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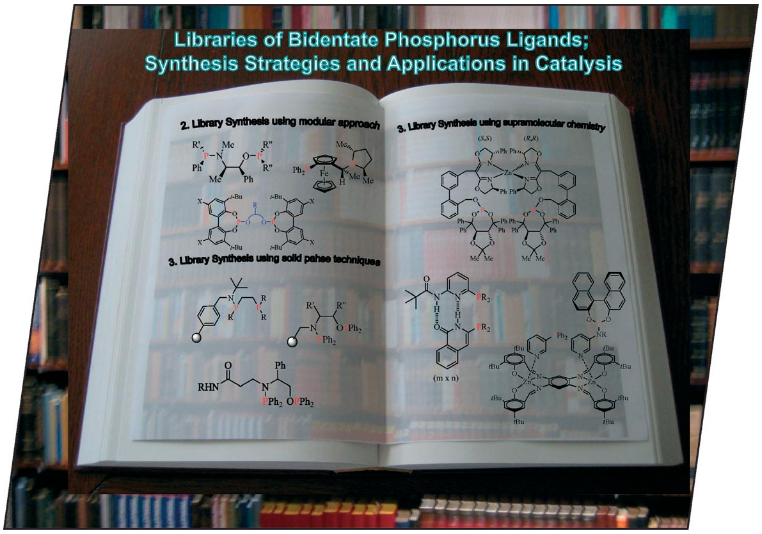
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows structures that represent three different ways of making phosphorus-based ligand libraries: modular synthesis, solid-phase synthesis and formation of ligands by assembly of smaller building blocks. These ligand libraries are important for the rapid identification of new catalysts for (asymmetric) conversions. In this Microreview on p. 2939 ff. J. N. H. Reek et al. show examples that illustrate these strategies.



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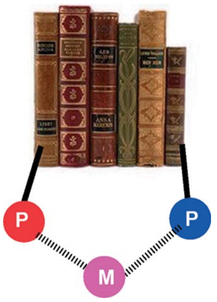
MICROREVIEW

Ligand Libraries

P. E. Goudriaan, P. W. N. M. van Leeuwen, M.-N. Birkholz, J. N. H. Reek* 2939–2958

Libraries of Bidentate Phosphorus Ligands; Synthesis Strategies and Application in Catalysis

Keywords: Ligand libraries / P ligands / Chelates / Supramolecular chemistry / Combinatorial chemistry / Asymmetric catalysis



The identification of suitable metal catalysts often translates directly to finding a proper ligand, which is enormously facilitated by the availability of ligand libraries. Bidentate P ligands are an important class the development of which is still challenging. In this review we discuss divergent synthesis, supported synthesis, and self-assembly as strategies to get ligand libraries.

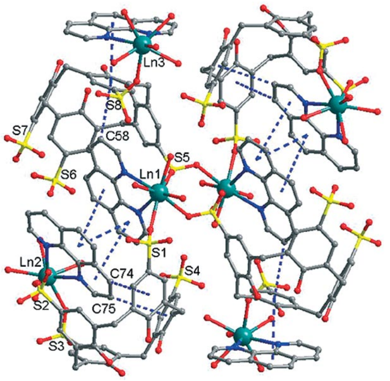
SHORT COMMUNICATIONS

Calixarene Bicapsules

W. Liao,* Y. Bi, S. Gao, D. Li, H. Zhang,* R. Dronskowski 2959–2962

Lanthanide-Hinged Calixarene Bicapsules: Discrete Hexanuclear Ln^{III}/Phenanthroline/*p*-Sulfonatocalix[4]arene Oligomers (Ln = Gd, Tb)

Keywords: Rare earths / Calixarenes / Supramolecular chemistry / Hydrothermal synthesis / Crsytal growth



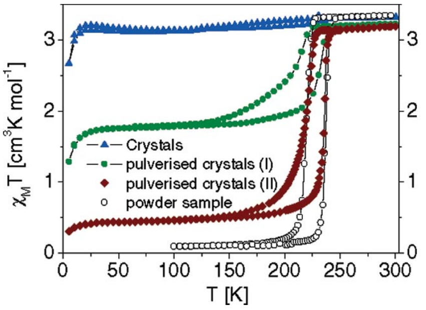
Two novel Ln^{III}–C4AS compounds have been synthesized, which contain the rarely reported Ln^{III}-hinged calixarene bicapsules. The Gd-containing sample exhibits a very weak antiferromagnetic interaction between the Gd^{3+} ions and the Tb-containing sample shows a characteristic Tb-centered luminescence, which indicates an efficient energy transfer from the calixarene unit to the Tb^{3+} ion.

