiophosphoryl triamide were synthesized according to literature methods.^[29–31] Freshly distilled POCl₃ (99%) or PSCl₃ (98%; both from Acros Organics, Geel, Belgium; 10–20 mL) were added directly and slowly to liquid ammonia in a flame-dried three-necked 1 L flask. Subsequently, the elimination of NH₄Cl from the products was carried out by a Soxhlet extraction with distilled Et₂NH in dry CH₂Cl₂ for 3 d. After drying in vacuo, OP(NH₂)₃ and SP(NH₂)₃ were available as starting materials in form of colourless, water sensitive powders. Their purity was verified by PXRD.

Ba₆P₁₂N₁₇O₉Br₃ was synthesized by a multicomponent system. In a typical procedure, BaBr₂ (35.7 mg, 0.120 mmol; Sigma–Aldrich, 99.999%), BaS (40.7 mg, 0.240 mmol; Sigma–Aldrich, 99.9%), OP(NH₂)₃ (27.4 mg, 0.288 mmol) and SP(NH₂)₃ (48.0 mg, 0.432 mmol) were thoroughly mixed and ground in an Ar-filled glove box (MBraun, Garching, Germany; H₂O ≤ 0.2 ppm, O₂ ≤ 1.0 ppm) and transferred into a silica glass ampoule (wall thickness 2 mm, inner diameter 11 mm). The evacuated and sealed ampoule (length around 11 cm), was heated in a tube furnace to 200 and 750 °C with dwell times of 12 and 48 h (heating and cooling rate: 1.0 K min^{−1}), respectively. The emerging condensation products NH₃ and H₂S were partially deposited as (NH₄)₂S at the places in the ampoule that cooled first. After breaking the ampoules, the samples were washed with water and *N,N*-dimethylformamide to remove NH₄Br, BaBr₂ and BaS. Ba₆P₁₂N₁₇O₉Br₃ was obtained as a heterogeneous, colourless, water and air resistant, nanocrystalline powder.

ADT Data Acquisition and Analysis: For data acquisition, the sample was suspended in ethanol and sprayed onto a carbon-coated copper grid using the sonifier described in ref.^[9] ADT was performed with a Tecnai F30 S-TWIN TEM equipped with a field emission gun working at 300 kV. Electron diffraction patterns were acquired with a CCD camera (14-bit GATAN 794MSC). EDX spectra were recorded in STEM mode and quantified with Emispec ESVision software.

ADT data acquisition was performed with a FISCHIONE tomography holder, using the acquisition module described in ref.^[7] STEM images and diffraction patterns were collected using a mild illumination setting. STEM images were collected by a FISCHIONE high angle annular dark field detector. Nano electron diffraction was performed with a 10 µm C2 condenser aperture with a 50 nm beam on the sample. ADT was coupled with precession of the electron beam (precession electron diffraction),^[9,17] performed using the NanoMEGAS SpinningStar unit. The precession angle was kept at 1.2°. The ADT3D^[8] software was used for data processing, which included geometrical parameter optimization, 3D diffraction volume reconstruction, 3D visualization, automated cell parameter determination and intensity integration. Ab initio structure solution was performed by direct methods implemented in SIR2008, included in the package IL MILIONE.^[18] Structure refinement was performed with the SHELX software.^[19]

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-423468.

Supporting Information (see footnote on the first page of this article): Results of MAPLE lattice energy calculations, diagrams of the coordination spheres of the Ba²⁺ ions and arrangement of the Br[−] ions.

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Ferrocene-Conjugated Oxidovanadium(IV) Complexes as Potent Near-IR Light Photocytotoxic Agents

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Ferrocene-conjugated oxidovanadium(IV) complexes [VO(Fc-tpy)(B)](ClO₄)₂ (**1–4**) and [VO(Ph-tpy)(dppz)](ClO₄)₂ (**5**) as a control [Fc = (η⁵-C₅H₄)Fe(η⁵-C₅H₅), Fc-tpy = 4'-ferrocenyl-2,2':6',2''-terpyridine, Ph-tpy = 4'-phenyl-2,2':6',2''-terpyridine, B = heterocyclic base: 2,2'-bipyridine (bpy in **1**), 1,10-phenanthroline (phen in **2**), dipyrroquinoxaline (dpq in **3**), dipyrrophenazine (dppz in **4**)] were prepared and their DNA binding, DNA photocleavage activity and photocytotoxicity studied. The crystal structure of [VO(Fc-tpy)(bpy)](PF₆)₂·3Me₂CO shows a vanadyl group in six-coordinate V^{IV}ON₅ coordination geometry, in which Fc-tpy and bpy display tridentate meridional and bidentate *N*-

donor axial-equatorial binding modes, respectively. The one-electron paramagnetic complexes exhibit a charge-transfer band near 590 nm in DMF. The V^{IV}/V^{III} redox couple in **1–4** appears near –0.7 V, whereas the Fc moiety shows a response near 0.6 V vs. SCE in DMF/0.1 M TBAP. The complexes are good binders to calf thymus DNA with K_b values of 10⁴–10⁶ M^{–1}. DNA melting and viscometric data suggest groove and/or partial intercalative DNA binding of the complexes. Complexes **3–5** display DNA photocleavage activity in near-IR light of 785 nm. Complex **4** shows significant photocytotoxicity in visible light (400–700 nm) in HeLa cells with low dark toxicity.

Introduction

Photodynamic therapy (PDT) is an emerging therapeutic technique for the treatment of cancer in the presence of light.^[1–5] In this process, selective light activation of the drug molecule (sensitizer) in the cancer cells produces reactive oxygen species (ROS), which damage the cancer cells and leave the unexposed normal cells unaffected. Photofrin[®] and its analogs, phthalocyanines and lutetium(III) texaphyrin (LUTRIN) are a few leading molecules in this treatment.^[1,6–8] The approved PDT drug Photofrin[®] generates singlet oxygen (¹O₂) species by energy transfer by a type-II pathway upon photoexcitation.^[9,10] The problems associated with Photofrin[®] and related organic dyes are skin- and hepatotoxicity, which limits their therapeutic potential.^[11,12] Biocompatible transition metal complexes, with their versatile coordination geometries and low-energy visible spectral bands, could be suitably designed to circumvent the drawbacks associated with Photofrin[®] and related organic PDT agents. Recent reports have shown that transi-

tion metal complexes are capable of photocleaving DNA in visible light and display significant photocytotoxicity.^[13–20] Some complexes are also known to show anaerobic DNA photocleavage activity.^[21,22] Among the new-generation platinum-based photoactive anticancer agents, platinum(IV) azide complexes are known to form reactive platinum(II) species on photoirradiation, which show desirable photocytotoxicity and low dark toxicity.^[23]

Among metal-based antitumor agents, rhodium and ruthenium complexes have been extensively studied to explore their photocytotoxicity in visible light in a variety of cancer cells.^[24–28] We have reported copper(II) and oxidovanadium(IV) complexes with a low-energy d–d band, which show DNA photocleavage activity within the PDT window of 620–800 nm.^[29–32] The use of bioorganometallic complexes in PDT is relatively unknown, although ferrocene and its conjugates have been used for medicinal purposes.^[33–38] Ferrocifen, the ferrocene-appended tamoxifen, is known to be more active in hormone-dependent breast cancer (ER+) and in ER– cases than tamoxifen.^[34] Several other ferrocene conjugates have been seen to show anticancer activity.^[35,36] Our use of the ferrocenyl moiety to design anticancer agents is based on its excellent stability in biological fluids, its redox activity and lipophilicity.^[33] Although ferrocene is nontoxic, its activation leads to the generation of species that can damage cancer cells.^[37] Photoinduced electron or charge transfer from the ferrocenyl moiety to a reducible metal centre or an organic chromophore leads to

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the activation of the ferrocenyl unit to form cytotoxic ROS. There are reports of non-ferrocenyl organometallic complexes photocleaving DNA in UV light; however, such complexes are not suitable for PDT considering the reduced tissue penetration of UV light compared to red light.^[13,39,40]

This work stems from our interest in designing complexes with a ferrocenyl moiety covalently linked to an oxidovanadium(IV) species to achieve photocytotoxic effects over a broad spectrum of visible light. Oxidovanadium(IV) complexes are known to show reduced dark toxicity in comparison to their copper(II) analogs.^[31,32] Copper(II) complexes are susceptible to reduction to form copper(I) species in the presence of cellular thiols, and the reduced species can generate reactive hydroxyl radicals, which cause cellular damage in the absence of light, thus having significant dark toxicity.^[41,42] Because of their dark toxicity, copper(II) complexes are generally not suitable for PDT applications. Oxidovanadium(IV) complexes, with the metal atom in its reduced oxidation state, are unlikely to show significant dark cytotoxicity, but could show significant photocytotoxicity due to the presence of a d–d band in the near-IR region. The presence of the ferrocenyl group is expected to augment the photocytotoxic effect. Herein, we present the synthesis, structure, DNA-binding and -cleavage activity and photocytotoxicity of the ferrocene-conjugated oxidovanadium(IV) complexes [VO(Fc-tpy)(B)](ClO₄)₂ (**1–4**), where Fc-tpy is 4'-ferrocenyl-2,2':6',2''-terpyridine and B is an *N,N*-donor heterocyclic base, viz. 2,2'-bipyridine (bpy in **1**), 1,10-phenanthroline (phen in **2**), dipyrido[3,2-*d*:2',3'-*f*]quinoxaline (dpq in **3**) and dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz in **4**) (Figure 1). We also prepared [VO(Ph-tpy)(dppz)](ClO₄)₂ (**5**), where Ph-tpy is 4'-phenyl-2,2':6',2''-terpyridine, as a control species to study the effect of the ferrocenyl moiety on the photocytotoxic activity of the oxidovanadium(IV) complexes. Complex **1** was structurally characterized by X-ray crystallography. Significant results of this work include the photocytotoxic effect observed for **4**, which comprises the ferrocenyl moiety and the dppz ligand. The complexes show significant DNA cleavage activity in red light of near-IR wavelength. Compounds that show similar DNA cleavage activity at near-IR wavelengths are rare in the literature.^[1,2,43,44]

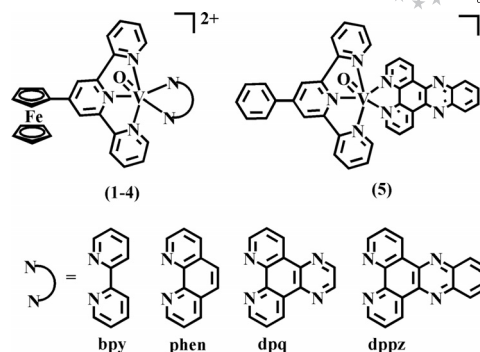


Figure 1. [VO(Fc-tpy)(B)](ClO₄)₂ (B = bpy in **1**, phen in **2**, dpq in **3**, dppz in **4**) and [VO(Ph-tpy)(dppz)](ClO₄)₂ (**5**).

Results and Discussion

Synthesis and General Properties

Complexes **1–4** were prepared in good yield (ca. 70%) by treating oxidovanadium(IV) perchlorate with the heterocyclic base (bpy in **1**, phen in **2**, dpq in **3** and dppz in **4**) and Fc-tpy in CHCl₃/EtOH (1:3, v/v) (Figure 1). Complex **5**, the phenyl analogue of **4**, was prepared as a control species. The complexes were characterized from spectral and analytical data. Selected physicochemical data are given in Table 1. The ESI mass spectra of the complexes in MeCN showed essentially the molecular ion peak of [VO(Fc-tpy)(B)]²⁺. A minor mass peak at *m/z* = 500 was also observed. This peak was assigned to [VO₂(Fc-tpy)]⁺, which seems to be formed during the mass spectral measurements. The IR spectra did not show any characteristic peaks for dioxovanadium units in the analytically pure samples. IR spectra showed the Cl–O stretching frequency of the perchlorate anion near 1090 cm^{−1} and the V=O stretching frequency in the range of 978–987 cm^{−1}.^[45] The complexes are one-electron paramagnetic species, which gives a magnetic moment value of ca. 1.6 μ_B due to the presence of a 3d¹ VO²⁺ moiety. The 1:2 electrolytic nature of the complexes was evidenced from conductivity data in *N,N*-dimethylformamide (DMF) at 25 °C. Cyclic voltammetry of the redox-active complexes in DMF/0.1 M tetrabutylammonium perchlorate (TBAP) showed a quasireversible Fc⁺/Fc redox

Table 1. Selected physicochemical data for **1–5**.

Complex	IR ^[a] [cm ^{−1}] ν(V=O)	ν(ClO ₄ [−])	λ _{max} [nm] (ε/dm ³ M ^{−1} cm ^{−1}) ^[b]	E _f [V] ^[c,d] (ΔE _p [mV])	E _p ^[c,e] [V]	μ _{eff} ^[f] [μ _B]
1	983	1096	580 (1710), 423 (740)	0.61(190)	−0.79	1.60
2	978	1095	593 (2200), 435 (1300)	0.62(215)	−0.72	1.58
3	984	1091	590 (3230), 430 (1620)	0.63(185)	−0.66	1.62
4	986	1093	589 (3320), 423 (1970)	0.62(178)	−0.65	1.61
5	987	1088	719(55)	—	−0.61	1.60

[a] In KBr. [b] In DMF. The d–d band near 720 nm for **1–4** could not be observed due to the presence of an intense charge-transfer band at ca. 590 nm. [c] Redox data in DMF/0.1 M TBAP. The potentials are vs. SCE. Scan rate = 50 mV s^{−1}. E_f = (E_{pa} + E_{pc})/2, ΔE_p = (E_{pa} − E_{pc}), where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. The ligand reduction data are: −1.40 V for **1**, −1.55 V for **2**, −1.68 and −1.92 V for **3**, −1.21 and −1.83 V for **4**, and −1.23 and −1.84 V for **5**. [d] Fc⁺/Fc redox couple. [e] Cathodic peak for the V^{IV}/V^{III} redox couple. [f] Magnetic moment at 298 K by using powdered solid samples of the complexes.

couple near 0.6 V and the V^{IV}/V^{III} couple as an irreversible reduction in the range from -0.61 to -0.79 V. A 200 mV anodic shift of the Fc^+/Fc potential from that of ferrocene ($E_f = 0.42$ V) could be due to the presence of the tpy moiety, which stabilizes the ferrocenyl unit. Complexes **3** and **4** exhibited two reductive responses at -1.21 and -1.83 V for dpq and -1.23 and -1.84 V for dppz, respectively. The redox data show the presence of a large potential window of 0.6 V to -0.7 V, which could reduce the undesirable chemical nuclease activity and dark cellular toxicity of the complexes.

In DMF, **1–4** exhibited a ferrocene-centred visible spectral band at ca. 430 nm and another intense band at ca. 590 nm, which is absent in the visible spectra of **5** and $Fc\text{-tpy}$ (L) (Figure 2). This charge-transfer band is associated with the ferrocenyl moiety and the terpyridyl vanadium(IV) moiety.^[46–48] The low-energy d–d absorption band for **1–4** was not observed possibly due to the presence of this intense band. Complex **5**, which lacks the ferrocenyl moiety, showed a low-energy oxido vanadium(IV)-centred d–d band at 720 nm in DMF (Figure 2). The ligand-centred electronic spectral bands were observed in the UV region. The band corresponding to dpq appeared at 340 nm, and dppz displayed two bands at 360 and 380 nm.^[49]

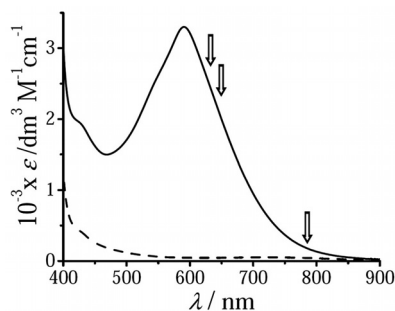


Figure 2. Electronic absorption spectra of **4** (solid line) and **5** (dashed line) in DMF. The arrows indicate the wavelengths of the laser light used for the photoinduced DNA cleavage studies.

X-ray Crystallography

X-ray quality single crystals of **1** as its PF_6^- salt (**1a**) were grown by layering hexane onto an acetone solution of **1a** at 4°C . Complex **1a** crystallized with three acetone molecules in the triclinic crystal system with space group $P\bar{1}$. An ORTEP view of the complex cation is shown in Figure 3. Selected bond lengths and angles are given in Table 2. The complex is a discrete monomeric species, in which the $Fc\text{-tpy}$ ligand shows a meridional binding mode, and bpy shows an axial–equatorial binding mode to the vanadium centre with a $V^{IV}ON_5$ coordination geometry. The two cyclopentadienyl rings of the ferrocenyl moiety in $Fc\text{-tpy}$ are in an eclipsed conformation. The $V\text{--}N$ bond *trans* to the $V=O$ group is significantly longer [$2.291(2)$ Å] than the other $V\text{--}N$ distances ($2.03\text{--}2.11$ Å).^[50] The $V\text{--}N$ bond length involving the central pyridyl ring of $Fc\text{-tpy}$ [$2.033(2)$ Å] is shorter than the other $V\text{--}N$ bonds, which involve the terminal pyridyl groups.

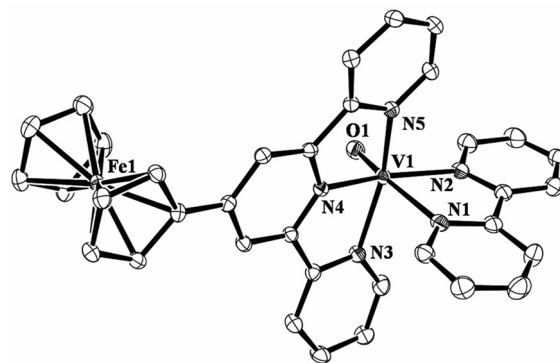


Figure 3. ORTEP view of the cationic complex of **1a**· $3\text{Me}_2\text{CO}$ showing 50% probability thermal ellipsoids and the numbering scheme for the metal and heteroatoms. The hydrogen atoms are not shown for clarity.

Table 2. Selected bond lengths [Å] and angles [$^\circ$] for **1a**· $3\text{Me}_2\text{CO}$.

$V(1)\text{--}O(1)$	1.5940(18)	$O(1)\text{--}V(1)\text{--}N(5)$	102.09(9)
$V(1)\text{--}N(1)$	2.291(2)	$N(1)\text{--}V(1)\text{--}N(2)$	73.10(8)
$V(1)\text{--}N(2)$	2.115(2)	$N(1)\text{--}V(1)\text{--}N(3)$	81.00(8)
$V(1)\text{--}N(3)$	2.118(2)	$N(1)\text{--}V(1)\text{--}N(4)$	87.76(8)
$V(1)\text{--}N(4)$	2.033(2)	$N(1)\text{--}V(1)\text{--}N(5)$	86.07(8)
$V(1)\text{--}N(5)$	2.109(2)	$N(2)\text{--}V(1)\text{--}N(3)$	105.76(8)
$Fe(1)\text{--}C_0^1$ [$Fe(1)\text{--}C_0^2$] ^[a]	1.644 [1.654]	$N(2)\text{--}V(1)\text{--}N(4)$	159.92(8)
$O(1)\text{--}V(1)\text{--}N(1)$	166.38(8)	$N(2)\text{--}V(1)\text{--}N(5)$	95.28(8)
$O(1)\text{--}V(1)\text{--}N(2)$	95.09(9)	$N(3)\text{--}V(1)\text{--}N(4)$	76.33(8)
$O(1)\text{--}V(1)\text{--}N(3)$	96.17(9)	$N(3)\text{--}V(1)\text{--}N(5)$	150.72(8)
$O(1)\text{--}V(1)\text{--}N(4)$	104.60(9)	$N(4)\text{--}V(1)\text{--}N(5)$	77.02(8)

[a] C_0^1 and C_0^2 are the two centroids of the cyclopentadienyl rings comprising atoms C(26)–C(30) and C(31)–C(35), respectively. The $Fe(1)\text{--}C$ distances are in the range of $2.033(2)\text{--}2.061(2)$ Å, which gives an average value of 2.047 Å.

DNA Binding Properties

The binding interaction of the complexes to calf thymus DNA was studied by electronic absorption titration, thermal denaturation and viscometric methods. The intrinsic equilibrium binding constant (K_b) of the complexes was determined from the spectral changes (hypochromism) in the ligand-centred absorption bands at ca. 260 nm upon addition of DNA (Figure 4). The extent of hypochromism gives a measure of the DNA binding affinity of the complexes.^[51] The complexes showed significant hypochromism of 15–23% with K_b values in the range of 8.5×10^4 to 1.1×10^6 M^{-1} . The binding strength of the complexes follows the order: **4** > **5** > **3** > **2** > **1** (Table 3). The high binding strength of **4** and **5** could be due to the presence of an extended planar phenazine moiety.

The thermal denaturation study gives a measure of the DNA duplex stability when bound to a complex. A DNA intercalator that stacks between two base pairs gives better duplex stability compared to the DNA groove binders.^[52] The observed increase in the calf thymus DNA melting temperature (T_m) on binding to the complexes is low ($\Delta T_m = 1\text{--}3^\circ\text{C}$) compared to that of the DNA intercalator ethidium bromide (EB, $\Delta T_m = 13^\circ\text{C}$) (Figure 5, Table 3). The DNA melting data suggest that the complexes are primarily groove-binding in nature, and the complexes that contain

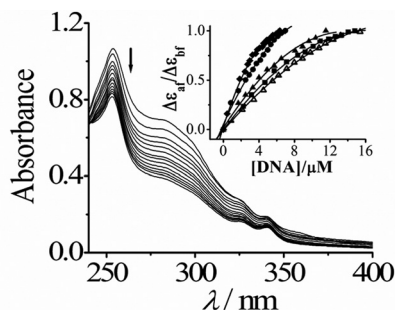


Figure 4. Absorption spectral traces of **3** in tris-HCl buffer (5 mM, pH = 7.2) on gradual addition of calf thymus DNA. Inset: Plot of $\Delta\epsilon_{at}/\Delta\epsilon_{bf}$ vs. [DNA] for **1** (Δ), **2** ($\blacksquare$), **3** ($\blacktriangle$), **4** ($\bullet$) and **5** ($\blacklozenge$).

Table 3. DNA binding data for **1–5**.

Complex	$K_b^{[a]}$ [M^{-1}] (s)	$\Delta T_m^{[b]}$ [$^{\circ}C$]
1	$(8.5 \pm 0.3) \times 10^4$ (0.02)	0.5
2	$(1.2 \pm 0.2) \times 10^5$ (0.03)	1.5
3	$(2.3 \pm 0.4) \times 10^5$ (0.08)	2
4	$(1.1 \pm 0.2) \times 10^6$ (0.18)	3
5	$(5.7 \pm 0.4) \times 10^5$ (0.03)	3.5

[a] The intrinsic equilibrium calf-thymus DNA binding constant and MvH fitting parameter (s) are from UV/Vis experiments. [b] Change in the calf thymus DNA melting temperature.

dppz showed partial intercalative binding. The DNA binding study was also carried out by viscosity measurements. The relative viscosity of the DNA solution increases with an increase in its contour length. A DNA intercalator, such as EB, has a significant effect on lengthening the DNA double helix upon intercalation, which causes a significant increase in the relative viscosity of the DNA solution.^[53] DNA groove binders and partial intercalators have only a minor effect. As shown in Figure 6, EB causes a significant increase in the relative specific viscosity $(\eta/\eta_0)^{1/3}$ (where η and η_0 are the specific viscosity of DNA in the presence and absence of the complex, respectively) of the calf thymus DNA in Tris-HCl buffer solution, whereas a minor groove binder, such as Hoechst dye, causes no apparent effect. Complexes **1–5** show a moderate increase in the relative specific viscosity of DNA, which indicates the groove-bind-

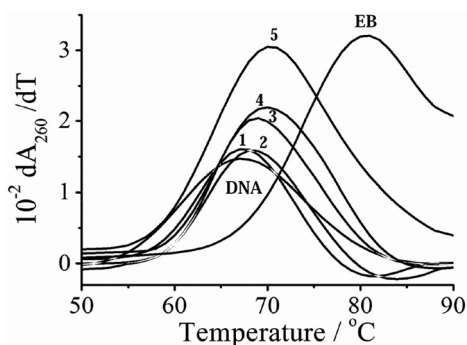


Figure 5. Thermal denaturation plots for calf thymus DNA (170 μM) alone and in the presence of **1–5** (17 μM) and EB (17 μM) in phosphate buffer (5 mM, pH = 6.8).

ing nature of **1–3** and partial intercalative binding mode of the dppz complexes (**4** and **5**). Ferrocenyl-containing **4** shows a marginally greater change in the relative specific viscosity than **5**, which has a pendant phenyl group.

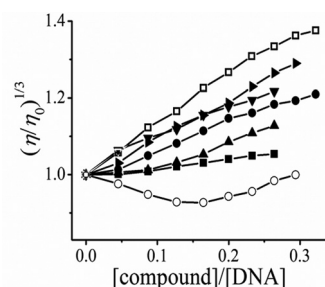


Figure 6. Effect of addition of an increasing concentration of EB ($\square$), **1** ($\blacksquare$), **2** ($\blacktriangle$), **3** ($\bullet$), **4** ($\blacktriangleright$), **5** ($\blacktriangledown$) and Hoechst 33258 ($\circ$) on the relative viscosity of calf thymus DNA (143 μM) in Tris-HCl buffer (5 mM, pH = 7.2) at 37 $^{\circ}C$.

Chemical Nuclease Activity

The oxidative pUC19 DNA cleavage activity of the complexes was studied in the dark in the presence of 3-mercaptopropionic acid (MPA) and glutathione (GSH) as reducing agents. The complexes showed moderate chemical nuclease activity at a high complex concentration of 35 μM (Figure 7). This could be due to the presence of the V^{IV}/V^{III} couple near -0.7 V vs. SCE. A similar extent of chemical nuclease activity was observed by using only 2.5 μM of a (bisphen)copper(II) species (Lanes 12 and 13 in Figure 7).^[41] The chemical nuclease activity of the complexes shows that the dpq and dppz complexes are more active than their phen and bpy analogs, which could be due to their higher DNA binding strengths.



Figure 7. Cleavage of SC pUC19 DNA [0.2 μg , 30 μM b.p. (base pairs)] by **1–4** (35 μM) and $[Cu(phen)_2(H_2O)](ClO_4)_2$ (5 μM) in the presence of MPA (0.5 mM) and GSH (0.5 mM) in Tris-HCl/NaCl buffer (50 mM, pH = 7.2) under dark reaction conditions. (a) Lane 1: DNA control; Lane 2: DNA + MPA; Lane 3: DNA + **1** + MPA; Lane 4: DNA + **2** + MPA; Lane 5: DNA + **3** + MPA; Lane 6: DNA + **4** + MPA; Lane 7: DNA + GSH; Lane 8: DNA + **1** + GSH; Lane 9: DNA + **2** + GSH; Lane 10: DNA + **3** + GSH; Lane 11: DNA + **4** + GSH; Lane 12: DNA + $[Cu(phen)_2(H_2O)](ClO_4)_2$ + MPA; Lane 13: DNA + $[Cu(phen)_2(H_2O)](ClO_4)_2$ + GSH. The concentration of the Cu^{II} complex is seven times less than that of the VO^{2+} complexes.

DNA Photocleavage

The photoinduced pUC19 DNA cleavage activity of the complexes was studied in Tris-HCl/NaCl buffer in red light

of 633, 647 and 785 nm. Selected DNA photocleavage data are listed in Table 4. Ferrocene-conjugated VO^{2+} **3** and **4** with dpq and dppz, respectively, showed significant DNA photocleavage activity at 647 nm (Figure 8). Complex **5**, with the absence of any visible absorption band near 600 nm, did not show any significant DNA cleavage activity in red light of 633 and 647 nm, whereas at near-IR light of 785 nm both **4** and **5** showed efficient DNA cleavage activity. The difference in the DNA photocleavage activity of the Fc-tpy and Ph-tpy complexes could be due to the presence of the ferrocenyl moiety, which shows an intense charge-transfer band near 600 nm. The DNA photocleavage activity of Ph-tpy-containing **5** at near-IR light could be due to the presence of a metal-centred low-energy d–d band at 720 nm. The DNA cleavage activity at near-IR light follows the order: **4** (Fc-tpy/dppz) > **5** (Ph-tpy/dppz) and **3** (Fc-tpy/dpq) >> **2** (Fc-tpy/phen) > **1** (Fc-tpy/bpy). The Fc-tpy and dppz ligands did not show any significant DNA photocleavage activity in red light. Complexes **1** and **2**, which contain photoinactive bpy and phen ligands, were poor photocleavers of DNA. The complexes did not show any apparent DNA cleavage activity in the dark. The metal-bound Fc-tpy moiety provides a broad visible spectral range for the complexes to show photoactivity in visible and near-IR light. In contrast, the metal-bound Ph-tpy moiety is active only at near-IR wavelengths.

Table 4. Selected SC pUC19 DNA (0.2 μg , 30 μM b.p.) cleavage data for **1–5** (35 μM).

Entry	Reaction conditions	% NC ^[a]	633 nm ^[b]	647 nm ^[b]	785 nm ^[b]
1	DNA control	3	2	3	
2	DNA + 1	30	16	16	
3	DNA + 2	45	22	26	
4	DNA + 3	73	73	60	
5	DNA + 4	82	85	71	
6	DNA + 5	20	18	62	

[a] NC = nicked circular form of pUC19 DNA. [b] Wavelengths of red light used for the DNA cleavage in air. Photoexposure time = 2 h.

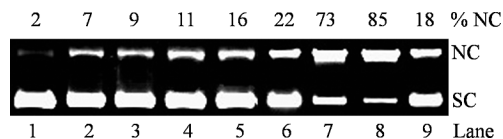


Figure 8. Gel electrophoresis showing the photoinduced DNA cleavage activity of **1–5** (35 μM) in red light of 647 nm by using SC pUC19 DNA (0.2 μg , 30 μM b.p.) for an exposure time of 2 h. Lane 1: DNA control; Lane 2: DNA + Fc-tpy (35 μM); Lane 3: DNA + dppz (35 μM); Lane 4: DNA + **4** (in dark); Lane 5: DNA + **1**; Lane 6: DNA + **2**; Lane 7: DNA + **3**; Lane 8: DNA + **4**; Lane 9: DNA + **5**.

The DNA-binding mode of **3** and **4** was studied in the presence of a DNA minor-groove binder, distamycin, and a major-groove binder, methyl green. A significant inhibition in the DNA photocleavage activity of **3** in red light of 647 nm was observed in the presence of distamycin, which

indicates the minor-groove-binding preference of **3**. Addition of distamycin had no apparent effect on the DNA photocleavage activity of **4**. Complex **4** showed a significant inhibition in the cleavage activity in the presence of methyl green, which indicates the major-groove-binding preference of **4**.

The mechanistic aspects of the DNA photocleavage activity of **4** were studied in red light of 647 nm in the presence of various additives, such as sodium azide and 2,2,6,6-tetramethyl-4-piperidone (TEMP) as singlet oxygen quenchers and dimethyl sulfoxide (DMSO), KI and catalase as hydroxyl radical scavengers. The addition of hydroxyl radical scavengers was found to inhibit the photoinduced DNA cleavage activity of **4**, which indicates the formation of hydroxyl radicals as the ROS (Figure 9). Upon oxidation, ferrocenyl compounds are known to produce hydroxyl radicals.^[37] It is likely that the ferrocenyl moiety in these complexes could become oxidized in red light in a photoredox pathway to generate ferricenium cationic species, which could lead to the formation of hydroxyl radicals from the degradation of the ferrocenium moiety.

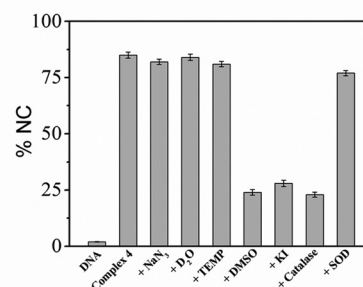


Figure 9. Bar diagram showing the photoinduced pUC19 DNA (0.2 μg , 30 μM b.p.) cleavage activity of **4** (35 μM) in the presence of different additives in red light of 647 nm for an exposure time of 2 h (NaN_3 , TEMP, KI = 0.5 mM; D_2O = 16 μL ; DMSO = 6 μL ; catalase = 4 units; SOD = 4 units).

Photocytotoxicity in HeLa Cells

The cytotoxicity of **2–5** was studied using HeLa cells by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. Complex **4** showed a significant PDT effect and gave IC_{50} values of 35.5 μM in the dark and 13.4 μM in visible light of 400–700 nm (Figure 10). The high photocytotoxic activity of **4** could be due to the presence of a ferrocenyl moiety, which is likely to cause better cellular uptake than the nonferrocenyl analog. Complex **5**, which lacks the ferrocenyl moiety, showed less cytotoxicity than **4** in the dark and light giving IC_{50} values of >100 μM and 26 μM , respectively. Complexes **2** and **3** are significantly less photocytotoxic than **4** in visible light. The free dppz ligand gave IC_{50} values of 58 μM in light and ca. 100 μM in the dark in HeLa cells.^[54] A comparison of the IC_{50} values of the complexes with Photofrin[®], cisplatin and other 3d-metal-based PDT agents showed that **4** is a potent organo-metallic PDT agent in red light (Table 5).

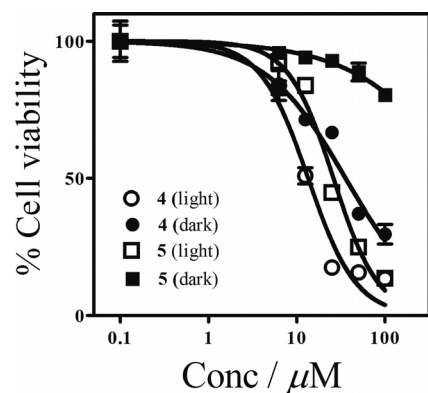


Figure 10. MTT assay plot showing the photocytotoxicity of **4** and **5** in HeLa cancer cells after 2 h incubation in the dark followed by photoirradiation with visible light (400–700 nm, 10 J cm^{-2}).

Table 5. Comparison of the IC_{50} values of **3–5** in HeLa cells with other compounds.

Complex	IC_{50} [μM] (in visible light) ^[a]	IC_{50} [μM] (in the dark)
2	46.1(± 1.1)	60.9(± 1.1)
3	35.5(± 1.0)	100
4	13.4(± 1.1)	35.5(± 1.0)
5	26.0(± 1.0)	100
[Cu(Fc-tpy)(dppz)](ClO ₄) ₂ ^[b]	3.7	10.5
Photofrin ^[c]	2.57	>25
Cisplatin ^[d]	–	7.2 ^[e]

[a] The light source used for **2–5** was a photoreactor of 400–700 nm. [b] Data from ref.^[30] [c] Data from ref.^[54b] [d] IC_{50} value after 24 h incubation taken from ref.^[54c] [e] IC_{50} value of cisplatin after 4 h incubation $70\text{ }\mu\text{M}$.

Nuclear Staining

Hoechst staining was performed to ascertain any changes in the nuclear characteristics due to cell death induced by **4** (Figure 11). To identify the possible involvement of apoptosis, the photoexposed HeLa cells with **4** ($15\text{ }\mu\text{M}$ for 4 h in the dark) were stained with Hoechst 33258 dye. A significant increase in the apoptotic nuclear morphology, such as extensive chromatin aggregation or nuclear condensation, was observed in the treated cells [Figure 11(e)] com-

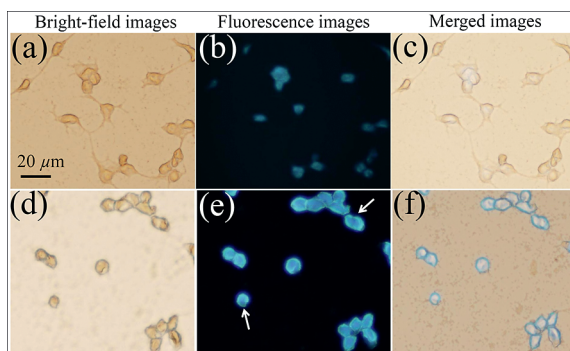


Figure 11. Hoechst 33258 staining of the nuclei of HeLa cells (2 h post photoexposure) treated with **4** in visible light (400–700 nm): panels (a), (b) and (c) are the untreated control cells, and (d), (e) and (f) are the cells treated with **4** ($15\text{ }\mu\text{M}$).

pared to the evenly stained nuclear contours of the normal HeLa cells [Figure 11(b)]. The control cells were found to be stained lightly and evenly with the dye. In contrast, treated HeLa cells 1 h after irradiation displayed intensely stained blue nuclei [Figure 11(b)]. This suggests chromatin condensation, which is a characteristic feature of apoptotic cells.^[55] The cell shrinkage from apoptosis is evidenced from the bright-field images of the cells treated with **4** compared to the untreated ones.

Conclusions

Ferrocene-conjugated oxidovanadium(IV) complexes of heterocyclic bases as a new class of near-IR light PDT agents were prepared and structurally characterized. The complexes, which have extended aromatic moieties, are efficient binders to calf thymus DNA, display red-light-induced pUC19 DNA cleavage activity. The dppz-containing complexes exhibit significant photocytotoxic effects in HeLa cells in visible light of 400–700 nm. The positive effect of the presence of a ferrocenyl moiety compared to its phenyl analog was observed from the higher photocytotoxicity of ferrocenyl-containing **4** than **5**. Except for bpy-containing **1**, all the other complexes showed good DNA binding. The dppz-containing complexes showed a partial intercalative DNA binding mode. The redox-active complexes showed cyclic voltammetric responses for the quasireversible Fc^+/Fc couple near 0.6 V and a cathodic response for the $\text{V}^{\text{IV}}/\text{V}^{\text{III}}$ couple near -0.7 V vs. SCE. This wide potential window is responsible for their moderate chemical nuclease activity at high complex concentration. The complexes are thus significantly less chemical-nuclease-active than their copper(II) analogs.

Complex **4** showed significant DNA photocleavage activity over a broad spectral range in red light of 633 and 647 nm and near-IR light of 785 nm. This is due to the presence of an intense charge-transfer band near 600 nm. This spectral feature of **4**, which remarkably mimics the solar spectral pattern for the wavelength range of 400–700 nm, is absent in its phenyl analog, **5**. The mechanistic data reveal the involvement of a hydroxyl radical pathway for the DNA photocleavage reactions, whereas organic PDT agents generally follow a singlet oxygen type-II pathway. The DNA photocleavage activity of the ferrocenyl conjugate **4** is significantly higher than its phenyl analog **5**. The photocytotoxic activity of **4** is also higher than **5**. The PDT effect observed for **4** in HeLa cells is of importance when compared to the IC_{50} values of organic PDT agents. As ferrocene is a poorly cytotoxic and biocompatible molecule, its conjugates of bioessential 3d-metal ions could be of potential use for biological applications in PDT using solar light.

Experimental Section

Materials and Methods: The reagents and chemicals were procured from commercial sources (SD Fine Chemicals, India; Sigma–Ald-

rich, USA) and used without further purification. Organic solvents were purified by standard procedures prior to use.^[56] Synthesis of the complexes was performed by using standard Schlenk techniques under nitrogen. Supercoiled (SC) pUC19 DNA (cesium chloride purified) was purchased from Bangalore Genie (India). Ferrocenecarbaldehyde, 2-acetylpyridine, calf thymus DNA, agarose (molecular biology grade), catalase, superoxide dismutase (SOD), TEMP, Hoechst 33258 [bis(benzimidazole) derivative], distamycin, methyl green and EB were purchased from Sigma–Aldrich (USA). Tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer solution was prepared by using deionized and sonicated triple-distilled water. 4'-Ferrocenyl-2,2':6',2''-terpyridine (Fc-tpy), 4'-phenyl-2,2':6',2''-terpyridine (Ph-tpy), dipyrro[3,2-*d*:2',3'-*f*]quinoxaline (dpq) and dipyrro[3,2-*a*:2',3'-*c*]phenazine (dppz) were prepared according to literature procedures.^[57–60] Elemental analysis was performed with a Thermo Finnigan FLASH EA 1112 CHNS analyzer. IR and electronic spectra were recorded with PerkinElmer Lambda 35 and PerkinElmer spectrum one 55 spectrophotometers, respectively. Room-temperature magnetic susceptibility data were obtained with a George Associates Inc. (Berkeley, USA) instrument by using Hg[Co(NCS)₄] as a standard. Diamagnetic corrections were carried out on the experimental susceptibility data.^[61] Molar conductivity measurements were carried out with a Control Dynamics (India) conductivity meter. Cyclic voltammetric measurements were made at room temperature with an EG&G PAR 253 VersaStat potentiostat/galvanostat by using a three-electrode configuration consisting of a glassy carbon working, platinum wire auxiliary, and saturated calomel reference (SCE) electrode with 0.1 M TBAP as the supporting electrolyte. ESI-MS measurements were carried out with a Bruker Daltonics make Esquire 300 Plus ESI model. CAUTION: As perchlorate salts are potentially explosive, only small quantities of the samples were used with due precautions.

Preparation of [VO(Fc-tpy)(B)](ClO₄)₂ [B = bpy (1), phen (2), dpq (3), dppz (4)] and [VO(Ph-tpy)(dppz)](ClO₄)₂ (5): Complexes 1–5 were prepared according to a general synthetic procedure in which an ethanol solution (10 mL) of vanadyl sulfate (VOSO₄, 0.16 g, 1.0 mmol) was treated with Ca(ClO₄)₂ (0.31 g, 1.0 mmol) and stirred for 45 min. Precipitated CaSO₄ was removed by filtration through Celite. To the blue filtrate was added slowly an ethanol solution (10 mL) of the heterocyclic base (bpy, 0.156 g; phen, 0.198 g; dpq, 0.232 g; dppz, 0.282 g; 1.0 mmol), and the resulting mixture was stirred for 15 min to obtain a greenish yellow solution. To this solution was added the terpyridyl ligand (Fc-tpy, 0.418 g; Ph-tpy, 0.324 g, 1.0 mmol) in a methanol/chloroform mixture (4:1, v/v, 10 mL) and the solution was stirred for 30 min to form a precipitate. The solid was collected by filtration, washed with cold CHCl₃ and MeOH and dried in vacuo over P₄O₁₀.

[VO(Fc-tpy)(bpy)](ClO₄)₂ (1): Yield 0.61 g, 73%. C₃₅H₂₇Cl₂Fe-N₅O₉V (837.98): calcd. C 50.09, H 3.24, N 8.34; found C 49.85, H 3.10, N 8.30. IR (KBr): $\tilde{\nu}$ = 3410 (br.), 3082 (br.), 1607 (s), 1541 (w), 1499 (w), 1473 (m), 1438 (m), 1253 (w), 1096 [vs, $\nu(\text{ClO}_4^-)$], 983 [m, $\nu(\text{V}=\text{O})$], 883 (w), 769 (s), 623 (m), 520 (s), 480 (w) cm⁻¹. ESI-MS (MeCN): m/z = 320 [1 – 2 ClO₄]²⁺. UV/Vis (DMF): λ_{max} ($\epsilon/\text{dm}^3\text{M}^{-1}\text{cm}^{-1}$) = 283 (15480), 423 (740), 580 (1710) nm. Molar conductance in DMF at 25 °C: Λ_{M} = 134 S m² M⁻¹; $\chi_{\text{M}}^{\text{corr}}$ = $1.073 \times 10^{-3} \text{ cm}^3 \text{ M}^{-1}$.

[VO(Fc-tpy)(phen)](ClO₄)₂ (2): Yield 0.65 g, 75%. C₃₇H₂₇Cl₂Fe-N₅O₉V (861.99): calcd. C 51.47, H 3.15, N 8.11; found C 51.21, H 3.32, N 8.01. IR (KBr): $\tilde{\nu}$ = 3433 (br.), 3078 (br.), 1606 (s), 1477 (w), 1428 (m), 1384 (w), 1258 (w), 1095 [vs, $\nu(\text{ClO}_4^-)$], 1035 (w), 978 [m, $\nu(\text{V}=\text{O})$], 850 (w), 791 (w), 726 (s), 623 (m), 523 (s) cm⁻¹.

ESI-MS (MeCN): m/z = 332 [2 – 2 ClO₄]²⁺. UV/Vis (DMF) λ_{max} ($\epsilon/\text{dm}^3\text{M}^{-1}\text{cm}^{-1}$) = 276 (50590), 435 (1300), 593 (2200) nm. Molar conductance in DMF at 25 °C: Λ_{M} = 138 S m² M⁻¹; $\chi_{\text{M}}^{\text{corr}}$ = $1.046 \times 10^{-3} \text{ cm}^3 \text{ M}^{-1}$.

[VO(Fc-tpy)(dpq)](ClO₄)₂ (3): Yield 0.64 g, 70%. C₃₉H₂₇Cl₂Fe-N₇O₉V (914.01): calcd. C 51.17, H 2.97, N 10.71; found C 50.84, H 2.58, N 10.52. IR (KBr): $\tilde{\nu}$ = 3432 (br.), 3090 (br.), 1606 (w), 1537 (w), 1500 (w), 1478 (w), 1437 (m), 1405 (w), 1390 (w), 1253 (w), 1091 [vs, $\nu(\text{ClO}_4^-)$], 984 [m, $\nu(\text{V}=\text{O})$], 796 (w), 729 (s), 623 (m), 523 (s), 442 (w) cm⁻¹. ESI-MS (MeCN): m/z = 358 [3 – 2 ClO₄]²⁺. UV/Vis (DMF): λ_{max} ($\epsilon/\text{dm}^3\text{M}^{-1}\text{cm}^{-1}$) = 278 (60910), 340 (890), 430 (1620), 590 (3230) nm. Molar conductance in DMF at 25 °C: Λ_{M} = 144 S m² M⁻¹; $\chi_{\text{M}}^{\text{corr}}$ = $1.1 \times 10^{-3} \text{ cm}^3 \text{ M}^{-1}$.