Hysteresis Induced by Grinding

B. Weber,* E. S. Kaps, C. Desplanches, J.-F. Létard 2963–2966

Quenching the Hysteresis in Single Crystals of a 1D Chain Iron(II) Spin Crossover Complex

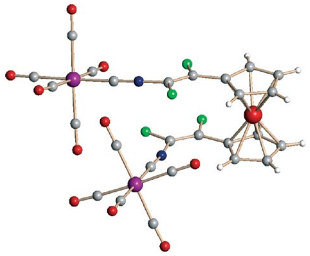
Keywords: Iron / N,O ligands / Magnetism / Solvent effects



For a 1D chain iron(II) complex unusual grinding effects are observed. The origin of those effects is investigated using magnetic measurements, X-ray powder diffraction and optical reflectivity studies.

Functionalized Cp Complexes

A highly efficient synthesis of fluorinated alkenyl isocyanide complexes with organometallic substituents is described. As long as the lithium organic substance, like for example 1,1′-dilithioferrocene, can be prepared there seems to be no limitations in the utility of this method. In the disubstituted ferrocene derivative the bulky substituents are in an almost eclipsed position.

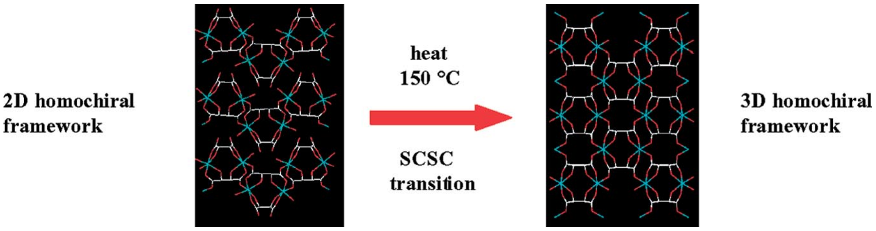


D. Lentz,* M. Mujkic,
S. Roth **2967–2970**

C–C Coupling Reactions of Pentacarbonyl(trifluoroethenyl isocyanide)chromium with Cyclopentadienyl Complexes

Keywords: Fluorine / Organometallic / Isocyanide / Cyclopentadienyl complexes / C–C coupling

Homochiral Coordination Polymers



A rare single crystal to single crystal (SCSC) transformation assisted by hydrogen bonding was induced thermally. A 2D homochiral coordination polymer $\{[Ni_2(\text{L-tar})_2(H_2O)_2](H_2O)_3\}_\infty$ was irreversibly converted into a 3D homochiral coordination polymer $\{Ni(\text{L-tar})\}_\infty$, and the structure was confirmed by X-ray crystallography and XRD.

P. Zhu, W. Gu, L.-Z. Zhang, X. Liu,*
J.-L. Tian, S.-P. Yan **2971–2974**

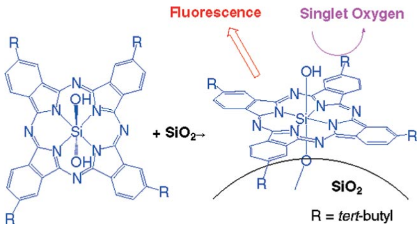
A Rare Thermally Induced Single Crystal to Single Crystal Transformation from a 2D Chiral Coordination Polymer to a 3D Chiral Coordination Polymer

Keywords: Crystal engineering / Coordination modes / Polymers

FULL PAPERS

Photoactive-Solid Phthalocyanines

Photophysical properties and surface structures of silica-gel-supported photofunctional (phthalocyaninato)silicon complexes ($SiPc\text{-}SiO_2$) have been investigated. By changing the amount of SiPcs, we have succeeded in preparing solid materials based on Pc complexes having both monomeric photophysical properties and a high ability for singlet-oxygen generation.



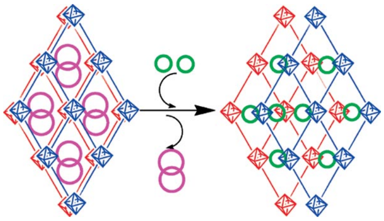
K. Ishii,* Y. Kikukawa, M. Shiine,
N. Kobayashi,* T. Tsuru, Y. Sakai,
A. Sakoda **2975–2981**

Synthesis and Photophysical Properties of Silica-Gel-Supported Photofunctional (Phthalocyaninato)silicon Complexes

Keywords: Phthalocyanine / Singlet oxygen / Photochemistry / Silica gel

Solvent-Mediated Ion Exchange

In the presence of different cations, 2D cluster-based coordination polymers can undergo ion-exchange and structural transformations through a solvent-mediated mechanism