[VO(Fc-tpy)(dppz)](ClO₄)₂ (4): Yield 0.66 g, 68%. C₄₃H₂₉Cl₂Fe-N₇O₉V (964.02): calcd. C 53.50, H 3.03, N 10.16; found C 53.28, H 2.82, N 9.91. IR (KBr): $\tilde{\nu}$ = 3423 (br.), 3074 (br.), 1605 (s), 1538 (w), 1499 (m), 1479 (m), 1440 (m), 1420 (w), 1384 (w), 1361 (w), 1252 (w), 1093 [vs, $\nu(\text{ClO}_4^-)$], 986 [m, $\nu(\text{V}=\text{O})$], 792 (w), 769 (w), 729 (s), 623 (m), 520 (s), 429 (w) cm⁻¹. ESI-MS (MeCN): m/z = 383 [4 – 2 ClO₄]²⁺. UV/Vis (DMF): λ_{max} ($\epsilon/\text{dm}^3\text{M}^{-1}\text{cm}^{-1}$) = 269 (112730), 361 (22610), 380 (22505), 423 (1970), 589 (3320) nm. Molar conductance in DMF at 25 °C: Λ_{M} = 143 S m² M⁻¹; $\chi_{\text{M}}^{\text{corr}}$ = $1.086 \times 10^{-3} \text{ cm}^3 \text{ M}^{-1}$.

[VO(Ph-tpy)(dppz)](ClO₄)₂ (5): Yield 0.54 g, 72%. C₃₉H₂₅Cl₂Fe-N₇O₉V (856.05): calcd. C 54.63, H 2.94, N 11.43; found C 54.34, H 2.85, N 11.66. IR (KBr): $\tilde{\nu}$ = 3411 (br.), 3066 (br.), 1606 (s), 1548 (w), 1497 (w), 1419 (m), 1360 (w), 1249 (w), 1088 [vs, $\nu(\text{ClO}_4^-)$], 987 [m, $\nu(\text{V}=\text{O})$], 796 (w), 772 (s), 731 (w), 624 (s), 495 (w), 428 (w). ESI-MS (MeCN): m/z = 329 [5 – 2 ClO₄]²⁺. UV/Vis (DMF): λ_{max} ($\epsilon/\text{dm}^3\text{M}^{-1}\text{cm}^{-1}$) = 270 (111000), 361 (14230), 380 (13790), 719 (55) nm. Molar conductance in DMF at 25 °C: Λ_{M} = 146 S m² M⁻¹; $\chi_{\text{M}}^{\text{corr}}$ = $1.073 \times 10^{-3} \text{ cm}^3 \text{ M}^{-1}$.

Solubility and Stability: All the complexes were soluble in DMF, MeCN and DMSO; moderately soluble in CH₂Cl₂ and MeOH. They were moderately stable in aqueous DMF and aqueous DMSO in the dark.

X-ray Crystallographic Procedures: Single crystals of **1a** were grown by layering hexane onto an acetone solution of **1a** at 4 °C for 4 d. A suitable crystal was mounted in a cryoloop under a stream of cold N₂ from the diffractometer cooling system. Unit-cell measurements and intensity data collections were performed at 90 K with a Bruker Smart Kappa APEX II CCD Area Detector by using graphite-monochromated Mo-K α (λ = 0.71073 Å) radiation. Data reduction included corrections for Lorentz and polarization effects by using a multiscan absorption correction program (SADABS).^[62] The crystal structure was solved and refined by using full-matrix least squares on F^2 (SHELX-97).^[63] Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated at their idealized positions riding on their carbon atoms. Selected crystallographic parameters are summarized in Table 6. A perspective view of the complex was obtained by using ORTEP-3 for windows.^[64] CCDC-797006 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DNA Binding Experiments: The experiments were carried out by using double-stranded calf thymus DNA in Tris-HCl buffer (pH = 7.2) and phosphate buffer (pH = 6.8). The purity of the DNA was estimated from the ratio of the absorbance values at 260 and

Table 6. Selected crystallographic data for **1a**·3Me₂CO.

Empirical formula	C ₄₄ H ₄₅ F ₁₂ FeN ₅ O ₄ P ₂ V
Crystal size [mm]	0.21 × 0.15 × 0.11
Fw [g mol ⁻¹]	1104.58
Crystal system	triclinic
Space group (no.)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	11.6198(5)
<i>b</i> [Å]	12.8904(5)
<i>c</i> [Å]	16.1821(6)
α [°]	90.774(2)
β [°]	97.445(2)
γ [°]	101.534(2)
<i>V</i> [Å ³]	2352.91(16)
<i>Z</i>	2
$2\theta_{\max}$ [°]	30.51
<i>T</i> [K]	90
<i>D</i> [g cm ⁻³]	1.559
λ [Å] (Mo- <i>K</i> α)	0.71073
μ [mm ⁻¹]	0.671
Data/restraints/parameters	13839/0/622
<i>R</i> (000)	1126
Goodness-of-fit on <i>F</i> ²	0.906
<i>R</i> (<i>F</i> _o) ^[a] [<i>I</i> > 2σ(<i>I</i>)]	0.0496
<i>wR</i> (<i>F</i> _o) ^[b] [<i>I</i> > 2σ(<i>I</i>)]	0.1110
<i>R</i> [all data] (<i>wR</i> [all data])	0.1083 (0.1371)
Largest diff. peak/hole [e Å ⁻³]	0.547/−0.535

[a] $R = \sum |F_o| - |F_c| / \sum |F_o|$. [b] $wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{0.5}$; $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$; *A* and *B* values are 0.0712 and 1.7344, respectively.

280 nm, which was found to be 1.9:1. This ratio indicated the lack of protein impurities in the DNA sample. The molar absorption coefficient (6600 dm³ mol⁻¹ cm⁻¹) of the calf thymus DNA at 260 nm was used to determine the DNA concentration.^[65] In UV/Vis absorption titration experiments, the complex concentration (25 μM) was kept constant, and the DNA concentration was varied from 0 to 16 μM. To cancel the effect of DNA absorption, equal quantities of DNA were added into the reference solution during the titration. The absorption coefficient (ϵ) of the complex solution in the absence of DNA, after each addition and saturation by DNA solution were recorded. The equilibrium DNA binding constants (*K*_b) of **1–5** were obtained from nonlinear fitting of the absorption coefficient data by the McGhee–von Hippel (MvH) method by using the equation of Bard and coworkers: $\Delta\epsilon_{\text{af}}/\Delta\epsilon_{\text{bf}} = \{b - (b^2 - 2K_b C_t [\text{DNA}]/s)^{0.5}\} / 2K_b$, where $b = 1 + K_b C_t + K_b [\text{DNA}]/2s$; *C*_t is the total concentration of the metal complex; *s* is the fitting parameter, ϵ_f , ϵ_a and ϵ_b are the molar extinction-coefficient values of the free complex in solution, complex bound to DNA at a definite concentration, and the complex in completely DNA bound form, respectively.^[66,67] The thermal denaturation experiments were carried out by monitoring the absorbance of calf thymus DNA at 260 nm in the presence and absence of the complexes. The temperature of the DNA solutions were varied from 40 to 90 °C at a scan rate of 1 °C min⁻¹. The melting temperatures (*T*_m) were calculated from the maxima of the derivative plots. In viscosity measurements, the flow time (*t*₀) of 3 mL Tris-HCl buffer alone was measured with a Schott Gerate AVS310 automated viscometer fixed with a thermostatic bath at a constant temperature of 37(±0.1) °C. The flow time (*t*) of the DNA in Tris-HCl buffer alone was also measured. A 100 μL volume of the complex solution from a stock solution of 200 μM in DMF was added gradually and the flow times were recorded thrice to an accuracy of 0.3 s with the automated timer and an average flow time (*t*_n) was calculated. Relative specific viscosity of DNA (η/η_0)^{1/3} was plotted against [complex]/[DNA], where $\eta = (t_n - t_0)$ and $\eta_0 =$

(*t* − *t*₀) are the viscosity of DNA in the presence and absence of the complex.^[68]

DNA Cleavage Experiments: The cleavage of supercoiled (SC) pUC19 DNA (0.2 μg, 30 μM, 2686 base pairs) by the complexes was studied in Tris-HCl buffer (50 mM, pH = 7.2) containing 50 mM NaCl. The samples were prepared in the dark. Different red-light sources were used for photoirradiation of the samples: 633 nm from a He-Ne laser (12 mW power), 647 nm from a continuous-wave Ar-Kr mixed-gas-ion laser (laser beam diameter = 1.8 mm, beam divergence = 0.70 mrad, Spectra Physics Water-Cooled Mixed-Gas Ion Laser Stabilite® 2018-RM) (100 mW laser power) and 785 nm from a diode laser (100 mW laser power, Model LQC785-100C from Spectra Physics with LD module). The solution path length of the irradiated sample solutions was ca. 5 mm. The sample solutions were incubated for 45 min prior to photoexposure and irradiation was performed for 2 h followed by quenching of the reaction by addition of a loading dye containing 30 mM ethylenediamine-tetraacetic acid (EDTA), 0.05% bromophenol blue, 0.05% xylene cyanol and 36% glycerol. Agarose gel electrophoresis was performed to separate the nicked circular (NC) part from the SC pUC19 DNA. Electrophoresis was carried out on a 0.8% agarose gel containing 1.0 μg mL⁻¹ EB in a dark room at 40 V in 1X TAE (Tris-acetate-EDTA) buffer for 2 h. The DNA cleavage products were visualized by UV light, photographed, and the band intensities were measured with a UVITECH Gel Documentation System after making due corrections for the low level of NC form present in the SC DNA sample and for the low affinity of EB to SC DNA compared to NC DNA.^[69] The observed error in measuring the band intensities varied within 3–5%. Mechanistic investigations were performed by using various external additives, such as KI (0.5 mM), NaN₃ (0.5 mM), TEMP (0.5 mM), DMSO (6 μL), SOD (4 units) and catalase (4 units). For the D₂O experiment, this solvent was used to dilute the sample to 20 μL. Experiments for the chemical nuclease study were carried out in a dark room in the presence of reducing agents, viz. GSH (5 mM) and MPA (5 mM). Incubation was carried out in the dark at 37 °C for 1 h.

Cell Cytotoxicity and Nuclear Staining: The photocytotoxicity of **2–4** was studied by using an MTT assay.^[70] About 1.0 × 10⁴ human cervical cancer HeLa cells were plated in a 96 well culture plate in Dulbecco's Modified Eagle Medium (DMEM) containing 10% FBS (fetal bovine serum). After 24 h of incubation at 37 °C in a CO₂ incubator, complexes of various concentrations in 1% DMSO were added to the cells, and incubation was continued in the dark for 2 h. The medium was subsequently changed to PBS (phosphate buffer saline), and photoirradiation was performed in visible light (400–700 nm) by using a Luzchem Photoreactor (Model LZC-1, Ontario, Canada) fitted with Sylvania 8 fluorescent white tubes with a fluence rate of 2.4 mW cm⁻² to provide a total dose of 10 J cm⁻². After photo exposure, PBS was replaced with DMEM-FBS buffer, and incubation was continued in the dark for a further 12 h. A 20 μL amount of 5 mg mL⁻¹ of MTT was added to each well, and incubation was continued for an additional 3 h. The culture medium was discarded, and formazan crystals were removed by adding 200 μL of DMSO. The absorbance at 595 nm was determined by using a BIORAD ELISA plate reader. The cytotoxicity of the test complex was measured as the percentage ratio of the absorbance of the treated cells to the untreated controls. The IC₅₀ values were determined by nonlinear regression analysis (GraphPad Prism 5.0). Hoechst staining was performed as described by Lee and Shacter.^[71] Briefly, the control and HeLa cells, which were treated with **4** (15 μM) in the dark for 4 h followed by irradiation with visible light of 400–700 nm (10 J cm⁻²) in a photoreactor, were fixed with 3.7% (v/v) paraformaldehyde in PBS at

25 °C for 10 min and stained with Hoechst 33258 dye (1 mg mL⁻¹ in PBS) for 5 min. After washing twice with PBS, the cells were examined by fluorescence microscopy (360/40 nm excitation and 460/50 nm emission filters). The apoptotic cells were identified by the presence of highly condensed or fragmented nuclei.

Supporting Information (see footnote on the first page of this article): ESI-MS spectra of 1–5 (Figures S1–S5), UV/Vis spectra (Figure S6), IR spectra (Figures S7–S11), cyclic voltammograms (Figures S12–S16), unit cell packing diagram (Figure S17), DNA binding plots (Figures S18–S19), gel electrophoresis diagrams (Figures S20–S24) and MTT plot (Figure S25).

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12-Membered Macrocycles Containing Ditelluroxane and Selenotelluroxane Units

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The reaction of benzeneseleninic acid with bis(*p*-methoxyphenyl)tellurium dihalide [halide = Cl (**1**), Br (**2**)] afforded colorless crystals in moderate yield. Single-crystal X-ray diffraction revealed the formation of 12-membered macrocycles [(*p*-MeO-C₆H₄)₂Te(μ-O)(μ-PhSeO₂)(μ₄-X)]₂ [X = Cl (**1**), Br (**2**)] where the halogen atoms, which are stabilized by Te–X interactions, cap the macrocycle on both sides. The reaction of NaI with **1** afforded the iodo-capped macrocycle [(*p*-MeO-C₆H₄)₂Te(μ-O)(μ-PhSeO₂)(μ₄-I)]₂ (**3**) in good yield. In the so-

lid-state structures of **1–3**, the alignment of the phenyl group on Se changes with respect to the macrocycle. Macrocycle **3** shows rare Se–π interactions, which lead to the formation of a supramolecular polymeric network. Further reaction of methaneseleninic acid with bis(*p*-methoxyphenyl)tellurium dichloride in methanol in the presence of triethylamine afforded a 12-membered macrocycle [(*p*-MeO-C₆H₄)₂Te(μ-O)(μ-MeSeO₂)(μ₄-Cl)]₂ (**4**), which is structurally similar to **1–3**.

Introduction

Diorganotellurium oxides are of immense interest because of their extensive applications in organic synthesis as oxygen transfer reagents.^[1] Another interesting aspect of diorganotellurium oxide/halides is their ability to form macrocycles, which results in the isolation of new telluroxane frameworks.^[2] Beckmann and coworkers have performed pioneering work in this field by carrying out reactions of diorganotellurium oxides with various protic ligands, such as carboxylates,^[3] phosphinates,^[4] sulfonates,^[4] and diorganosilane diols,^[5] which resulted in the formation of products that show rich structural variation. Beckmann and coworkers have also shown that solutions of di-*p*-anisyltellurium oxide and di-*tert*-butyltin oxide can absorb gaseous CO₂ rapidly, which resulted in the formation of tellurastannoxanes that evolved the absorbed CO₂ at low temperatures.^[6] Chandrasekhar and coworkers have investigated the reaction of a cyclic phosphinic acid with diorganotellurium dihalide, which led to the assembly of an unprecedented 12-membered macrocycle, which is capped by halogen atoms on both sides;^[7] the authors suggest that these macrocycles can be considered as analogues of “inverse crowns”^[8] and “anti-crowns”.^[9] This report is fascinating as changing the organic group bound to the phosphorus atom of the phosphinic acid had a profound effect on the reactivity of phosphinic acid with diorganotellurium dihalides/oxide precursors, which led to the isolation of

products with completely different structural forms. Recently, we and others have investigated the chemistry of heavier main-group metal oxo clusters and the reactivity of organostibonic acids with various protic ligands, such as silanols and pyrazolyl phenols, which resulted in the formation of interesting organoantimony oxo clusters and cages.^[10] Christou and coworkers have proposed the use of benzeneseleninic acid as a protic ligand as, unlike phosphinates and sulfonates, seleninates consist not only of a three-coordinate central atom but also have a stereoactive lone pair on the central selenium atom, unlike carboxylates.^[11a] The reaction of benzeneseleninic acid with [Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄] resulted in the formation of polynuclear clusters, [Mn₇O₈(O₂SePh)₈(O₂CMe)(H₂O)] and [Mn₇O₈(O₂SePh)₉(H₂O)], which are basically built from a new [Mn₇O₈]⁹⁺ core and exhibit interesting magnetic properties.^[11b,11c] Benzeneseleninic acid has been used as a protic ligand for the synthesis of compounds containing Sn–O–Se bonds.^[12] In [Mn₇O₈(O₂SePh)₈(O₂CMe)(H₂O)] and [Mn₇O₈(O₂SePh)₉(H₂O)] the organoseleninates bind to the transition metal in a chelating fashion, whereas in the latter compounds that contain Sn–O–Se bonds, they coordinate to the tin atoms in a monodentate binding mode. Despite these interesting observations, reports of the use of organoseleninic acid as a protic ligand are scarce. Singh and coworkers have carried out the condensation reaction of bis(*o*-formylphenyl)selenide/telluride with primary amines followed by reduction, which led to the formation of fused macrocycles that can bind to a variety of transition metal ions.^[13] Despite these efforts on the isolation of interesting tellurium- and selenium-based macrocycles, compounds that contain Se–O–Te motifs are rare.^[14] Hence, we investigated the reactivity of organoseleninic acid with diorgano-

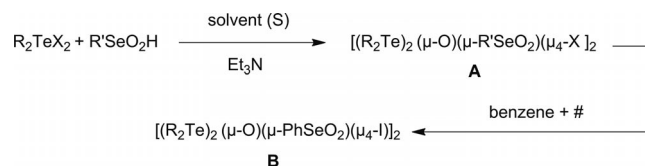
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tellurium dihalide with primarily two objectives: (a) to investigate the effect of changing the protic acid from phosphinic to seleninic acid on the structure of the product of their reaction with diorganotellurium dihalides and (b) the effect of changing the organic group bound to selenium on the structure of the products. Herein, we report the synthesis and structural characterization of 12-membered macrocycles that contain both Te–O–Te and Se–O–Te bonds: $[(p\text{-MeO-C}_6\text{H}_4)_2\text{Te}(\mu\text{-O})(\mu\text{-RSeO}_2)(\mu_4\text{-X})_2]$ [R = Ph (**1**, **2**, **3**), Me (**4**); X = Cl (**1**), Br (**2**), I (**3**), Cl (**4**)].

Results and Discussion

The syntheses of **1–3** were adapted from literature methods.^[7] Benzeneseleninic acid and bis(*p*-methoxyphenyl)-tellurium dihalide [halide = Cl (**1**), Br (**2**)] were stirred in benzene for 12 h at room temperature in the presence of triethylamine (Scheme 1). Filtration followed by slow evaporation of the solvent afforded colorless crystals in moderate yield. Unlike **1** and **2**, iodo-capped $[(p\text{-MeO-C}_6\text{H}_4)_2\text{Te}(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu_4\text{-I})_2]$ (**3**) could not be synthesized by reaction of the corresponding diorganotellurium diiodide with benzeneseleninic acid. Instead, **3** was synthesized from the reaction of **1** with sodium iodide (Scheme 1).^[7] $[(p\text{-MeO-C}_6\text{H}_4)_2\text{Te}(\mu\text{-O})(\mu\text{-MeSeO}_2)(\mu_4\text{-Cl})_2]$ (**4**) was synthesized following a similar method to **1** and **2** except that methanol was used as the solvent in place of benzene.



S = benzene (**1**, **2**), methanol (**4**)
 A: R = MeOC₆H₄, R' = Ph (**1,2**), Me (**4**), X = Cl (**1,4**), Br (**2**)
 B: R = MeOC₆H₄; # = **1** + NaI

Scheme 1.

Macrocycles **1–4** were characterized by standard analytical and spectroscopic techniques. ⁷⁷Se NMR spectra (CDCl₃) show single resonances at nearly identical chemical shifts for **1**, **2**, and **3** (1167 ppm), which suggests that the selenium atoms are in identical environments. The ¹²⁵Te NMR spectra (CDCl₃) also show single resonances but a slight upfield shift is observed on going from **1** to **2** to **3** with chemical shifts of 1211, 1196, and 1182 ppm, respectively. This variation in the ¹²⁵Te NMR spectra can be assigned to the decrease in electronegativity on going from chlorine to bromine to iodine.^[15] ⁷⁷Se NMR and ¹²⁵Te NMR spectra (CDCl₃) of **4** show single resonances at 1182 ppm, which suggests that the selenium and tellurium atoms are in identical environments.

Single-crystal X-ray diffraction revealed the formation of 12-membered macrocycles **1–4** where halogen atoms, which are stabilized by Te–X interactions, cap the macrocycle on both sides. The crystallographic data and selected metric parameters for **1**, **2**, **3**, and **4** are given in Tables 1 and 2. Macrocycles **1–4** crystallize in the triclinic space group *P*1̄

and are 12-membered rings that consist of a Te₄Se₂O₆ framework, which is built from two ditelluroxane units and two seleninate groups [Figure 1 (**1**) and Supporting Information, Figures S1 (**2**), S2 (**3**), and S3 (**4**)]. Charge neutralization for the dicationic macrocycle comes from the halide ions that are present above and below the macrocycle in a capping fashion held together by Te–X interactions. The average Te–X distances in **1**, **2**, **3**, and **4** are 3.380, 3.465, 3.688, and 3.362 Å, respectively, which fall in the range reported in the literature.^[7,16] The average Te–O distances of the ditelluroxane units in **1**, **2**, **3**, and **4** are 1.980(3), 1.977(2), 1.989(4), and 1.979(3) Å, respectively, which are slightly longer than those found in a sulfonate-based macrocycle^[4] and are almost similar to those found in ditelluroxane macrocycles based on phosphinate ligands.^[4,7] The Te–O–Te angles in **1**, **2**, **3**, and **4** are 123.88(2), 126.90(1), 122.15(2), and 126.70(13)°, respectively, and the O–Te–O angles are 168.12(1), 166.62(7), 168.43(2), and 166.95(10)°, respectively, which fall in the ranges reported in the literature.^[7,17] The average Se–O distances in **1**, **2**, **3**, and **4** are 1.678(4), 1.690(2), 1.690(4), and 1.683(3) Å, respectively, and the O–Se–O bond angles are between 105.5 and 107.7°. The Se–O distances are similar to those in an organotin seleninate ester^[12] and slightly shorter than those found in a Mn₇ cluster.^[11a]

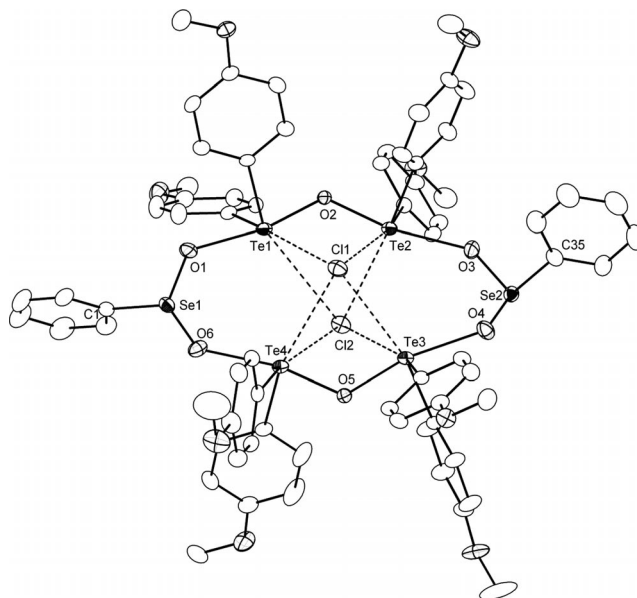


Figure 1. ORTEP representation of **1**. Thermal ellipsoids are shown at 30% probability.

The major change in the solid-state structures on going from Cl-capped **1** to Br-capped **2** and I-capped **3** is the orientation of the Se–Ph group, which changes dramatically with respect to the macrocyclic core (Figure 2). Investigating the torsion angles between the oxygen atoms bound to selenium (O1–Se1 and O6–Se1 in **1**) and the carbon atoms of the phenyl ring (C1–C2 and C1–C6 in **1**) led to interesting observations. The torsion angles in **1** for C2–C1⋯Se1–O1 and C2–C1⋯Se1–O6 are –100.3(5) and 151.8(4)°, which

fall in the range classified as *–syn-clinal* and *+anti-periplanar*, respectively. The torsion angles for the Se–O bond to the carbon atom of the ring on the other side (i.e. C1 and C6 in **1**) are $-26.6(5)$ ($C6-C1\cdots Se1-O6$) and $81.3(5)^\circ$ ($C6-C1\cdots Se1-O1$). In this case, the torsion angles fall in the range classified as *–syn-periplanar* and *+syn-clinal*, respectively. In **1**, as the entire macrocycle is present in the asymmetric unit, the torsion angles between the oxygen atoms bound to the second selenium atom ($O3-Se2$ and $O4-Se2$) and the carbon atoms of the phenyl ring ($C40-C35$ and $C36-C35$) differ from those that involve Se1, those that involve Se2 fall in the ranges classified as *+anti-clinal*, *–anti-clinal*, *+syn-clinal*, and *–syn-clinal*. In **2** and **3**, as only half of the macrocycle appears in the asymmetric unit, investigating the torsion angles of the oxygen atoms bound to selenium and the carbon atoms of the selenium-bound phenyl ring on one side of the macrocycle is sufficient to understand the orientation of the selenium-attached phenyl group with respect to the macrocycle. In **2**, the $C2-C1\cdots Se1-O1$ and $C2-C1\cdots Se1-O2$ torsion angles are $-70.8(3)$ and $178.5(3)^\circ$, which can be classified as *–syn-clinal* and *+anti-periplanar*, respectively. Although the torsion angles in **2** have the same classification as those of **1**, the values of the torsion angles themselves vary considerably (nearly 30°) compared with identical atoms in **1**. If one looks at the torsion angles of Se–O to the carbon atoms of the ring on the other side, the angles are $-4.3(3)$ ($C6-C1\cdots Se1-O2$) and $106.4(3)^\circ$ ($C6-C1\cdots Se1-O1$), respectively. Here, the torsions angles fall in the range classified as *–syn-periplanar* and *+anti-clinal*, respectively. In **3**, the $C2-C1\cdots Se1-O3$ and $C2-C1\cdots Se1-O1$ torsion angles are $-17.6(5)$ and $-124.8(5)^\circ$, which fall in the ranges classified as *–syn-periplanar* and *–anti-clinal*, respectively. In comparison with **1** and **2**, the classification of the torsion angles for similar atoms in **3** varies considerably. The torsion angles of the Se–O bond to the carbon atom of the ring on the other side are $57.9(5)$ ($C6-C1\cdots Se1-O1$) and $165.13(5)^\circ$ ($C6-C1\cdots Se1-O3$), which fall in the ranges classified as *+syn-clinal* and *+anti-periplanar*, respectively. These torsion angles and their classifications for **1**, **2**, and **3** indicate the dramatic change in the orientation of the selenium-bound phenyl group with respect to the macrocyclic ring (Figure 2).

This variation in the position of the Se atom and the subsequent orientation of the Se–Ph group to the macrocyclic core leads to the observation of interesting weak interactions in the solid state. In **2**, intramolecular $\pi-\pi$ stacking^[18] is observed between the phenyl ring attached to selenium with one of the aromatic rings attached to tellurium (Figure S4). Furthermore, an edge-to-face CH– π interaction^[19] between the tellurium-attached phenyl rings and benzene present as solvent of crystallization is also observed (Figure S4). The $\pi-\pi$ and edge-to-face CH– π bond lengths are 3.957 and 2.826 Å, respectively. Although the intramolecular $\pi-\pi$ stacking distance between the phenyl centroids (3.957 Å) in **2** is slightly greater than the sum of the van der Waals radii (3.800 Å), it can be considered as a weak $\pi-\pi$ interaction as the aromatic rings are attached to strong electron-withdrawing groups. The dihedral angle be-

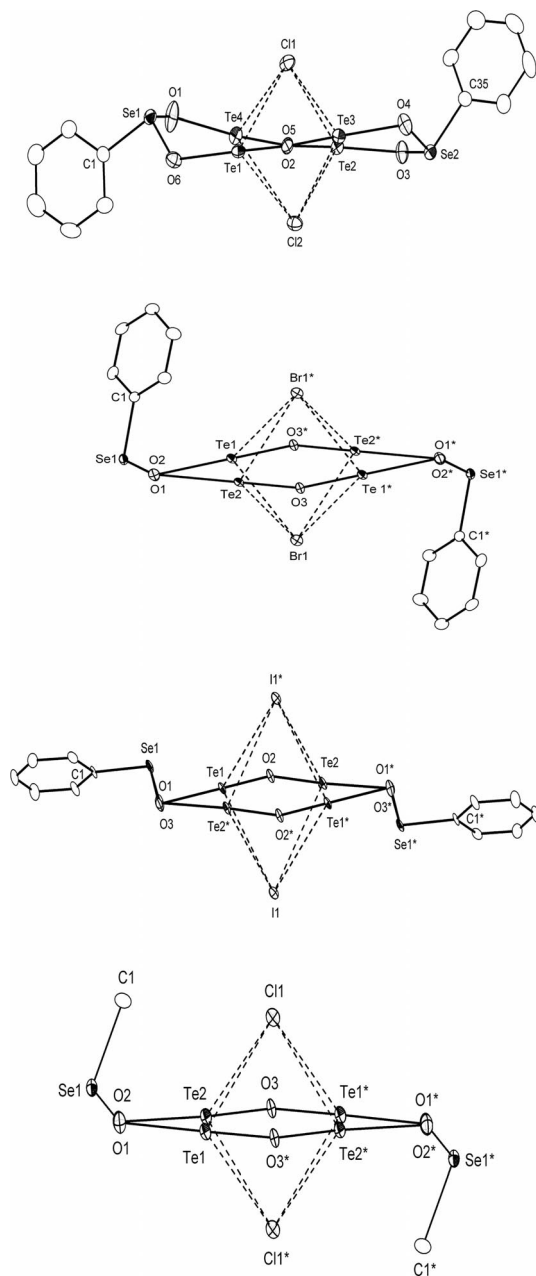


Figure 2. ORTEP representations of **1**, **2**, **3**, and **4**, which show the orientation of the Se–Ph (**1**, **2**, **3**) and Se–Me (**4**) bonds with respect to the macrocycle. Thermal ellipsoids are shown at 30% probability. Aromatic groups on tellurium atoms are omitted for clarity.

tween the two interacting aromatic ring planes is 16.51° , which is within the agreeable limits for the interaction to be considered as $\pi-\pi$ stacking.

The consequence of the variation in the orientation of the selenium-attached phenyl ring to the macrocycle leads to interesting intramolecular interactions, which result in the formation of a polymeric supramolecular structure in **3** (Figure 3). This arises from the Se– π interactions (3.508 Å), the distance of which is much less than the sum of the van der Waals radii (3.80 Å). Although Te– π interactions are well documented,^[20] Se– π interactions are rare.^[21] Hence, the supramolecular pattern observed in **3** is a rare example

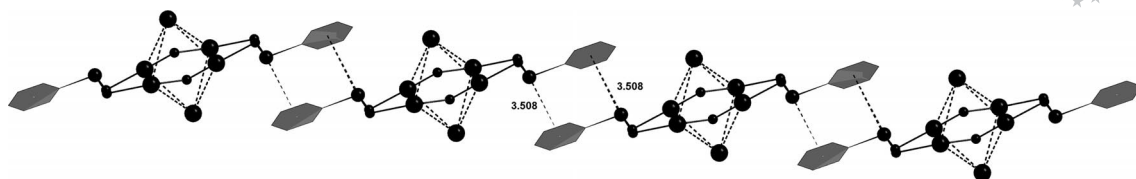


Figure 3. Supramolecular structure of **3**, which shows Se– π interactions.

of Se– π interactions between a tetravalent selenium to the π cloud of an aromatic ring. A recent report^[21b] on a systematic study of the interactions of divalent selenium with aromatic rings in small molecules states that, similar to well-known divalent sulfur–aromatic ring interactions, selenium–aromatic ring interactions can play an important role in complex formation between drug molecules that contain selenium atoms and protein active sites that contain aromatic side chains, which can facilitate drug delivery.

Conclusions

12-Membered macrocycles that consist of a $\text{Te}_4\text{Se}_2\text{O}_6$ framework have been isolated and structurally characterized. Halogen atoms, which are stabilized by Te–X interactions, cap both sides of the cationic macrocycle to provide charge neutrality. To the best of our knowledge, **1–4** are the first structurally characterized examples of compounds that contain both Te–O–Te and Se–O–Te units and hence belong to a unique class of macrocycles. Changing the protic acid from phosphinic to seleninic acid and changing the organic group on the selenium atom did not have any profound effect on the structure of the product on reaction with diorganotellurium dihalides, which is contrary to that observed with phosphinic acids. Interestingly, on going from **1** to **2** to **3** the spatial orientation of the phenyl group bound to selenium varies with respect to the macrocyclic ring because of the variation of the halogen and its steric and electronic requirements. The consequence of this structural variation is the formation of interesting weak interactions in the structures of **2** and **3** (intra- and intermolecular, respectively), whereas no such interactions are observed in that of **1**.

Experimental Section

Reagents and General Procedures: Tellurium tetrachloride, benzeneseleninic acid, and methaneseleninic acid were purchased from Sigma Aldrich Ltd. Solvents and other general reagents were purchased from commercial sources and purified according to standard procedures. Bis(*p*-methoxyphenyl)tellurium dihalide (*p*-OMeC₆H₄TeCl₂ or *p*-OMeC₆H₄TeBr₂) was synthesized according to a literature procedure.^[22]

Instrumentation: IR spectra were recorded with a JASCO-5300FT-IR spectrometer as KBr pellets. ¹H, ¹³C, ¹²⁵Te, and ⁷⁷Se NMR spectra were recorded with a Bruker AVANCE^{III} 400 instrument. Elemental analysis was performed with a Flash EA Series 1112 CHNS analyzer. Single-crystal X-ray diffraction data collection was car-

ried out at 100(2) K with a Bruker Smart Apex CCD area detector system [λ (Mo- K_α) = 0.71073 Å] with a graphite monochromator (see Tables 1 and 2). The data were reduced using SAINTPLUS, and the structures were solved using SHELXS-97^[23] and refined using SHELXL-97.^[24] All non-hydrogen atoms were refined anisotropically.

CCDC-840166 (for **1**), -840167 (for **2**), -840168 (for **3**), and -840169 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1 and 2: Benzeneseleninic acid and triethylamine were added to of benzene (15 mL), and the mixture was stirred for 5 min to obtain a clear solution. To this was added bis(*p*-methoxyphenyl)-tellurium dihalide (*p*-OMeC₆H₄TeCl₂ or *p*-OMeC₆H₄TeBr₂) and the solution immediately became turbid. Stirring was continued for 12 h. The solution was filtered to remove the triethylamine hydrochloride formed during the reaction. The filtrate was allowed to stand at room temperature for a week, and colorless block-like crystals were obtained.

[(*p*-OMeC₆H₄)₂Te]₂(μ -O)(μ -PhSeO₂)(μ -Cl)₂ (1**):** Following the procedure above, benzeneseleninic acid (0.15 g, 0.80 mmol), triethylamine (0.12 mL, 0.88 mmol), and bis(*p*-methoxyphenyl)tellurium dichloride (0.33 g, 0.80 mmol) afforded **1** [0.17 g, 46%, based on bis(*p*-methoxyphenyl)tellurium dichloride]. M.p. 150–152 °C. C₆₈H₆₆Cl₂O₁₄Se₂Te₄ (1846.49): calcd. C 44.23, H 3.60; found C 44.16, H 3.68. ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, 16 H), 7.37 (m, 10 H), 6.80 (d, 16 H), 3.80 (s, 24 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.18, 135.08, 130.78, 129.27, 128.78, 128.33, 125.90, 114.50, 55.32 ppm. ⁷⁷Se NMR (76.3 MHz, CDCl₃): δ = 1167.23 (s) ppm. ¹²⁵Te NMR (126.3 MHz, CDCl₃): δ = 1211.90 (s) ppm. IR (KBr): 3057.45 (w), 2930.14 (w), 1585.63 (s), 1564.41 (m), 1493.04 (s), 1452.53 (m), 1292.42 (s), 1253.84 (s), 1178.61 (s), 1057.09 (m), 1020.44 (m), 823.68 (m), 788.96 (m), 748.45 (m), 659 (w), 513.11 (m), 476 (m) cm^{−1}.

[(*p*-OMeC₆H₄)₂Te]₂(μ -O)(μ -PhSeO₂)(μ -Br)₂·2C₆H₆ (2**):** Following the procedure above, benzeneseleninic acid (0.15 g, 0.80 mmol), triethylamine (0.12 mL, 0.88 mmol), and bis(*p*-methoxyphenyl)tellurium dibromide (0.40 g, 0.80 mmol) afforded **2** [0.22 g, 53% based on bis(*p*-methoxyphenyl)tellurium dibromide]. M.p. 230–232 °C. C₆₈H₆₆Br₂O₁₄Se₂Te₄ (1935.39): calcd. C 42.20, H 3.43; found C 42.31, H 3.38. ¹H NMR (400 MHz, CDCl₃): δ = 7.78 (d, 16 H), 7.42 (m, 5 H), 7.20 (m, 5 H), 6.76 (d, 16 H), 3.79 (s, 24 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.88, 135.96, 130.73, 129.29, 128.75, 128.34, 125.98, 114.03, 55.25 ppm. ⁷⁷Se NMR (76.3 MHz, CDCl₃): δ = 1167.86 (s) ppm. ¹²⁵Te NMR (126.3 MHz, CDCl₃): δ = 1196.33 (s) ppm. IR (KBr): 3063.24 (w), 2943.64 (w), 2831.76 (m), 1585.63 (s), 1575.98 (m), 1493.04 (s), 1460.25 (m), 1439.03 (m), 1402.38 (m), 1294.35 (s), 1253.84 (s), 1176.68 (s), 1059.02 (m), 1020.44 (m), 821.75 (m), 788.96 (m), 748.45 (w), 653.93 (w), 515.04 (s), 480.32 (w), 441.74 (s) cm^{−1}.

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **2**, **3**, and **4**.

1		2		3		4	
Te(1)–O(1)	2.329(4)	Te(1)–O(1)	2.2976(2)	Te(1)–O(1)	2.357(4)	Te(1)–O(1)	2.283(3)
Te(1)–O(2)	1.982(3)	Te(1)–O(3)*	2.0067(2)	Te(1)–O(2)	1.989(4)	Te(1)–O(3)#	1.994(3)
Te(1)–C(7)	2.124(5)	Te(1)–C(7)	2.110(3)	Te(1)–C(7)	2.102(6)	Te(1)–C(2)	2.110(4)
Te(1)–C(14)	2.136(5)	Te(1)–C(14)	2.107(3)	Te(1)–C(14)	2.100(6)	Te(1)–C(9)	2.121(4)
Te(2)–O(2)	1.994(3)	Te(2)–O(2)	2.506(2)	Te(2)–O(2)	1.989(4)	Te(2)–O(2)	2.409(3)
Te(2)–O(3)	2.348(4)	Te(2)–O(3)	1.9477(2)	Te(2)–O(3)*	2.349(4)	Te(2)–O(3)	1.964(3)
Te(2)–C(21)	2.126(5)	Te(2)–C(21)	2.112(3)	Te(2)–C(21)	2.113(6)	Te(2)–C(16)	2.112(4)
Te(2)–C(28)	2.131(5)	Te(2)–C(28)	2.113(3)	Te(2)–C(28)	2.119(6)	Te(2)–C(23)	2.126(4)
Te(3)–O(4)	2.342(4)	Se(1)–O(1)	1.7101(2)	Se(1)–O(1)	1.689(4)	Se(1)–O(1)	1.689(3)
Te(3)–O(5)	1.975(3)	Se(1)–O(2)	1.671(2)	Se(1)–O(3)	1.691(4)	Se(1)–O(2)	1.677(3)
Te(3)–C(41)	2.132(5)	Se(1)–C(1)	1.937(3)	Se(1)–C(1)	1.925(6)	Se(1)–C(1)	1.928(4)
Te(3)–C(48)	2.108(5)	O(1)–Te(1)–O(3)*	165.12(7)	O(1)–Te(1)–O(2)	168.84(2)	O(3)#–Te(1)–O(1)	164.48(1)
Te(4)–O(5)	1.970(3)	C(7)–Te(1)–C(14)	94.45(1)	C(7)–Te(1)–C(14)	95.0(2)	C(2)–Te(1)–C(9)	99.65(2)
Te(4)–O(6)	2.361(4)	O(2)–Te(2)–O(3)	168.12(7)	O(2)–Te(2)–O(3)*	168.02(2)	O(2)–Te(2)–O(3)	169.43(1)
Te(4)–C(55)	2.106(5)	C(21)–Te(2)–C(28)	93.99(1)	C(21)–Te(2)–C(28)	94.6(2)	C(16)–Te(2)–C(23)	93.95(2)
Te(4)–C(62)	2.112(5)	O(1)–Se(1)–O(2)	107.77(1)	O(1)–Se(1)–O(3)	105.5(2)	O(1)–Se(1)–O(2)	107.04(1)
Se(1)–C(1)	1.938(5)	C(1)–Se(1)–O(1)	100.04(1)	C(1)–Se(1)–O(1)	98.8(2)	C(1)–Se(1)–O(1)	100.12(2)
Se(1)–O(1)	1.677(4)	C(1)–Se(1)–O(2)	101.89(1)	C(1)–Se(1)–O(3)	98.7(2)	C(1)–Se(1)–O(2)	101.49(2)
Se(1)–O(6)	1.681(4)	Se(1)–O(1)–Te(1)	124.77(1)	Se(1)–O(1)–Te(1)	110.62(2)	Se(1)–O(1)–Te(1)	125.50(1)
Se(2)–C(35)	1.920(5)	Se(1)–O(2)–Te(2)	135.98(1)	Te(1)–O(2)–Te(2)	122.15(2)	Se(1)–O(2)–Te(2)	129.82(1)
Se(2)–O(3)	1.668(4)	Te(2)–O(3)–Te(1)*	126.90(1)	Se(1)–O(3)–Te(2)*	113.6(2)	Te(2)–O(3)–Te(1)#	126.70(1)
Se(2)–O(4)	1.688(4)						
O(1)–Te(1)–O(2)	169.20(1)						
C(7)–Te(1)–C(14)	96.73(2)						
O(2)–Te(2)–O(3)	167.57(1)						
C(21)–Te(2)–C(28)	96.72(2)						
O(4)–Te(3)–O(5)	167.60(1)						
C(41)–Te(3)–C(48)	97.32(2)						
O(5)–Te(4)–O(6)	168.11(1)						
C(55)–Te(4)–C(62)	99.91(2)						
C(1)–Se(1)–O(1)	101.4(2)						
C(1)–Se(1)–O(6)	98.4(2)						
O(1)–Se(1)–O(6)	105.7(2)						
C(35)–Se(2)–O(3)	100.2(2)						
C(35)–Se(2)–O(4)	98.5(2)						
O(3)–Se(2)–O(4)	107.45(2)						
Te(1)–O(1)–Se(1)	130.7(2)						
Te(1)–O(2)–Te(2)	123.69(2)						
Te(2)–O(3)–Se(2)	143.7(2)						
Te(3)–O(4)–Se(2)	126.32(2)						
Te(3)–O(5)–Te(4)	124.07(2)						
Te(4)–O(6)–Se(1)	124.31(2)						

Symmetry transformations used to generate equivalent atoms, *: $1 - x, 1 - y, 1 - z$; #: $1 - x, 2 - y, 1 - z$.

[(*p*-OMeC₆H₄)₂Te]₂(μ-O)(μ-PhSeO₂)(μ₄-I)₂·7C₆H₆ (3**):** Sodium iodide (0.008 g, 0.053 mmol) was added to a solution of **1** (0.052 g, 0.028 mmol) in benzene (15 mL), which was stirred for 24 h. The solution became orange-yellow. The mixture was filtered, and the filtrate was allowed to stand at room temperature to afford colorless block-like crystals. Yield: 0.05 g (69% based on **1**). M.p. 216–218 °C. C₆₈H₆₆I₂O₁₄Se₂Te₄ (2029.39): calcd. C 40.24, H 3.27; found C 40.14, H 3.32. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (m, 16 H), 7.24 (m, 10 H), 6.78 (d, 16 H), 3.80 (s, 24 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.87, 136.26, 131.51, 130.97, 129.19, 128.93, 126.00, 113.96, 55.26 ppm. ⁷⁷Se NMR (76.3 MHz, CDCl₃): δ = 1166.72 (s) ppm. ¹²⁵Te NMR (126.3 MHz, CDCl₃): δ = 1182.96 (s) ppm. IR (KBr): 3065.3 (w), 2959.92 (w), 2932.95 (w), 2835.62 (m), 1584.43 (m), 1567.74 (s), 1492.05 (s), 1493.30 (s), 1438.85 (m), 1293.72 (s), 1252.76 (s), 1177.32 (s), 1088.85 (w), 1060.34 (m), 1022.90 (m), 821.63 (s), 788.72 (m), 749.20 (w), 649.54 (w), 588.00 (m), 506.23 (m), 477.60 (w) cm⁻¹.

[(*p*-OMeC₆H₄)₂Te]₂(μ-O)(μ-MeSeO₂)(μ₄-Cl)₂·2C₆H₆ (4**):** Methaneseleninic acid (0.123 g, 0.968 mmol) and triethylamine (0.15 mL, 1.08 mmol) were added to methanol (15 mL), and the mixture was stirred for 5 min to obtain a clear solution. To this was added bis(*p*-methoxyphenyl)tellurium dichloride (0.400 g, 0.968 mmol), and the solution was warmed to obtain a clear solution. Stirring was continued at room temperature for 12 h. The solution was filtered and the solvent removed from the filtrate under reduced pressure to obtain a white solid. This solid was dissolved in benzene, and the solution was filtered to remove triethylamine hydrochloride. The filtrate allowed to stand at room temperature for 2 days to afford colorless block-like crystals of **4** [0.23 g, 55% based on bis(*p*-methoxyphenyl)tellurium dichloride]. M.p. 180–182 °C. C₅₈H₆₂Cl₂O₁₄Se₂Te₄ (1722.35): calcd. C 40.45, H 3.63; found C 40.35, H 3.68. ¹H NMR (400 MHz, CDCl₃): δ = 7.8 (d, 16 H), 6.8 (d, 16 H), 3.8 (s, 24 H), 2.2 (s, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.00, 135.75, 128.34, 114.26, 55.29, 40.99

Table 2. Crystallographic data for **1**, **2**, **3**, and **4**.