J.-J. Zhang, Y. Zhao, S. A. Gamboa,
M. Muñoz, A. Lachgar* **2982–2990**

Solvent-Mediated Ion Exchange and Structural Transformations of Cluster-Based Coordination Polymers

Keywords: Cluster compounds / Metal *salen* complexes / Coordination polymers / Structural modification / Self-assembly

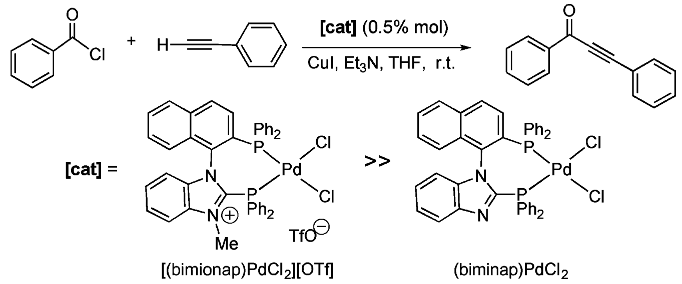
CONTENTS

Proximally Cationic Ligands

N. Debono, Y. Canac,* C. Duhayon, R. Chauvin* **2991–2999**

An Atropo-Stereogenic Diphosphane Ligand with a Proximal Cationic Charge: Specific Catalytic Properties of a Palladium Complex Thereof

Keywords: Cations / Donor character / Phosphane ligands / Homogeneous catalysis / Palladium



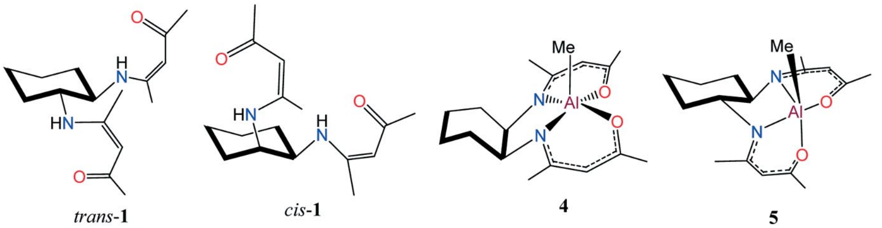
The P-conjugated cationic charge does not suppress the coordinating character of the hybrid bimionap ligand. This feature was shown to induce specific catalytic properties (with respect to its neutral biminap analogue) in Sonogashira-type coupling reactions.

Bis(ketiminato)aluminum Complexes

C. Huang, L.-F. Hsueh, P. Kuo, H. M. Lee, C. Uno, J. Huang,* C.-Y. Tu, C.-H. Hu,* G. Lee, C. Hung **3000–3008**

Aluminum Complexes Containing Cyclohexane-1,2-diyl Linked Bis(ketiminato) Ligands and Proton-Promoted Demethylation

Keywords: Aluminum / Bis(ketiminato) ligands / Diaminocyclohexane / Demethylation



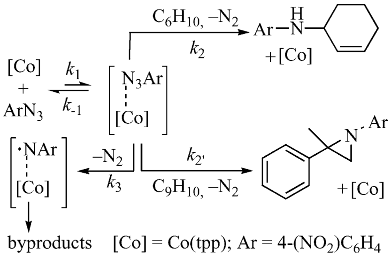
A series of cyclohexane-1,2-diyl linked bis(ketiminato)aluminum complexes containing cyclohexane-1,2-diyl linked bis(ketiminato) ligands were synthesized, and their subsequent reactions were also studied.

Mechanism of Amination

A. Caselli, E. Gallo, S. Fantauzzi, S. Morlacchi, F. Ragaini, S. Cenini* **3009–3019**

Allylic Amination and Aziridination of Olefins by Aryl Azides Catalyzed by Co^{II}(tpp): A Synthetic and Mechanistic Study

Keywords: Cobalt / Porphyrinoids / Azides / Homogeneous catalysis / C–H activation



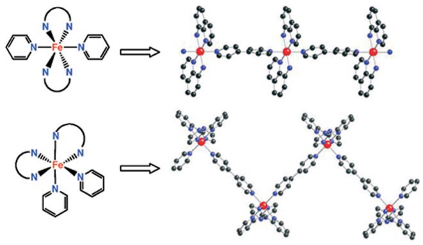
Co^{II}(tpp) catalyzes the reaction of aromatic azides with nonactivated olefins to yield allylic amines or aziridines in moderate-to-good yields. The reaction mechanism was investigated and found to proceed through reversible coordination of the aryl azide to the Co^{II}–porphyrin complex. The often postulated "nitrene" complex is not an intermediate in this reaction.