	1	2	3	4
Formula	C ₆₈ H ₆₆ Cl ₂ O ₁₄ Se ₂ Te ₄	C ₉₂ H ₉₀ Br ₂ O ₁₄ Se ₂ Te ₄	C ₁₁₀ H ₁₀₈ I ₂ O ₁₄ Se ₂ Te ₄	C ₇₀ H ₇₄ Cl ₂ O ₁₄ Se ₂ Te ₄
<i>f</i> _w	1846.43	2247.78	2576.08	1878.51
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Crystal size [mm]	0.18 × 0.16 × 0.10	0.20 × 0.16 × 0.12	0.20 × 0.16 × 0.12	0.16 × 0.16 × 0.10
<i>a</i> [Å]	13.943(3)	13.400	13.466	10.958
<i>b</i> [Å]	15.726(3)	13.813	14.102	11.839
<i>c</i> [Å]	17.826(3)	13.964	15.170	14.670
<i>α</i> [°]	83.057(3)	105.21	91.41	107.63
<i>β</i> [°]	69.493(3)	100.85	115.60	94.69
<i>γ</i> [°]	67.539(2)	113.06	93.75	104.30
<i>V</i> [Å ³]	3382.8(10)	2168.1	2588.0	1732.1
<i>Z</i>	2	1	1	1
<i>d</i> _{calcd.} [Mg m ⁻³]	1.813	1.722	1.653	1.801
<i>μ</i> [mm ⁻¹]	2.926	3.156	2.477	2.859
<i>F</i> (000)	1792	1100	1262	916.0
<i>θ</i> range for data collection [°]	1.22 to 25.12	1.60 to 25.02	1.45 to 25.07	1.48 to 25.13
Reflections collected/unique	32316/11937	14953/7568	24560/9119	16845/6127
<i>R</i> (int.)	0.0533	0.0198	0.0548	0.0476
Data/restraints/parameters	11937/0/819	7568/0/518	9119/0/599	6127/0/420
GoF on <i>F</i> ²	0.987	1.087	1.023	1.013
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0411/0.0988	0.0248/0.0646	0.0507/0.1290	0.0338/0.0756
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0535/0.1057	0.0268/0.0656	0.0630/0.1367	0.0400/0.0785
largest diff peak/hole [e Å ⁻³]	2.083/−1.377	0.831/−1.105	2.829/−2.074	1.072/−0.525

ppm. ⁷⁷Se NMR (76.3 MHz, CDCl₃): δ = 1182.04 (s) ppm. ¹²⁵Te NMR (126.3 MHz, CDCl₃): δ = 1182.01 (s) ppm. IR (KBr): 3067.09 (w), 2934.00 (w), 2833.69 (w), 1585.63 (m), 1493.04 (s), 1460.25 (w), 1400.45 (m), 1292.42 (s), 1249.99 (s), 1176.68 (s), 1060.94 (w), 1022.36 (m), 873.83 (w), 823.68 (s), 787.03 (m), 750.38 (m), 671.29 (m), 588.34 (w), 511.18 (s), 439.81 (m) cm⁻¹.

Supporting Information (see footnote on the first page of this article): Molecular structures of **2**, **3**, and **4**, π–π stacking and edge-to-face CH–π interactions in the structure of **2**.

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From an Octakis(3-cyanopropyl)silsesquioxane Building Block to a Highly COOH-Functionalized Hybrid Organic–Inorganic Material

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Keywords: Organic–inorganic hybrid composites / Sol-gel processes / Hydrogen bonds / Ion chelation / Nanostructures / Silsesquioxanes / Silicon / Solid-state NMR spectroscopy

A new nanostructured and highly COOH-functionalized hybrid organic–inorganic material has been synthesized by the hydrolysis of oligomeric octahedral silsesquioxane (POSS), which contains eight cyanopropyl groups. The hybrid, elemental building block oligomeric octakis(3-cyanopropyl)silsesquioxane (**CN-POSS**) was synthesized from oligomeric octakis(3-chloropropyl)silsesquioxane (**Cl-POSS**) by an exchange reaction. The formation and nanostructuring of the COOH-functionalized hybrid material were induced by non-covalent hydrogen bonding between **COOH-POSS** units without decomposition of the core. The material has been fully characterized by scanning electron microscopy, FTIR

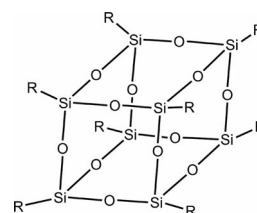
and ^1H , ^{13}C , and ^{29}Si solid-state NMR spectroscopy, X-ray diffraction, and elemental analysis, which confirm that the POSS core remains intact after each chemical modification step. Thermogravimetric analysis indicates that the organic units are thermally stable up to 200 °C. The activation energy related to the proton conductivity of **COOH-POSS** has been evaluated and confirms the presence of strong hydrogen bonds. Finally, the accessibility and adsorption capacity of the COOH groups towards transition metal ions have been demonstrated and underline the potential of these hybrid materials in extraction chemistry.

Introduction

The development of new nanostructured materials based on the self-assembly of well-defined molecular building blocks represents a very exciting research field.^[1] Nanomaterials have potential applications in a myriad of fields, such as biomedical or optoelectronic applications.^[2] The rational design of the molecular building blocks (geometry, functional units, etc) offers new pathways to tune the structure and the properties of the final material. In this context, the supramolecular approach, which exploits molecular recognition processes based on a wide variety of intermolecular interactions (π – π stacking, hydrogen bonding, halogen bonding, and metal–ligand coordination), can lead to the organization of these individual molecules (building blocks) into controlled macroscopic systems.^[3]

Based on this approach, our group has developed a large number of hybrid organic–inorganic materials prepared from molecular precursors (organosilanes) by using the hydrolytic sol–gel process.^[4,5,6] This sol–gel process, which

consists of inorganic polymerization of molecular precursors under mild chemical conditions, is a very convenient pathway for this approach.^[7] This process is totally compatible with all types of organic or inorganic units (molecules, complexes, polymers, biochemicals, and even biological units),^[8] which opens a wide range of possible applications. We have recently reported the synthesis of self-organized hybrid organic–inorganic materials and their potential applications for extraction chemistry due to their excellent chelating properties towards transition metals.^[5,9] These excellent properties were attributed to the high local organization of the hybrid material. In continuation of these studies, we have focused our attention on polyhedral oligomeric silsesquioxanes (POSS), especially the octameric silsesquioxane $\text{R}_8(\text{SiO}_{1.5})_8$ -based hybrid materials. Due to its unique eightfold symmetry and rigid cubic-structure, POSS that bears eight corner groups (T_8) has attracted a great deal of interest (Scheme 1).^[10]



Scheme 1. Octameric silsesquioxane unit.

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The organization of the eight ligands in a spherical environment, which can be fine-tuned by changing the nature of the organic spacer, offers the opportunity for POSS to act as a nanobuilding block. Thus, a vast number of polyhedral frameworks have been synthesized, which cover a wide range of applications such as electronic materials,^[11] catalysts,^[12] heat resistant materials,^[13] molecular machines,^[14] and biomedicines.^[15]

Herein, we described a new type of COOH-functionalized organic–inorganic hybrid material based on oligomeric octapropionic acid silsesquioxane (**COOH-POSS**). Although a wide variety of octasilsesquioxanes derivatives have been developed, carboxylic-functionalized T₈ compounds are still scarce.^[16] The interest in carboxylic acid stems from the finding that this group is one of the most important motifs used in crystal engineering for the self-assembly of organic molecular building blocks.^[17] As expected, **COOH-POSS** self-assembled into a nanostructured material through the in situ formation of strong hydrogen bonds between the COOH groups during the hydrolysis of the CN units. The low proton mobility of the material has been confirmed by conductivity measurements. Finally, the chelating ability of the sodium salt of this hybrid material (**COONa-POSS**) towards transition metal ions has been examined from aqueous solutions for potential applications in extraction chemistry.

Results and Discussion

Oligomeric octakis(3-chloropropyl)silsesquioxane (**Cl-POSS**) was obtained by hydrolysis and polycondensation of 3-chloropropyltrimethoxysilane in methanol under acidic conditions in 30% yield (Scheme 2). Treatment of **Cl-POSS** with a large excess of NaCN in the presence of a catalytic amount of 18-crown-6 in acetonitrile afforded oligomeric octakis(3-cyanopropyl)silsesquioxane (**CN-POSS**) in 98% yield after purification (Scheme 2). **CN-POSS** was fully characterized by ¹H, ¹³C{¹H}, and ²⁹Si{¹H} magic angle spinning (MAS) NMR and IR spectroscopy, thermogravimetric analysis (TGA), and elemental analysis. The charac-

teristics of **CN-POSS** obtained by this method are very similar to those of the material obtained by hydrosilylation of H₈O₁₂Si₈.^[18]

The hydrolysis of the nitrile groups in **CN-POSS** was achieved quantitatively in the presence of sulfuric acid (Scheme 2), which led to **COOH-POSS** as a white powder. To verify the stability of the framework of the T₈ structure under these acidic conditions, **Cl-POSS** was treated with 9 M H₂SO₄ as described above. The recovered solid remained soluble in MeCN, acetone, and CHCl₃. Analysis by NMR spectroscopy and MALDI-TOF MS, and the narrow polydispersity (*M_n* = 946, *M_w*/*M_n* = 1.01) of the gel permeation chromatography (GPC) profile of **Cl-POSS** after this acidic treatment confirm unambiguously that no decomposition of the POSS core occurs (see Supporting Information for the GPC profile, Figure S1). Indeed, cage decomposition, scrambling, and rearrangement have mostly been reported under basic rather than acidic conditions.^[19]

TGA of **CN-POSS** and **COOH-POSS** were conducted from 25–800 °C under air (Figure 1). The progressive weight losses assigned to the decomposition of the organic groups are around 50% for **CN-POSS** and 60% for

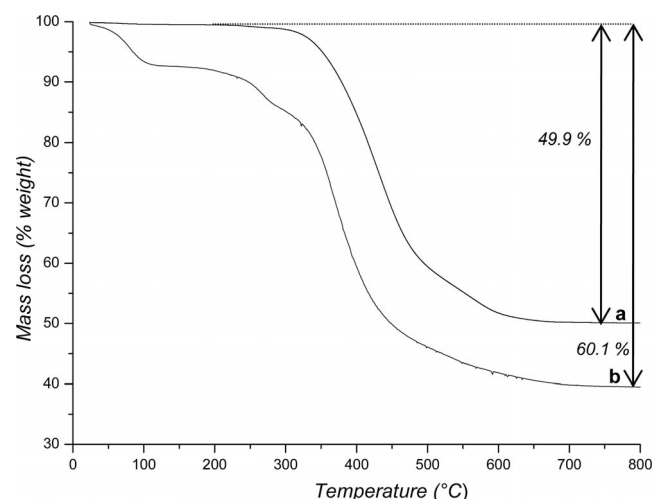
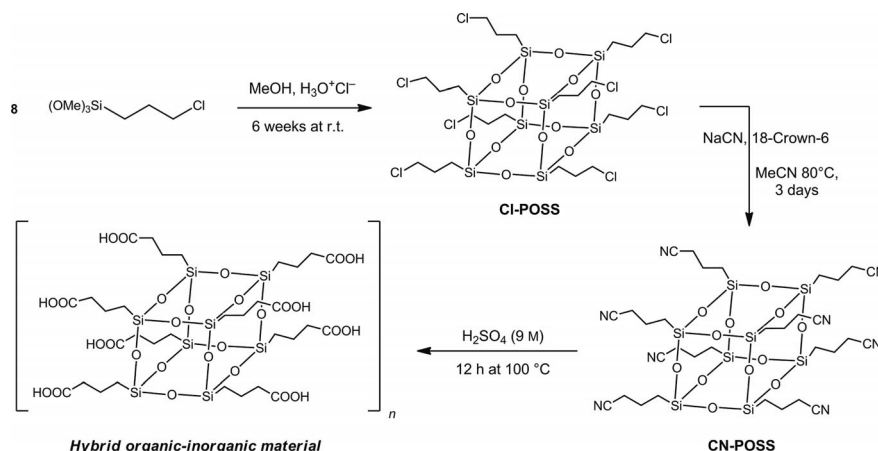


Figure 1. TGA curves of **CN-POSS** (a) and **COOH-POSS** (b).



Scheme 2. Preparation of **Cl-POSS**, **CN-POSS**, and **COOH-POSS**.

COOH-POSS. These values are close to the theoretical values (56% for **CN-POSS** and 63% for **COOH-POSS**) and in agreement with the results of the elemental analysis.

COOH-POSS is not soluble in any solvent even at high temperature. Thus, **COOH-POSS** was characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ MAS NMR spectroscopy. The POSS scaffold is ideal for characterization by NMR spectroscopy using the three standard nuclei (^1H , ^{13}C , ^{29}Si) as, due to the symmetry of the entire structure, all eight silicon centers and the eight organic chains become equivalent to each other and yield a simple set of unique signals. The ^{29}Si cross-polarization (CP)-MAS NMR spectrum of **COOH-POSS** revealed the presence of one peak (Figure 2) at -68 ppm, which is attributed to T_3 [$\text{CSi}(\text{OSi})_3$] substructures. The absence of a resonance at around -100 ppm, which corresponds to Q substructures, denotes that no cleavage of the Si-C bonds occurred during hydrothermal treatment.

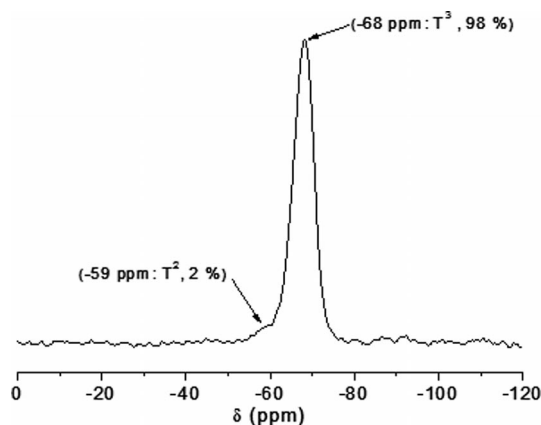


Figure 2. ^{29}Si single-pulse solid-state NMR spectrum of dry **COOH-POSS**.

The ^{13}C CP-MAS NMR spectrum of **COOH-POSS** shows that the organosiloxane units remain intact. Three signals (13, 19, and 37 ppm) are assigned to the propyl spacer and that at 180 ppm is attributed to the carbonyl resonances of the carboxylic acid groups (Figure 3). The absence of a peak at 120 ppm unambiguously demonstrates

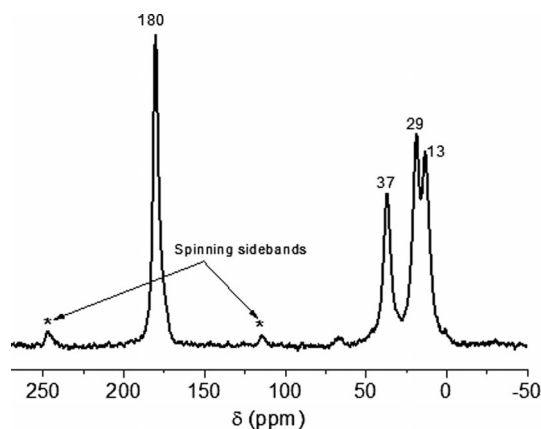


Figure 3. ^{13}C CP-MAS solid state NMR spectrum of dry **COOH-POSS**.

the complete hydrolysis of the nitrile groups.^[20,21,22] The weak signal at around 60 ppm could be due to an esterification reaction between the COOH groups and EtOH (washing solvent).

The ^1H MAS NMR spectrum of **COOH-POSS**, which was obtained at a spinning rate of 40 kHz, is presented in Figure 4 (a). From this spectrum, all the protons present in **COOH-POSS** could be established. Four signals can be clearly distinguished at 0.84, 1.81, 2.32, and 10.20 ppm. The first three peaks correspond to protons of the propyl chain and can be attributed to $\text{SiCH}_2\text{CH}_2-$, $\text{SiCH}_2\text{CH}_2\text{CH}_2-$, and $\text{SiCH}_2\text{CH}_2\text{CH}_2-$, respectively. The resolved peak at 10.20 ppm is assigned to the acidic proton of the COOH groups. A shift to low field is well-known when strong hydrogen bonding interactions exist.^[23] Thus, the peak at 10.20 ppm indicates that the COOH end groups self-assemble into hydrogen bonded pairs. In addition, no signals from residual water (at around 5 ppm)^[24] were observed. This observation is in good agreement with previous work that demonstrated that dehydration of a sample could be achieved by rapid sample rotation in a solid-state NMR probe.^[23a]

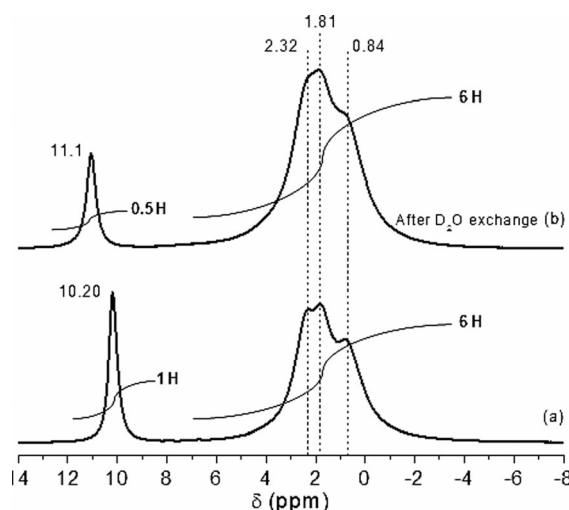


Figure 4. ^1H single-pulse solid-state NMR spectra of **COOH-POSS** before (a) and after D_2O exchange (b). Spinning speed: 40 kHz.

The composition of **COOH-POSS** was also inferred from the results of C, H, and Si elemental analysis. The amounts of C, H, and Si were found to be close to theoretical values, which confirms the integrity of the POSS core. In addition, the absence of nitrogen indicates the complete hydrolysis of the cyano groups.

The formation of COOH groups was further confirmed by FTIR spectroscopy. The IR spectrum of **COOH-POSS** exhibits an intense band at 1703 cm^{-1} , which is assigned to the stretching vibration of the C=O bonds of the carboxylic acid groups. An intense, broad band between 3250 and 2900 cm^{-1} , which corresponds to OH stretching vibrations, was also observed (Figure S2). Moreover, no absorbance in the region around 2243 cm^{-1} , which is characteristic of nitrile groups, was discerned in the IR spectrum. This unam-

biguously indicates that the acid hydrolysis of the nitrile groups was complete.

The peak observed at 1703 cm^{-1} for the $\text{C}=\text{O}$ bonds is lower than that expected (1740 cm^{-1}) for free COOH groups.^[25] This diminution can be explained by the formation of hydrogen bonds in **COOH-POSS**. This type of hydrogen bonding has already been noted for lamellar hybrid materials obtained by self-assembly.^[26] All these observations can be interpreted by the formation of a 3D network through noncovalent hydrogen bonding interactions between the carboxylic acid groups of different **COOH-POSS** units (Scheme 3).

The strength of the hydrogen bonds was evaluated by proton–deuterium exchange of the COOH groups. Treatment of **COOH-POSS** with D_2O at room temperature led to the replacement of 50% of protons by D after 30 min (Figure 4b).

In order to see whether the modification of the cubes changes the surface and to determine the morphologies of materials at microscopic scale, scanning electron microscopy (SEM) measurements were performed on **CN-POSS** and **COOH-POSS**. The SEM images show that the compounds have very different morphologies and surfaces. Large particles with dimensions of several micrometers were observed for **CN-POSS** (Figure 5 A), and an aggregation of small ($1\text{ }\mu\text{m}$), homogeneous particles were observed for **COOH-POSS** (Figure 5, B). This aggregation was confirmed by nitrogen adsorption measurements that indicate a Brunauer–Emmett–Teller surface area about $20\text{ m}^2\text{ g}^{-1}$ for **COOH-POSS** (Figure S3) and $0\text{ m}^2\text{ g}^{-1}$ for **CN-POSS**.

The XRD pattern for **CN-POSS** (Figure 6) exhibits a low-angle diffraction peak at $q = 5.81\text{ nm}^{-1}$, which corresponds to a d -spacing of $10.8\text{ }\text{\AA}$.^[27] This distance is characteristic of the diameter of octafunctional octasilsesquioxanes.^[28] The weak peak observed at $q = 16.50\text{ nm}^{-1}$, which

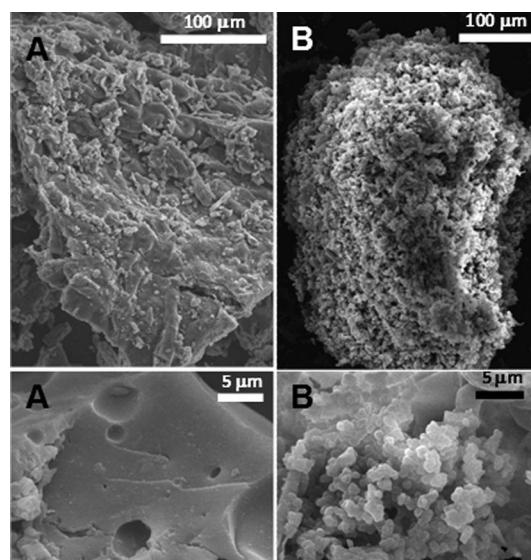
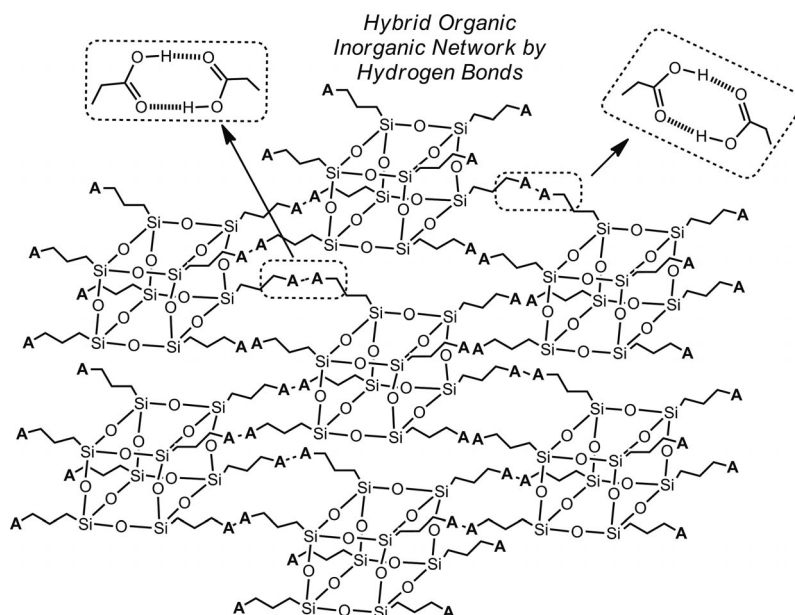


Figure 5. SEM images of **CN-POSS** (A) and **COOH-POSS** (B).

corresponds to $3.8\text{ }\text{\AA}$, can be attributed to the siloxane bonds of the POSS core.^[29,30] Interestingly, the XRD pattern of **COOH-POSS** (Figure 6) showed that the structure is less ordered in comparison to that of **CN-POSS**, with a diffraction peak at $q = 5.47\text{ nm}^{-1}$ and a d -spacing of $11.5\text{ }\text{\AA}$. This shift ($0.7\text{ }\text{\AA}$) can be explained by the increase of the size of the octameric units.

The conductivity properties of **COOH-POSS** were assessed by complex impedance spectroscopy (CIS). Figure 7 illustrates the Arrhenius diagram for the dc conductivity of **COOH-POSS**, which is the semilogarithmic plot of the dc conductivity vs. the inverse absolute temperature. The dc conductivity values were extracted from the dc plateau of



Scheme 3. Illustration of **COOH-POSS**.

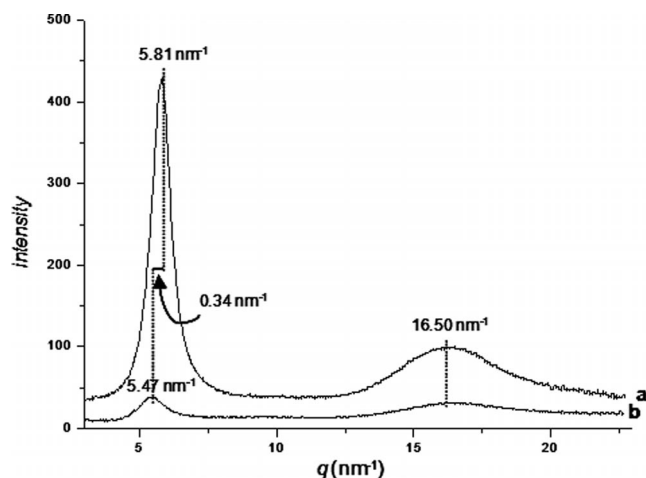
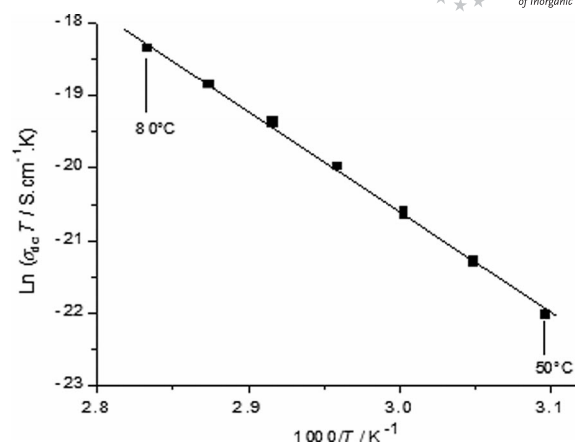


Figure 6. XRD patterns of CN-POSS (a) and COOH-POSS (b).

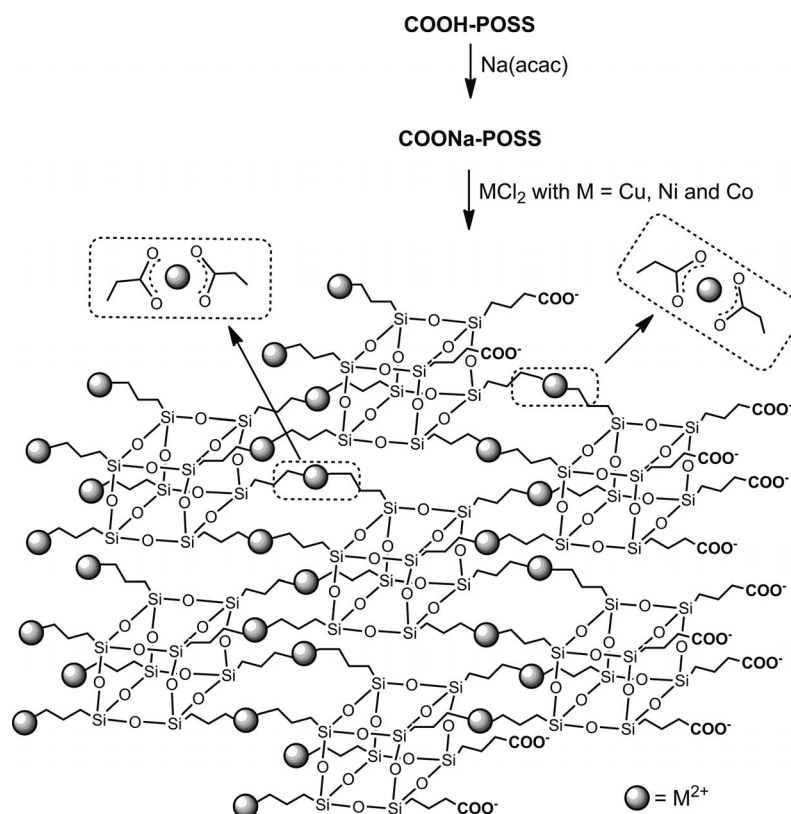
the global conductivity signal (Figure S4). The conductivity is likely to correspond to long-range redistribution or diffusion of protons that arise from the COOH groups. The relatively low values of the *dc* conductivity indicate that **COOH-POSS** is poorly conductive. This unusual behavior may be explained by the low mobility of the protons. According to Equation (1), the Arrhenius plot gives the activation energy (E_a) of the conductivity process:

$$\sigma_{dc} = (\sigma_0/T) \exp(-E_a/kT)$$

Figure 7. $\ln(\sigma_{dc} \times T)$ vs. $1000/T$ for dry COOH-POSS in the range 50–80 °C.

where σ_{dc} is direct current (*dc*) conductivity at a given temperature (T), σ_0 is *dc* conductivity at infinite temperature, k is the Boltzmann constant, and T is the temperature. E_a corresponds to the activation energy required for the creation of the proton charge carrier followed by its migration from its trapping site to another site. In the case of **COOH-POSS**, the so-obtained E_a value is 1.20 eV, which is high compared to those reported for dehydrated proton-conducting membranes ($0.40 < E_a$ [eV] < 0.85 eV).^[31,32]

This result suggests that protons in **COOH-POSS** are strongly confined to the hosting sites of the functionalized

Scheme 4. Schematic representation of **COOM-POSS** after ion-exchange.

POSS. This behavior corresponds fairly well with the existence of strong hydrogen bonds between the carboxylic acid groups of the different **COOH-POSS** units as highlighted by the FTIR data.

Finally, the accessibility of the carboxylic acid groups in **COOH-POSS** and their ion-exchange behavior were investigated. Direct transition metal ion uptake by **COOH-POSS** was attempted but failed. Therefore, to study the chelating ability of this material towards transition metal ions, the carboxylic acid groups were deprotonated and sodium carboxylate salts were formed, which would be expected to serve as binding sites for various cations. **COOH-POSS** was easily transformed into **COONa-POSS** by treatment with sodium acetylacetonate in ethanol at 25 °C (Scheme 4).

This exchange reaction was confirmed by energy dispersive spectroscopy (EDS). In fact, the Na/Si molar ratio was found to be 0.97, which is very close to the theoretical ratio (1) and indicates that the COOH groups were accessible. The ^{29}Si MAS NMR spectrum of **COONa-POSS** showed only one peak at -67.7 ppm and the absence of signals in the Q region, which indicated that the treatment did not affect the siloxane bonds in the POSS cage (Figure S5).

The chelating ability of **COONa-POSS** was tested towards copper, cobalt, and nickel salts. **COONa-POSS** was treated with aqueous solutions of CuCl_2 , CoCl_2 , and NiCl_2 at room temperature for 10 h (Scheme 4). The resulting solids were collected by filtration and washed with water to eliminate any uncomplexed salts, which led to **COOM-POSS** ($M = \text{Cu}, \text{Co}, \text{and Ni}$) hybrid materials. **COOCu-POSS**, **COOCu-POSS**, **COONi-POSS** were obtained as blue, purple, and green powders, respectively. The content of the transition metal ions was estimated by EDS. The M/Si molar ratios were found to be 0.48, 0.49, and 0.48, respectively, which revealed the incorporation of one M^{2+} per two carboxylate units as expected. In addition, for all the materials after chelation, the sodium content in **COOM-POSS** was found to be very low (< 50 ppm), which shows that all the carboxylate groups were operative.

Conclusions

Organic–inorganic hybrid materials that were highly functionalized with carboxylic acid groups were synthesized by hydrolysis of the CN groups of polyhedral oligomeric silsesquioxane (POSS), which contains eight cyanopropyl groups, and its molecular structure was fully characterized. We showed that this material was constituted by the association of several units of POSS that are connected by hydrogen bonds. The presence of these bonds was evidenced by ^1H MAS NMR and IR spectroscopy and the high activation energy of the proton conductivity process. Furthermore, **COONa-POSS** was proved to be highly efficient in the chelation of transition metal ions, which could be of particular interest for ion separation and sequestration.

Experimental Section

General Procedures: All reactions were carried out under air. (3-Chloropropyl)trimethoxysilane, NaCN, and 18-crown-6 were purchased from Aldrich and used as supplied.

Characterization: Solid-state NMR spectra for ^{29}Si and ^{13}C were recorded with a Varian VNMRs 300 Solid spectrometer at 7.05 T. A 7.5 mm MAS probe was used with a spinning rate of 5 kHz. Single-pulse experiments with continuous-wave ^1H decoupling were used for ^{29}Si NMR spectroscopy, with a $2\ \mu\text{s}\ \pi/2$ pulse duration, and a recycle delay of 60 s. A recycle delay of 200 s was found necessary to allow full ^{29}Si relaxation, although this did not lead to any change in the relative ratios of the individual components on spectral decomposition. Thus, data with recycle delay of 60 s can be considered as quantitative. For ^{13}C NMR spectroscopy, CP MAS experiments with a continuous-wave ^1H decoupling were acquired with 5 s recycle, $5\ \mu\text{s}\ \pi/2$ (^1H) pulse duration, and 3 ms contact time. The ^{29}Si and ^{13}C nuclei were referenced to SiMe_4 at 0 ppm. ^1H NMR spectra were recorded with a Varian VNMRs 600 (14.1 T) Solid spectrometer. A 1.6 mm MAS probe was used for ^1H nuclei with a spinning rate of 40 kHz. Single-pulse experiments were also used for ^1H nuclei with $2\ \mu\text{s}\ \pi/2$ pulse duration and a recycle delay of 5 s. The ^1H chemical shifts were referenced to tetrakis(trimethylsilyl)silane (single peak at 0.2 ppm). Solid-state NMR spectra were fitted using the Dmfit program.^[33] The average molecular weight and molecular weight distribution of the resulting POSS after acid treatment of **Cl-POSS** was measured using size exclusion chromatography (SEC) with a system equipped with a guard column, PLgel 500, 10^3 , 10^4 columns (Polymer Laboratories), and a differential refractive-index detector (Waters). The eluant used was tetrahydrofuran at a flow rate of $1\ \text{mL}\ \text{min}^{-1}$ at 30 °C. Polystyrene standards (Polymer Laboratories) ranging from 1400 to $1300 \times 10^3\ \text{g}\ \text{mol}^{-1}$ were used to calibrate the SEC. Powder XRD experiments were carried out with a high resolution Bonse–Hart camera with two germanium channel cuts for very small q values. The wavelength used was $1.542\ \text{\AA}$ (Cu-K_α radiation). SEM images were obtained with a Hitachi S2600N microscope. TGA profiles were recorded between 25 and 700 °C with a slope of $5\ ^\circ\text{C}/\text{min}$ under air with a Netzsch STA 409 PC apparatus using ca. 10 mg samples in Pt pans. Elemental analysis of C, H, and N was performed by the Service Mesures Physiques (Montpellier, France) and the Service Central d'Analyse (CNRS, Vernaison, France). EDS was performed with an environmental scanning electronic microscope FEIQuanta200FEG coupled with an Oxford INCA analyzer at UM2. CIS: Isothermal conductivity measurements were performed in the 10^{-2} – 10^6 Hz range with a Novocontrol dielectric alpha analyzer. The temperature of the sample, 20–80 °C, was controlled by a Quatro Novocontrol system by a nitrogen flux. In order to avoid the use of high mechanical pressure, CIS experiments were not carried out on pellets prepared from compressed powder. Instead, we employed a cell similar to that generally used for liquids. About 100 mg of **COOH-POSS** was poured on to the lower electrode of the cell, very gently pressed by the upper metallic electrode, and then inserted in the cryostat of the impedancemeter. According to TGA results, the sample was dehydrated in situ at 80 °C for 1 h under dry nitrogen flux before the conductivity measurements were performed.

Synthesis of Oligomeric Octakis(3-chloropropyl)silsesquioxane (Cl-POSS): This compound was prepared by hydrolysis and polycondensation of (3-chloropropyl)trimethoxysilane according to a literature procedure.^[34]

Synthesis of Oligomeric Octakis(3-cyanopropyl)silsesquioxane (CN-POSS): A solution of **Cl-POSS** (10.00 g, 9.65 mmol) in acetonitrile

(50 mL) was added dropwise to a hot solution of NaCN (9.46 g, 193.0 mmol) and 18-crown-6 (0.20 g, 1.93 mmol) in acetonitrile (300 mL). The resulting mixture was heated to reflux with stirring for 7 d. The reaction mixture was cooled to room temperature, and the salts were eliminated by filtration. MeCN was evaporated under vacuum, and the sticky residue was washed with pentane (5 × 50 mL) to yield **CN-POSS** (8.90 g, 98%) as a white powder. ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$): δ = 0.90 (m, 16 H, SiCH_2), 1.81 (m, 16 H, SiCH_2CH_2), 2.50 (t, $^3J_{\text{HH}}$ = 12.0 Hz, 16 H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CN}$) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (40 MHz, $[\text{D}_6]\text{acetone}$): δ = −69.2 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $[\text{D}_6]\text{acetone}$): 12.1 (SiCH_2), 20.2 [$(\text{SiCH}_2\text{CH}_2)$ and $(\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CN})$], 120.0 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 2941, 2884 and 2799 ($\nu_{\text{C-H}}$), 2243 (ν_{CN}), 1152 and 1029 ($\nu_{\text{Si-O-Si}}$) cm^{-1} . $\text{C}_{32}\text{H}_{48}\text{N}_8\text{O}_{12}\text{Si}_8$ (961.40): calcd. C 39.98, H 5.03, N 11.65, Si 23.37; found C 39.50, H 5.12, N 11.02, Si 22.82. MALDI-TOF MS: m/z = 984.20 $[\text{M} + \text{Na}]^+$. TGA: weight loss of 49.9% between 25 and 700 °C.

Synthesis of Oligomeric Silsesquioxane-octapropionic Acid (COOH-POSS): To **CN-POSS** (6.00 g, 6.25 mmol) was added sulfuric acid solution (9 M, 150 mL) at room temperature. The mixture was stirred at 25 °C for 1 h and 100 °C for 10 h. The reaction mixture was cooled to room temperature before water (400 mL) was added. The solid was recovered by filtration and washed with water (3 × 100 mL), acetone (50 mL), and ether (50 mL). After drying at 120 °C under vacuum for 12 h, **COOH-POSS** (6.90 g, 99%) was obtained as a white powder. ^{13}C NMR (75 MHz, CP-MAS): δ = 13.0 (SiCH_2), 19.1 (SiCH_2CH_2), 37.0 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{COOH}$) and 180.0 (COOH) ppm. ^{29}Si NMR (60 MHz, CP-MAS): δ = −68.8 ppm. ^1H NMR (600 MHz, MAS): δ = 0.84, 1.81, 2.32 (3s, 6 H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$) and 10.20 (s, 1 H, COOH) ppm. IR (v, KBr): $\tilde{\nu}$ = 3250–2700 ($\nu_{\text{O-H}}$ of carboxylic acid), 2944 and 2800 ($\nu_{\text{C-H}}$), 1703 ($\nu_{\text{C=O}}$), 1105 and 1008 ($\nu_{\text{Si-O-Si}}$) cm^{-1} . $\text{C}_{32}\text{H}_{56}\text{O}_{28}\text{Si}_8$ (1113.45): calcd. C 34.52, H 5.07, Si 20.18; found C 33.25, H 5.26, Si 20.33. TGA: weight loss of 60.1% between 25 and 800 °C.

Proton Exchange Study of COOH-POSS with D₂O: **COOH-POSS** (25 mg) was added to of D₂O (4 mL) at room temperature under an argon atmosphere. The resulting suspension was stirred for 30 min and filtered under argon. The obtained solid was dried at 100 °C under vacuum for 20 h. ^1H NMR (600 MHz, MAS): δ = 0.84, 1.81, 2.32 (3s, 6 H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$) and 11.10 (s, 0.5 H, COOH) ppm.

Synthesis of the Sodium Salt of COOH-POSS (COONa-POSS): A solution of sodium acetylacetonate (2.0 g, 16.26 mmol) in dry EtOH (20 mL) was added at room temperature to a suspension of **COOH-POSS** (2.25 g, 2.03 mmol) in dry EtOH (20 mL). The mixture was stirred at 25 °C for 10 h. The resulting solid was collected by filtration and washed twice with hot EtOH (20 mL) to remove acetylacetonate. After drying, **COONa-POSS** (2.57 g, 2.00 mmol, 98%) was obtained as a white powder. ^{29}Si NMR (60 MHz, CP-MAS): δ = −67.7 ppm. EDS analysis (atomic): Na/Si = 0.97.

Synthesis of the Copper(II) Salt of COOH-POSS (COOCu-POSS): **COONa-POSS** (0.50 g, 0.39 mmol) was added to a solution of CuCl_2 (0.31 g, 2.33 mmol) in water (20 mL) at room temperature. After 10 h of stirring at 25 °C, the solid was collected by filtration, washed with water (4 × 10 mL), and dried under vacuum to give **COOCu-POSS** (0.50 g, 0.37 mmol, 95%) as a blue powder. EDS analysis (atomic): Na/Si = 0 and Cu/Si = 0.48.

Synthesis of the Cobalt(II) Salt of COOH-POSS (COOCu-POSS): This material was prepared according to the procedure described for **COOCu-POSS**. A purple solid was obtained in 95% yield. EDS analysis (atomic): Na/Si = 0 and Co/Si = 0.49.

Synthesis of the Nickel(II) Salt of COOH-POSS (COONi-POSS): This material was prepared according to the procedure described for **COOCu-POSS**. A green solid was obtained in 96% yield. EDS analysis (atomic): Na/Si = 0 and Ni/Si = 0.48.

Supporting Information (see footnote on the first page of this article): GPC profile of **Cl-POSS** after acid treatment. ATR FTIR spectrum for **COOH-POSS**. Nitrogen adsorption–desorption isotherms at 77 K for **COOH-POSS**. Real part of the global conductivity (σ_{ac}) as a function of the frequency (f) of dry **COOH-POSS** at different temperatures. ^{29}Si CP-MAS NMR spectrum of **COONa-POSS**.

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Thermal and Photochemical Reactions of Azidoruthenium(III) Complexes of Macrocyclic Tertiary Amines and the Structure of the (Phosphoraniminato)ruthenium(III) Complex *trans*-[Ru(14-TMC)(N₃)-(NPh₃)]⁺

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Keywords: Ruthenium / N ligands / Macrocyclic ligands / Azides / Nitrides

The bis(azido)ruthenium(III) complexes, *trans*-[Ru(L)(N₃)₂]⁺ [L = 14-TMC (**1**) and 16-TMC (**4**)] have been prepared. These complexes undergo facile thermal or photo-decomposition in RCN (R = Me, Bu, Ph, 4-MePh, 2-MeOPh) solutions to produce the corresponding azidoruthenium(II) complexes *trans*-[Ru(L)(N₃)(RCN)]⁺ [L = 14-TMC, R = Me (**2a**), Bu (**2b**), Ph (**2c**), 4-MePh (**2d**), 2-MeOPh (**2e**); L = 16-TMC, R = Me (**5a**), Ph (**5b**)] and *cis*-[Ru(Tet-Me₆)(N₃)(MeCN)]⁺ (**6**). Complex **1** reacted with PPh₃, by a nitrogen atom transfer reaction, to

give *trans*-[Ru(14-TMC)(N₃)(NPh₃)]⁺ (**3**) in 80 % yield. The crystal structures of **2e**(PF₆), **3**(PF₆) and **5b**(ClO₄) have been determined by X-ray diffraction analysis. Complex **3** is the first structurally characterized (phosphoraniminato)ruthenium(III) complex with Ru–N distances of 1.991(7)–2.014(6) Å and a nearly linear Ru–N–P moiety [$\angle$ Ru–N–P = 168.2(5)–171.5(6)°]. Density functional theory (DFT) calculations on **3** and the proposed [Ru^V(14-TMC)(N)(N₃)]⁺ intermediate have been performed.

Introduction

The transformation of metal azides to metal nitrides involving a two-electron oxidation of the metal center and a release of N₂ is a useful strategy for the preparation of reactive metal-nitrido complexes.^[1–2] Notable recent examples include the photolysis at low temperature of azido-Fe^{III} and Fe^{IV} complexes of macrocyclic amine ligands to generate the respective nitrido-Fe^V and Fe^{VI} complexes,^[3–6] and the structural characterization of tetrahedral nitrido-Fe^V complexes.^[7] However, there are only a handful of examples of azidoruthenium complexes; *cis*-[Ru^{III}(en)₂(N₃)₂]⁺ and *cis*-[Ru^{III}(trien)(N₃)₂]⁺ (en = ethylene diamine; trien = triethylenetetramine) were reported in 1970 by Basolo and Pearson, and reactive ruthenium nitrene or imido intermediates were proposed in the thermal or photolytic decomposition reactions of azidoruthenium complexes.^[8] Since then, azidoruthenium complexes bearing bipyridine,^[9] thiolate, thioether,^[10] and tetradentate anionic N₂O₂ ligands,^[11] and azido diruthenium complexes^[12] have been studied. Caulton et al. have reported the crystal structure of the square

planar [(PNP)Ru^{IV}N] complex that was formed by the decomposition of [(PNP)Ru^{II}N₃] [PNP = (tBu₂PCH₂-SiMe₂)₂N].^[13a]

Over the past decades, we have been studying the synthesis and reactivities of oxygen- and nitrogen-multiple bonded ruthenium and osmium complexes that are supported by tertiary amine ligands.^[14] Macrocyclic tertiary amine ligands are optically transparent in the UV/Vis spectral region, and are electrochemically inert upon coordination to metal ions. In this work, we report the synthesis of a series of azido-Ru^{II} and Ru^{III} complexes supported by tertiary amine ligands, and their thermal and photolytic decomposition reactions (Figure 1). A proposed mechanism for these

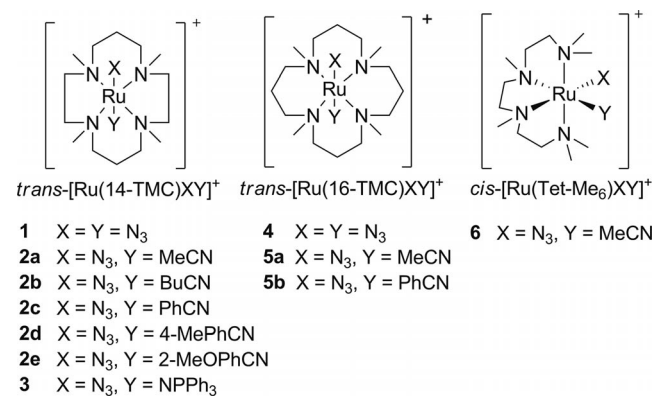


Figure 1. Azidoruthenium(II) and (III) complexes that have been prepared in this work.

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reactions that involves a nitridoruthenium(V) intermediate is discussed.

Results and Discussion

Synthesis and Characterization

Complex **1** was prepared by the reaction of *trans*-[Ru(14-TMC)Cl₂]Cl (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) with 10 equiv. of NaN₃ in a MeOH/H₂O mixture at 0 °C, and upon addition of NaPF₆ to the mixture **1** was isolated as a PF₆[−] salt in 90% yield. Complex **1**(PF₆) is a bright red solid that is light sensitive both in solution and in the solid state. It is stable for weeks when kept in the dark at −20 °C, as revealed by UV/Vis spectrophotometry.

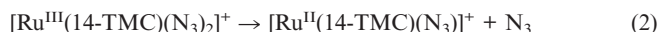
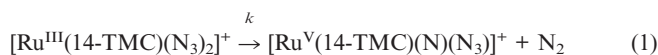
Treatment of *trans*-[Ru(16-TMC)Cl₂]Cl (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with zinc amalgam, NaN₃, followed by air oxidation, afforded a red species tentatively assigned as *trans*-[Ru(16-TMC)(N₃)₂]⁺ (**4**). However, attempts to isolate **4** in a pure form were not successful, and this species was found to have a short lifetime (half-life ca. 300 s) at room temperature. The direct reaction between *trans*-[Ru(16-TMC)Cl₂]⁺ with excess NaN₃ to produce **4** was not successful, presumably due to the low reactivity of the chloride ligand towards substitution reactions. Attempts to prepare *cis*-[Ru(Tet-Me₆)(N₃)₂]⁺ (Tet-Me₆ = 1,1,4,7,10,10-Hexamethyltriethylenetetramine) resulted in the formation of a solid that exploded upon mechanical impact, and this product was not isolated.

The UV/Vis spectrum of **1** shows two absorption bands at 583 and 408 nm, bands that can be assigned to N₃[−] → Ru^{III} ligand to metal charge transfer (LMCT) transitions. It is also pertinent to compare these absorption λ_{max} values with the LMCT transition energy of *trans*-[Ru(14-TMC)Br₂]⁺ in MeCN (λ_{max} = 471 nm) and *trans*-[Ru(14-TMC)(NCS)₂]⁺ in MeCN (λ_{max} = 594 nm), which reveal that N₃[−] has an optical electronegativity comparable to NCS[−].^[13] For **1**, The Ru^{III/II} redox process is reversible on the cyclic voltammetric timescale with E^{1/2} = −0.59 V vs. Cp₂Fe⁺⁰ and with an E^{1/2} value comparable to that of the *trans*-[Ru(14-TMC)Cl₂]⁺⁰ couple (E^{1/2} = −0.62 V vs. Cp₂Fe⁺⁰).^[15] Complex **1** exhibits one ν_{as}(N₃) band in its spectrum with a stretching frequency of 2047 cm^{−1}, which is similar to ν_{as}(N₃) frequencies for other metal complexes containing terminal azide ligand such as *trans*-[Cr(14aneN₄)(N₃)₂]PF₆ (2085, 2069 cm^{−1}, 14aneN₄ = 1,4,8,11-tetraazacyclotetradecane),^[16] *trans*-[Mn(14aneN₄)(N₃)₂]ClO₄ (2069, 2047 cm^{−1})^[17] and *trans*-[Fe(14aneN₄)(N₃)₂]PF₆ (2044 cm^{−1}).^[18] This assignment is further supported by the expected shift of this peak to 2035 cm^{−1} in the spectrum of *trans*-[Ru(14-TMC)(¹⁵N¹⁴N¹⁴N₂)₂]⁺ (¹⁵N labeled **1**).

The ESI-MS spectrum of **1** in MeCN shows a cluster peak that can be attributed to the molecular cation of **1** at *m/z* 442, this value is equivalent to that calculated for **1** with a formula of C₁₄H₃₂N₁₀Ru and with the most abundant ¹⁰²Ru isotope, furthermore the spectrum has the expected

isotope pattern. Cluster peaks located at *m/z* = 400, 414 and 428 are assigned to [Ru(14-TMC)(N₃)₂]⁺, [Ru(14-TMC)(N)(N₃)₂]⁺ and [Ru(14-TMC)(N₂)(N₃)₂]⁺, respectively. The presence of [Ru(14-TMC)(N₃)₂]⁺ and [Ru(14-TMC)(N)(N₃)₂]⁺ is probably due to in-source fragmentation. The detection of [Ru(14-TMC)(N₃)(N₂)₂]⁺ is attributed to the reaction of [Ru(14-TMC)(N)(N₃)₂]⁺ with **1** (see kinetics section).

Collision induced dissociation (CID) of metal azide complexes is known to generate metal nitride species with the expulsion of N₂ in the gas phase.^[19–20] In this work, the collisional activation of **1** lead to mass differences (Δ*m*) of −28 and −42, associated with the major fragmentation pathway, in the CID spectra recorded over the whole range of collision energies. To further confirm the mass differences of 28 and 42, we performed CID of the mass selected ion of ¹⁵N labeled **1** at *m/z* 444, which is mainly attributed to [¹⁰²Ru(14-TMC)(¹⁵N¹⁴N¹⁴N₂)₂]⁺. The fragmentation of [¹⁰²Ru(14-TMC)(¹⁵N¹⁴N¹⁴N₂)₂]⁺ induced ¹⁴N¹⁴N and ¹⁴N¹⁵N losses (Δ*m* = −28 and −29), the peaks for which were equal in intensity, as well as the expulsion of neutral ¹⁵N¹⁴N¹⁴N (Δ*m* = −43). These results reveal that the azido group of the complex could be eliminated via an oxidative pathway [Equation (1)] and a reductive pathway [Equation (2)].



As depicted in Figure 2, loss of N₂ is readily observed at a collision energy nominally set to E_{CM} = 0 eV, indicating that the activation energy of this pathway is the lowest of the two. By increasing E_{CM}, the relative abundance of [1]-N₂ gradually increased. In contrast, the loss of the azido ligand is less sensitive to the experimental conditions we investigated. We propose that the ionic fragment [1]-N₂ formed in the reaction could correspond to the *trans*-

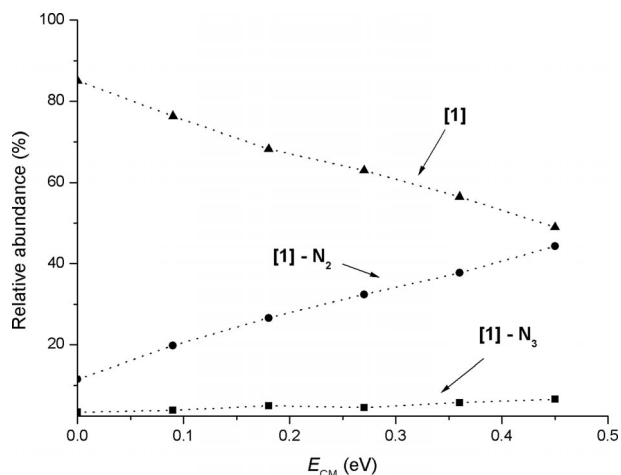
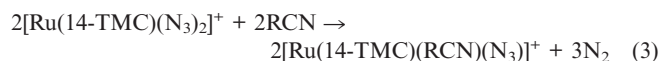


Figure 2. Collision induced fragmentation of mass selected [1]⁺ as a function of collision energy (center of mass frame). [1]-N₂ and [1]-N₃ are [Ru^V(14-TMC)(N)(N₃)₂]⁺ and [Ru^{II}(14-TMC)(N₃)₂]⁺, respectively.

$[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]^+$ cation. Although isolation of *trans*- $[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]^+$ has not been realized so far, the mass spectroscopic data suggests considerable thermal stability of *trans*- $[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]^+$ in the gas phase (see DFT calculation section). A similar finding has been reported for the CID of $[\text{Fe}(\text{cyclam-acetato})(\text{N}_3)]^+$ (cyclam-acetato = 1,4,8,11-tetraazacyclotetradecane-1-acetato).^[20]

Thermally Induced Decomposition of $[\text{Ru}(\text{L})(\text{N}_3)_2]^+$ in RCN

Decomposition of $[\text{Ru}(\text{L})(\text{N}_3)_2]^+$ (L = 14-TMC, 16-TMC, Tet-Me₆) in RCN at room temperature gave the $[\text{Ru}(\text{L})(\text{N}_3)(\text{RCN})]^+$ complexes in good to excellent yields. In MeCN, complex **1** gradually decomposed with the evolution of gas, and converted to **2a** after 24 h. GC-MS analysis confirmed that the evolved gas was N₂, 1.5 ± 0.1 mol of which was produced per mol of **1**. The reaction is depicted by [Equation (3)].



With *trans*- $[\text{Ru}(14\text{-TMC})(^{15}\text{N}^{14}\text{N}^{14}\text{N}_2)]^+$, the N₂ released was found to be a mixture of $^{14}\text{N}^{14}\text{N}$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}^{15}\text{N}$ in the ratio of 5.5:6:1, indicating that both N atoms come from the coordinated N₃[−] ligand. This ratio is consistent with the pathway involving reaction of $[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]$ with **1** (calculated $^{14}\text{N}^{14}\text{N}$: $^{14}\text{N}^{15}\text{N}$: $^{15}\text{N}^{15}\text{N}$ = 5: 6: 1). A slightly higher value of $^{14}\text{N}_2$ found in experimental data is attributed to a leak of the gas syringe. A pathway that involves the homolytic cleavage of a Ru–N₃ bond with the generation of an azide radical that subsequently reacts with another azide radical to produce N₂ is not favored. This is because the presence of a 70 fold excess of acrylamide, a well known trapping agent for the azide radical,^[9] did not cause any decrease in the production of N₂ in the thermal decomposition reaction.

The rate of decomposition of **1**(PF₆) in MeCN was examined by UV/Vis spectrophotometry (Figure 3). Spectral

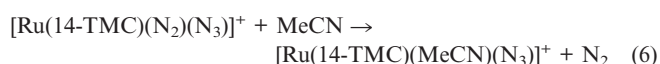
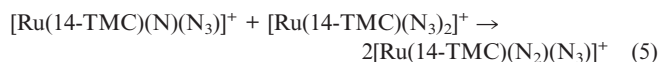
changes with an isosbestic point at 291 nm were observed. The intense charge-transfer bands at 409 and 538 nm gradually decreased in intensity with the concomitant formation of a new band at 246 nm. The decomposition of **1** followed first order kinetics [Equation (2)]. The pseudo first order rate constant (k_{obs}) was independent of the initial concentration of **1**, which was in the range of 0.05–1.0 mM [Table 1 and Equation (4)].

$$-\text{d}[\text{Ru}(14\text{-TMC})(\text{N}_3)_2]^+/\text{d}t = k_{\text{obs}}[\text{Ru}(14\text{-TMC})(\text{N}_3)_2]^+ \quad (4)$$

Table 1. Rate constants for the decomposition of **1**.

Entry	Temperature [K]	[1] [mM]	k_{obs} [s ^{−1}]
1	287	0.10	2.62×10^{-5}
2	292	0.05	7.06×10^{-5}
3		0.1	7.12×10^{-5}
4		0.25	6.48×10^{-5}
5		0.50	6.44×10^{-5}
6		1.0	6.24×10^{-5}
7	301	0.1	2.30×10^{-4}
8	307	0.1	6.12×10^{-4}
9	312	0.1	1.34×10^{-3}
10	319	0.1	2.48×10^{-3}

We propose that the rate determining step in the decomposition of **1** is the cleavage of the N–N bond of the azide ligand with the subsequent formation of $[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]^+$ and N₂ [Equation (1)]. $[\text{Ru}^{\text{V}}(14\text{-TMC})(\text{N})(\text{N}_3)]^+$ reacts with another molecule of **1** to give two molecules of $[\text{Ru}(14\text{-TMC})(\text{N}_3)(\text{N}_2)]^+$, the latter further decomposes to give **2a** [Equation (5) and Equation (6)]. Thus, the rate of decomposition of **1** is directly related to the rate of formation of **2a** [Equation (7)].



$$k_{\text{obs}} = 2k \quad (7)$$

We determined the effect of temperature over the 287–319 K range on the thermal decomposition of **1** in MeCN. A good linear correlation was obtained for the Eyring plot of $\ln(k/T)$ vs. $1/T$. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 25.9 ± 1.2 kcal mol^{−1} and 9.4 ± 4.0 cal mol^{−1} K^{−1}, respectively. The positive value for $\Delta S^\ddagger$ indicates a gain in entropy, which is consistent with the dissociation of N₂ from the azide ligand [Equation (1)]. It is pertinent to compare the activation parameters for **1** with those for the decomposition of other metal azide complexes e.g. $[\text{Cp}^*_2\text{Mo}(\text{N}_3)_2]$ (Cp* = C₅Me₅ anion): $\Delta H^\ddagger = 26.6 \pm 0.2$ kcal mol^{−1} and $\Delta S^\ddagger = 3.5 \pm 0.7$ cal mol^{−1} K^{−1};^[21] *cis*- $[\text{Ru}^{\text{III}}(\text{en})(\text{N}_3)_2]\text{PF}_6$: $\Delta H^\ddagger = 23.8$ kcal mol^{−1}, $\Delta S^\ddagger = -2$ cal mol^{−1} K^{−1};^[8] *cis*- $[\text{Ru}^{\text{III}}(\text{trien})(\text{N}_3)_2]\text{PF}_6$: $\Delta H^\ddagger = 22.9$ kcal mol^{−1}, $\Delta S^\ddagger = -2$ cal mol^{−1} K^{−1}.^[8] The $[\text{Cp}^*_2\text{Mo}(\text{N}_3)_2]$ system also has a positive $\Delta S^\ddagger$ value. The reason for the discrepancy in the $\Delta S^\ddagger$ value determined by Basolo and ours is not clear, but

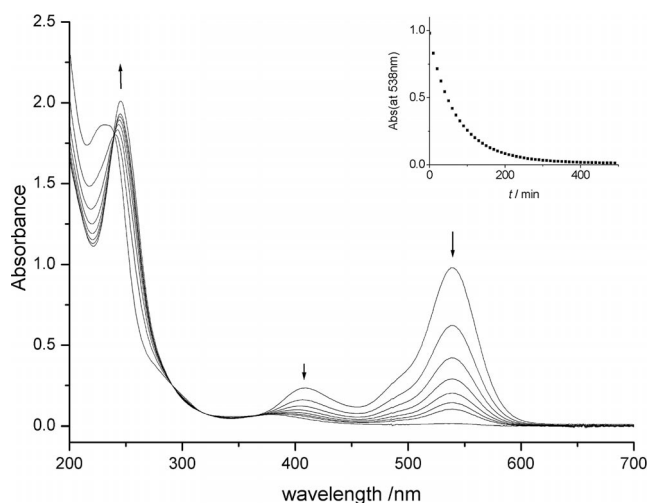


Figure 3. Time resolved UV/Vis spectral changes observed for **1**(PF₆) (0.1 mM) in MeCN at 301 K. Insert is the absorbance trace monitored at 538 nm.

we note that the two azide ligands in *cis*-[Ru^{III}(en)(N₃)₂]⁺ and *cis*-[Ru^{III}(trien)(N₃)₂]⁺ are in a *cis*-configuration whereas in **1** they are in a *trans*-configuration.

Structure of **2e**(PF₆)

In the structure of **2e** the four methyl groups of the macrocyclic 14-TMC ligand adopt a “3-up and 1-down” or *R,S,R,R* geometry; three methyl groups are in a *syn* orientation with the 2-MeOPhCN ligand. The average Ru–N(amine) distance is 2.143 Å. The Ru–N(2-MeOPhCN) distance in **2e** [1.955(3) Å] is significantly shorter than the Ru–N(MeCN) distance in *trans*-[Ru(14-TMC)(O)(MeCN)]²⁺ [2.149(6) Å] revealing that Ru^{IV}=O has a larger *trans* effect than Ru^{II}–N₃.^[22] The length of the Ru–N(azide) bond in **2a** [2.107(10) Å]^[23] is comparable to that within **2e** [2.115(3) Å] (Figure 4).

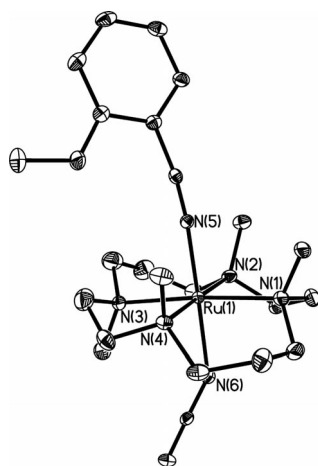


Figure 4. Molecular structure of the **2e** cation (ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity). Selected bond lengths [Å]: Ru1–N(1) 2.136(3), Ru(1)–N(2) 2.139(3), Ru(1)–N(3) 2.160(3), Ru(1)–N(4) 2.136(3), Ru(1)–N(5) 1.955(3), Ru(1)–N(6) 2.115(3).

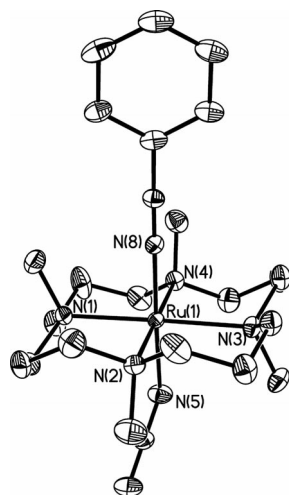


Figure 5. Molecular structure of the **5b** cation (ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] for **5b**: Ru(1)–N(1) 2.239(4), Ru(1)–N(2) 2.257(4), Ru(1)–N(3) 2.266(4), Ru(1)–N(4) 2.241(4), Ru(1)–N(5) 2.084(5), Ru(1)–N(8) 1.958(4).

Structure of **5b**(ClO₄)

In **5b**, the methyl groups of the macrocyclic 16-TMC ligand adopt a “2-up and 2-down” or *R,R,S,S* geometry, and the average Ru–N(amine) bond length is 2.251 Å. The lengths of the Ru–N(azide) and Ru–N(PhCN) bonds are 2.084(5) and 1.958(4) Å, respectively (Figure 5).

Thermal Decomposition of **1** in the Presence of PPh₃

It is well documented that phosphane compounds react with electrophilic metal nitride complexes.^[1,24] In this work, a Ru^{III} phosphoraniminato complex was obtained in 80% yield when PPh₃ was added to **1**. The direct reaction of **1** with PPh₃ to produce **3** is unlikely since there is no significant change in the rate of decomposition of **1** in the presence of PPh₃. Thus, our results indicate that complex **3** was produced by a nitrogen atom transfer reaction between electrophilic *trans*-[Ru^V(14-TMC)(N)(N₃)]⁺ and PPh₃. The IR spectrum of **3** exhibits a peak at 1167 cm^{−1} that is assignable to ν(P=N). A similar ν(P=N) value has been reported for [Ru(NPPPh₃)L(py)Cl] [L = 2,6-bis(hydroxy-2,2-diphenylethyl)pyridine], ν(P=N) = 1160 cm^{−1}.^[23] This ν(P=N) assignment is also supported by the expected shift of this peak to 1152 cm^{−1} in the spectrum of ¹⁵N labeled complex **3**.

Crystal Structure of **3**(PF₆)

A perspective view of the structure of **3**(PF₆) and selected bond lengths and bond angles for this complex are shown in Figure 6. There are two crystallographically independent units per unit cell. In both units the methyl groups of the

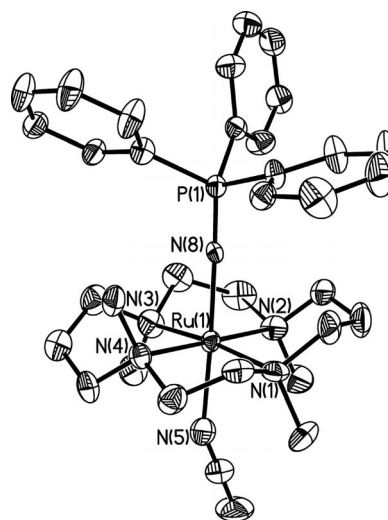


Figure 6. Molecular structure of one of two crystallographically independent **3** cations (ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°] (values for the second independent molecule are given in square parentheses): Ru(1)–N(5) 2.069(9) [2.078(8)], Ru(1)–N(8) 2.014(6) [1.991(7)], P(1)–N(8) 1.542(7) [1.551(7)], ∠Ru(1)–N(8)–P(1) 168.2(5) [171.5(6)].

macrocyclic 14-TMC ligand adopt a “3-up and 1-down” or *R,S,R,R* geometry; one methyl group is facing the NPPH_3 group. The Ru–N(phosphoraninato) distances are 1.991(7)–2.014(6) Å, and the Ru–N–P bond angles are 171.5(6) and 168.2(5)° (see DFT calculations section). Both the linear M–N–P and short M–NPPH₃ distances (1.65–1.86 Å) are generally found in metal phosphoraninato complexes and are indicative of the multiple bond character of the M–N bonds.^[24]

Photo-Induced Decomposition of **1**

The decomposition of **1** in MeCN can be activated by light irradiation. When a MeCN solution of **1** was irradiated with a 300 W Xenon lamp with a low pass filter at 400 nm in an Ar atmosphere at 273 K the solution underwent a rapid color change from red to yellow that was observed within 5 min. The light activated decomposition of **1** gave **2a** as the major product, which was accompanied by a small amount of $\text{trans-[Ru(14-TMC)(MeCN)}_2\text{]}^{2+}$ ($m/z = 220$) that was detected in the resultant solution by ESI-MS analysis. Quantitative determination of the light induced decomposition of **1** showed that 1.5 ± 0.1 mol of N_2 was produced per mol of ruthenium complex. No decrease in the production of N_2 was observed for the photo-induced decomposition of **1** in the presence of a 70 fold excess of acrylamide.^[9]

Density Functional Theory (DFT) Calculations

DFT calculations are a useful tool for understanding and rationalizing the electronic structure of metal complexes. In this work, ESI-MS studies revealed that **1** underwent expulsion of N_2 to afford $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$ upon collisional activation. Attempts to isolate and characterize $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$ were not successful. In order to obtain more information about the electronic structure of $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$, DFT (BP/TZ2P) calculations were performed. In addition, the crystal structure of **3** determined by us reveals a long Ru–NPPH₃ distance and that the Ru–N–P moiety is nearly linear, findings that are not commonly encountered in the literature.^[23] We performed DFT (BP/TZ2P) calculations on **3** to rationalize its structure. The calculations are described as follows.

Complex $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$

Among the seven optimized conformers of $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$ in the doublet state (see Supporting Information, Figure S1), the energy of the conformer with “two-up, two-down” or *R,R,S,S* geometry, which displays compromise between steric hindrance and the tension of ethylene and 1,3-propenyl groups, was found to be the lowest. A *R,R,S,S* geometry for 14-TMC was found for the $\text{trans-[Ru}^{\text{IV}}\text{(14-TMC)(O)(NCO)]}^+$ cation.^[25] The quartet and sextet states of this conformer were also calculated and were found to be unfavorable since their energy values are

40.2 and 90.6 kcal/mol greater, respectively, than that of the doublet state.

In $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$, the computed $\text{Ru}^{\text{V}}\equiv\text{N}$ distance of 1.723 Å is comparable to the $\text{Ru}^{\text{V}}\equiv\text{N}$ distances of 1.74/1.78 Å found in nitridoruthenium(V) complexes of a *meso*-octamethylporphyrinogen tetraanion,^[26] but is longer than the $\text{Ru}^{\text{VI}}\equiv\text{N}$ distances reported in the literature that range from 1.59 to 1.66 Å.^[1,27–29] On the basis of the DFT calculations (Figure 7), the highest singly occupied molecular orbital (SOMO) is best considered to be one of the Ru–N π^* antibonding orbitals. Occupancy of these π^* orbitals reduces the Ru–N bond order, thus accounting for the “elongated” Ru–nitrido distance in $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$.

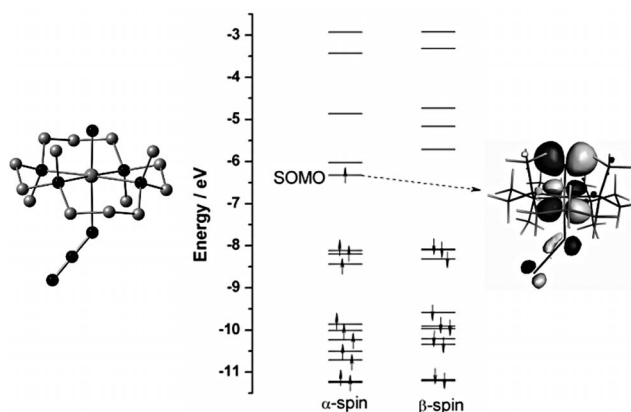


Figure 7. Left: Optimized structure of $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$ calculated with BP/TZ2P, hydrogen atoms have been omitted. Right: Kohn–Sham (KS) Molecular orbital diagram for $\text{trans-[Ru}^{\text{V}}\text{(14-TMC)(N)(N}_3\text{)]}^+$.

Complex $\text{trans-[Ru(14-TMC)(NPPH}_3\text{)(N}_3\text{)]}^+$ (**3**)

In this work, DFT (BP/TZ2P) calculations on **3** and the simplified model complex $\text{trans-[Ru(14-TMC)(NPH}_3\text{)(N}_3\text{)]}^+$ (Model 1), in which the phenyl groups are replaced by H atoms, were performed (Figure 8). The doublet state of **3** is most favorable as the quartet and sextet states are 31.3 and 67.0 kcal/mol higher in energy than the doublet state, respectively. The quality of the optimized structure

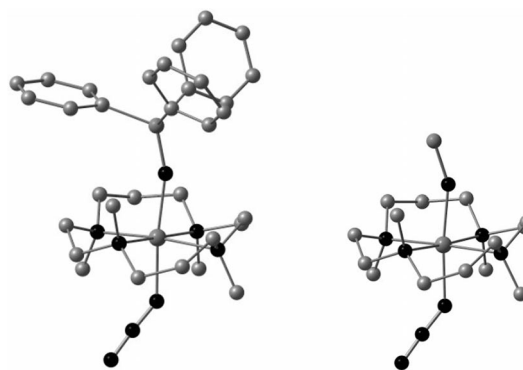


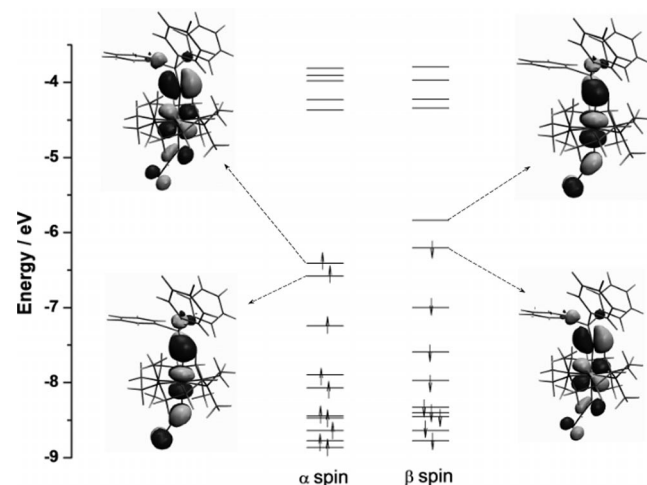
Figure 8. Optimized structures of complex **3** (left) and a simplified model of **3** (Model 1, right). These structures were calculated with BP/TZ2P. Hydrogen atoms have been omitted.

Table 2. The NBO descriptors for the bonds involving the (phosphoraniminato)-N atom within **3**; the hybrid contributions of the nitrogen atom (h_N), percentage polarization toward the nitrogen atoms (c_{N^2}) and the occupancy number (occ.) are given.

	Character	α Spin h_N	c_{N^2} [%]	Occ.	β Spin h_N	c_{N^2} [%]	Occ.
BD _{P-N}	σ_{P-N}	$s^{36.7}p^{63.0}$	68.1	0.987	$s^{38.3}p^{61.4}$	67.8	0.988
BD _{Ru-N}	π_{Ru-N}	—	—	—	$p^{99.8}$	70.7	0.918
LP _N	$\sigma_{donor \rightarrow Ru}$	$s^{33.3}p^{66.7}$	—	0.810	$s^{31.6}p^{68.4}$	—	0.813
	$2p_N$	$s^{10.2}p^{89.6}$	—	0.885	$s^{29.7}p^{70.1}$	—	0.878
	$2p_N'$	$s^{19.3}p^{80.3}$	—	0.878	—	—	—

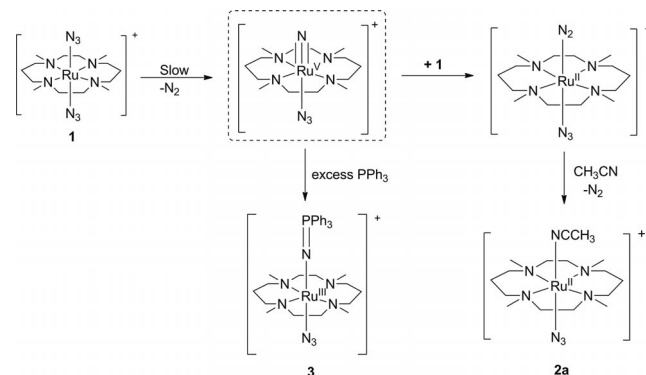
was checked by comparing it with the crystal structure of **3** determined by X-ray diffraction analysis. The calculated Ru–N(phosphoraniminato) distance and Ru–N–P angle are 2.069 Å and 162.3°, which are in agreement with the experimental values (Ru–N 1.991–2.014 Å and $\angle$ Ru–N–P 168.2–171.6°).

The frontier Kohn–Sham (KS) molecular orbitals (Figure 9) show that there are three singly occupied MOs that feature antibonding interactions between the Ru and (phosphoraniminato)-N atoms. Occupancy of these orbitals would reduce the Ru–N(phosphoraniminato) bond order causing elongation of the Ru–N(phosphoraniminato) bond. In addition, natural bond orbital (NBO) analysis (Table 2) showed that all σ bonds (σ_{P-N} in both spin states, and $\sigma_{donor \rightarrow Ru}$ in both spin states) involving the (phosphoraniminato)-N atom have a contribution from sp^2 orbitals of the (phosphoraniminato)-N atom. These findings suggest the (phosphoraniminato)-N atom prefers to adopt an sp^2 -hybridized state. Indeed, this observation is further supported by the fact that in Model 1, in which the structure is subject to less steric hindrance than the other computationally determined structures, the Ru–N(phosphoraniminato) distance is shortened from 2.069 to 2.017 Å, and the angle $\angle$ Ru–N–P is reduced from 162.3 to 157.1°. Thus, the long length of the Ru–N(phosphoraniminato) bond in **3** may be due to a combination of both electronic and steric effects.

Figure 9. Diagram of the frontier KS molecular orbitals of **3**.

Conclusions

In this work, we have synthesized azidoruthenium(II) and (III) complexes that are supported by chelating macrocyclic tertiary amine ligands, and have studied their thermal and photo-decomposition. On the basis of ESI-MS results, kinetic measurements, and a trapping experiment we propose that an electrophilic ruthenium(V) nitride species is generated in these processes, as depicted in Scheme 1.



Scheme 1.

Experimental Section

General: All reagents and solvents were of analytical grade unless otherwise stated. $RuCl_3 \cdot xH_2O$ (Strem), $Na^{15}N^{14}N^{14}N$ (98 atom-%, Cambridge Isotope), triphenylphosphane (Aldrich), butyronitrile (Aldrich), benzonitrile (Aldrich), 2-methylbenzonitrile (Aldrich), 2-methoxybenzonitrile (Aldrich) were obtained from commercial sources and were used as received. MeCN was purified and dried before use. Water was purified with a nanoPure system (Barnstead, USA).

Caution! Metal azides are potentially explosive and should be handled only in small quantities (< 100 mg) and with appropriate precautions.

Infrared spectra were recorded with KBr discs or Nujol mulls on a Nicolet 20 SXC FTIR spectrophotometer. UV/Vis spectra were recorded on a HP 8453 diode array spectrophotometer. GC–MS measurements were carried out on an Agilent 6890N gas chromatograph interfaced with an Agilent 5973 mass selective spectrometer. Electro-spray ionization (ESI) mass spectrometry was performed on a hybrid Q-ToF mass spectrometer (Q-STAR XL, Applied Biosystems, collision gas: Ar). NMR spectra were obtained with a Bruker Avance 400 pulsed Fourier transform instrument. Element-

tal analyses were performed by the Institute of Chemistry of the Chinese Academy of Sciences or MEDAC Ltd, UK.

trans-[Ru(14-TMC)(N₃)₂]PF₆ (1**(PF₆)).** NaN₃ (70 mg) in H₂O (1 mL) was added to a methanolic solution (9 mL) of *trans*-[Ru(TMC)Cl₂]Cl (50 mg, 0.108 mmol) at 0 °C. After 5 min of vigorously stirring, the color of the solution changed from yellow to bright red. Addition of a saturated aqueous solution of NaPF₆ (1 mL) gave a bright red solid, **1**(PF₆). The solid was collected by filtration and washed with water and methanol. The solid is stable at –20 °C for weeks; yield 90%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2047. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (MeCN): 235 (16000), 408 (1900), 488 (sh, 2200), 538 (8100). C₁₄H₃₂F₆N₁₀PRu (586.51): calcd. C 22.43, H 4.84, N 20.56; found C 22.90, H 4.73, N 20.28. ESI-MS: m/z = 442 [M]⁺. ¹⁵N Labeled form of **1**: *trans*-[Ru(14-TMC)-(¹⁵N¹⁴N¹⁴N)₂]PF₆. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2035.

trans-[Ru(L)(N₃)RCN]PF₆, L = 14-TMC, R = Me (2a**), Bu (**2b**), Ph (**2c**), 4-MePh (**2d**), 2-MeOPh (**2e**); L = 16-TMC, R = Me (**5a**), Ph (**5b**)).** [Ru(L)(N₃)₂]PF₆ (100 mg) was dissolved in RCN (15 mL) with gentle stirring. After 24 h, the bright red solution gradually changed to yellow and gas bubbles evolved at room temperature. The solution was concentrated under vacuum and a yellow solid was obtained by slow diffusion of Et₂O into the RCN solution.

Complex 2a(PF₆). Yellow solid; yield 99%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2068, $\nu(\text{C}\equiv\text{N})$ 2239. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 252 (15500), 379 (520). C₁₆H₃₅F₆N₈PRu·0.5MeCN (**2a**·PF₆·0.5MeCN): calcd. C 31.69, H 6.07, N 19.64; found C 31.47, H 6.02, N 19.35. ESI-MS: m/z = 441 [M]⁺ and 400 [M – MeCN]⁺. ¹⁵N Labeled form: *trans*-[Ru(14-TMC)(¹⁵N¹⁴N¹⁴N)(MeCN)]PF₆. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2054, $\nu(\text{C}\equiv\text{N})$ 2241. ESI-MS: m/z = 441 [M]⁺ and 400 [M – MeCN]⁺.

Complex 2b(PF₆). Orange-yellow solid; yield 80%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2064, $\nu(\text{C}\equiv\text{N})$ 2218. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 259 (18000), 379 (770). C₁₄H₃₂F₆N₇PRu (544.49): calcd. C 36.36, H 6.58, N 18.16; found C 36.28, H 6.55, N 17.90. ESI-MS: m/z = 483 [M]⁺ and 400 [M – BuCN]⁺.

Complex 2c(PF₆). Orange solid; yield 78%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2062, $\nu(\text{C}\equiv\text{N})$ 2187. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 229 (17000), 271 (15000), 366 (sh, 8200), 400 (11000). C₂₀H₃₇F₆N₇PRu (621.59): calcd. C 38.95, H 5.76, N 17.30; found C 39.14, H 5.68, N 17.04. ESI-MS: m/z = 503 [M]⁺ and 400 [M – PhCN]⁺.

Complex 2d(PF₆). Orange solid; yield 76%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2073, $\nu(\text{C}\equiv\text{N})$ 2172. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 232 (16000), 266 (17000), 358 (sh, 6900), 395 (9800). C₂₁H₃₉F₆N₇PRu (635.62): calcd. C 39.94, H 5.94, N 16.94; found C 40.02, H 5.84, N 16.65. ESI-MS: m/z = 517 [M]⁺ and 400 [M – 4-MePhCN]⁺.

Complex 2e(PF₆). Orange solid; yield 81%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2073, $\nu(\text{C}\equiv\text{N})$ 2172. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 234 (11000), 271 (12000), 401 (7400). C₂₁H₃₉F₆N₇OPRu (651.62): calcd. C 5.80, H 5.80, N 16.54; found C 39.12, H 4.34, N 16.97. ESI-MS: m/z = 533 [M]⁺ and 400 [M – 2-MeOPhCN]⁺.

Complex 3(PF₆). **1**(PF₆) (50 mg, 0.085 mmol) was dissolved in MeCN (15 mL). PPh₃ (559 mg, 2.13 mmol) was added to the solution while it was stirred. After 24 h, the solution developed a yellow color. After removal of the solvent by rotary evaporation, the yellow solid that had formed was washed with Et₂O, and was recrystallized by slow diffusion of Et₂O into a MeCN solution of the product (56 mg); yield 80%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2073, $\nu(\text{N}=\text{P})$ 1167. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (MeCN): 245 (22000), 380 (900), 530 (610). C₃₆H₅₃F₆N₁₀P₂Ru·2MeCN: calcd. C 47.89, H 5.92, N 15.51; found C 47.10, H 5.90, N 15.35. ESI-MS: m/z = 676 [M]⁺ and 648 [M – 28]⁺.

Complex 4(PF₆). A mixture of *trans*-[Ru(16-TMC)Cl₂]Cl (100 mg, 0.203 mmol) and zinc amalgam (0.5 g, 1.88 mmol) in methanol (15 mL) was refluxed for 1 h in an Ar atmosphere. A solution of NaN₃ (132 mg, 2.03 mmol) in H₂O (1 mL) was added, and the reaction mixture was stirred at 80 °C for about 1 h. The solution was cooled to room temperature and filtered. Addition of a saturated aqueous solution of NaPF₆ (1 mL) to the reaction mixture gave a bright red solid. The solid was collected by filtration and washed with water. The solid is stable at –20 °C for a few days; yield ca. 50%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2035.

Complex 5a(PF₆). Yellow solid; yield 90%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2066, $\nu(\text{C}\equiv\text{N})$ 2241. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 245 (6800), 431 (250). C₁₈H₃₉F₆N₈P₂Ru (644.57): calcd. C 35.23, H 6.41, N 18.26; found C 36.39, H 6.53, N 17.95. ESI-MS: m/z = 469 [M]⁺ and 428 [M – MeCN]⁺.

Complex 5b(ClO₄). Yellow solid. Crystals suitable for X-ray crystallography were grown by slow diffusion of Et₂O into a PhCN solution of **5b**(ClO₄); yield 72%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2065, $\nu(\text{C}\equiv\text{N})$ 2187. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 232 (12000), 259 (10000), 344 (5400), 386 (5200). C₂₃H₄₁N₈Ru·ClO₄: calcd. C 43.84, H 6.56, N 17.78; found C 43.53, H 6.65, N 17.62. ESI-MS: m/z = 531 [M]⁺ and 428 [M – PhCN]⁺.

Complex 6(PF₆). *cis*-[Ru(Tet-Me₆)Cl₂]PF₆ (100 mg, 0.183 mmol) was mixed with silver toluene-*p*-sulfonate (0.112 g, 0.402 mmol) in water (15 mL). The suspension was stirred and heated to 100 °C for 1 h, or until no further silver chloride precipitated, to leave a clear orange supernatant solution. After AgCl was removed, the filtrate was cooled in an ice bath. A deep red solution was obtained when NaN₃ (0.35 g, 17 mmol) was added to the solution. Addition of an aqueous solution of NH₄PF₆ (saturated, 2 mL) gave a red precipitate, proposed to be *cis*-[Ru(Tet-Me₆)(N₃)₂]PF₆. Without further purification, the red precipitate was redissolved in MeCN, and the solution stirred overnight. The solid that formed was collected after vacuum evaporation of the solvent. Yellow crystals were obtained by recrystallization of the crude product from MeCN/Et₂O; yield 37%. IR (KBr): $\nu_{\text{as}}(\text{N}_3)$ 2045, $\nu(\text{C}\equiv\text{N})$ 2249. UV/Vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH₂Cl₂): 231(10380), 408 (sh, 380). C₁₄H₃₃F₆N₈PRu (559.50): calcd. C 30.05, H 5.94, N 20.03; found C 29.95, H 5.77, N 19.83. ESI-MS: m/z = 415 [M]⁺ and 374 [M – MeCN]⁺.

Single Crystal Structure Determinations: X-ray diffraction data for **5b**(ClO₄) were collected on a Bruker X8 Proteum diffractometer with Cu-K α radiation (1.54178 Å), and the X-ray diffraction data for **2e**(PF₆) and **3**(PF₆) were collected on a Bruker Smart CCD 1000 with graphite monochromated Mo-K α radiation (0.71073 Å). The images were interpreted and the peak intensities were integrated with the PROTEUM2 suite or DENZO program. The structures were solved by direct method employing the SHELXS-97 program.^[30] The structure refinements were performed on F^2 by a full-matrix least-squares technique. The positions of the H atoms were calculated based on riding modes, and the H atoms were refined with their thermal parameters equal to 1.2 times those of the associated C atoms, and they participated in the calculation of final R indices. In the final stages of the least-square refinements all non-hydrogen atoms were refined anisotropically (Table 3).

CCDC-833472 [for **2e**(PF₆)], -833473 [for **3**(PF₆)], -833474 [for **5b**(ClO₄)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Kinetic Measurements: Experiments were performed on a Hewlett-Packard 8453 diode array spectrophotometer. The decay of **1** was

Table 3. Crystallographic data for **2e**(PF₆), **3**(PF₆) and **5b**(ClO₄).

	2e (PF ₆)	3 (PF ₆)·MeCN	5b (ClO ₄)
Formula	C ₂₂ H ₃₆ N ₈ ORuF ₆ P	C ₃₄ H ₅₀ N ₉ P ₂ F ₆ Ru	C ₂₃ H ₄₁ N ₈ RuClO ₄
Color, habit	yellow, block	yellow, bar	orange, plate
<i>M</i> _r [g mol ⁻¹]	674.63	861.84	630.15
Temperature (K)	100	301	100
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> na2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	13.486(2)	19.725(4)	16.5262(11)
<i>b</i> [Å]	13.909(3)	9.683(2)	13.0711(6)
<i>c</i> [Å]	14.582(3)	40.215(8)	13.3390(7)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	90	90	109.949(2)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	2735.3(9)	7681(3)	2708.5(3)
<i>Z</i>	4	8	4
<i>D</i> _{calcd.} [g cm ⁻³]	1.638	1.491	1.545
<i>F</i> (000)	1380	3560	1312
Theta range for data collection [°]	2.5 to 28.0	2.0 to 27.5	2.8 to 65.7
Reflections collected	17319	46889	19499
Independent reflections	6490	15763	4573
Data/parameters/restraints	6490/352/21	15763/945/927	4573/338/0
GoF	1.01	1.01	1.14
<i>R</i> ₁ ^[a] [<i>I</i> > 2σ(<i>I</i>)]	0.0391	0.0803	0.059
<i>wR</i> ₂ ^[b] [<i>I</i> > 2σ(<i>I</i>)]	0.0927	0.2068	0.155
Residual peak/hole (e Å ⁻³)	0.73 and -0.42	2.57 and -1.40	1.94 to -0.84

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

monitored at 538 nm. The reaction followed first order kinetics and the first order rate constant, k_{obs} , was obtained by nonlinear least-squares fits of the A_t vs. t data with the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-kt)$, where A_0 and A_∞ are the initial and final absorbance values, respectively.

ESI-MS Measurements: ESI-MS experiments were performed with a hybrid Q-ToF mass spectrometer (Q-STAR XL, Applied Biosystems). For the experiments, micromolar solutions of **1** in MeCN were freshly prepared and were introduced to the ESI source through a capillary fitted with a syringe pump (ca. 5 μ L min⁻¹). Nitrogen was the nebulizing gas. For CID at low collision energies, the ions of interest were mass selected in Q1, interact with argon (collision gas) in the quadrupole under nearly single collision conditions, which are typically 2×10^{-4} mbar, and with adjustable collision energy ($E_{lab} = 0$ –15 eV). The collision energy in the center-of-mass frame (E_{cm}) was determined by $E_{cm} = E_{lab} [m_c/(m_c + m_i)]$, where E_{lab} = kinetic energy of the ion that is provided by the electric fields in the mass spectrometer, m_c = mass of the collision gas atom, and m_i = mass of the ion.

Calculations: Full geometry optimizations of the title compounds were carried out with the BP86 (Becke exchange^[31] and Perdew correlation^[32]) functional and an uncontracted triple- ζ Slater-type orbital, including two sets of polarization functions as the basis sets (TZ2P), for all the atoms. The zero order regular approximation (ZORA)^[33] was adopted in all calculations to account for the scalar relativistic effect. The energy gradient convergence criterion was set to 10^{-4} au during optimizations. All DFT calculations were executed with the Amsterdam Density Functional (ADF 2008.01) program.^[34] PBE0 functional^[35] with the cooperation of the basis set def2-TZVP were employed to conduct single-point calculations for NBO analyses (with NBO 5.0^[36]), and these calculations were accomplished with the Gaussian 03 program suite.^[37]

Supporting Information (see footnote on the first page of this article): Figure showing the different configurations of the four methyl groups of the 14-TMC ligand in trans-[Ru^V(14-TMC)(N)(N₃)]⁺.

Acknowledgments

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