Spin-Crossover Polymers

B. Le Guennic, G. S. Matouzenko, S. A. Borshch* **3020–3023**

Topology of Spin-Crossover Polymers and Mutual Influence of Ligands

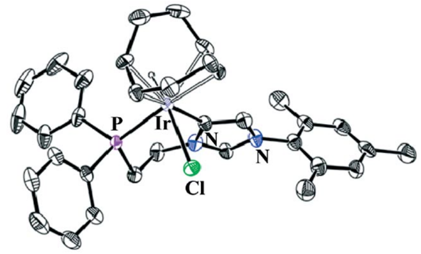
Keywords: N ligands / Coordination modes / Chain structures / Density functional calculations / Spin crossover



Density functional calculations demonstrate that the structure of spin-crossover polymers is determined by the Fe^{II} ion coordination mode, which is dependent on the metal–ligand π-interactions.

(Carbene)iridium Complexes

Phosphane–imidazolium salts added to the iridium complex [Ir(COD)(μ-Cl)]$_2$ without the need of a base and led to hydridoiridium(III) complexes containing "abnormal" carbene ligands, through C–H insertion at the C5 position of the imidazolium ring.



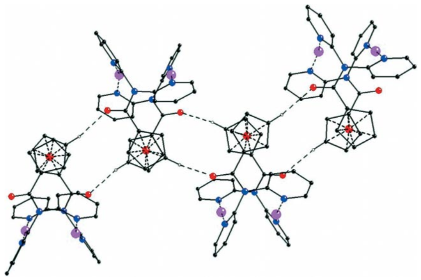
J. Wolf, A. Labande,* J.-C. Daran, R. Poli* **3024–3030**

Reactivity of Phosphane–Imidazolium Salts Towards [Ir(COD)Cl]$_2$: Preparation of New Hydridoiridium(III) Complexes Bearing Abnormal Carbenes

Keywords: Carbenes / Phosphane ligands / Iridium / Hydrides / C–H activation

Bis(pyridyl)amino–Ferrocene Ligands

The synthesis and complexation properties of {[bis(2-pyridyl)amino]carbonyl}ferrocene and 1,1′-bis{[bis(2-pyridyl)amino]carbonyl}ferrocene ligands have been studied. The structures show the formation of supramolecular arrays through hydrogen bonding.

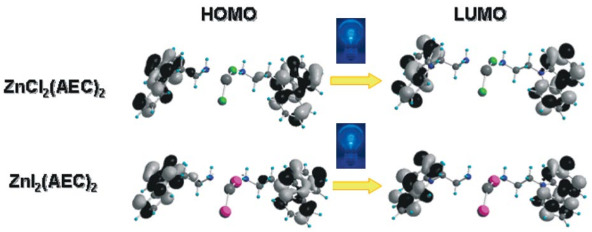


J. E. Aguado, O. Crespo, M. C. Gimeno,* P. G. Jones, A. Laguna, Y. Nieto **3031–3039**

Metal Complexes with Mono- and Bis{[bis(2-pyridyl)amino]carbonyl}ferrocene Ligands

Keywords: Gold / Silver / Copper / Sandwich complexes / N ligands

Hybrid Materials



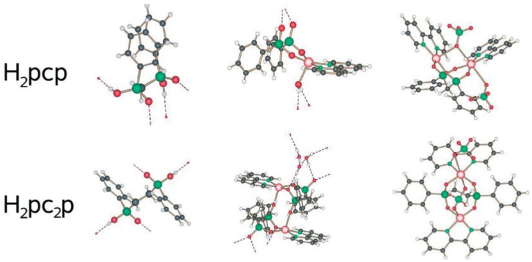
The organic–inorganic hybrid materials $ZnCl_2(AEC)_2$ (**1**), $ZnI_2(AEC)_2$ (**2**), $CdI_2(AEC)_2$ (**3**), and $HgI_2(AEC)_2$ (**4**) were synthesized. The crystal structures of **1**·CH_3CN and **2**·CH_3CN reveal quasi-1D inorganic frameworks. The optical energy gaps of these materials are influenced by the AEC ligands; compounds **1**, **2**, and **3** give deep-blue emissions from the AEC ligands, whereas **4** does not emit light.

W. Wang, J. Qiao,* G. Dong, L. Wang, L. Duan, D. Zhang, Y. Qiu* **3040–3045**

Metal Halide/N-Donor Organic Ligand Hybrid Materials with Confined Energy Gaps and Emissions

Keywords: Organic–inorganic hybrid composites / Halides / Luminescence

Phosphinate Complexes



The structures of a series of Cu^{II}-(2,2′bipy) complexes with two closely related diphosphinates $[O_2(Ph)P{-}alkyl{-}P\{Ph(O_2)\}]^{2-}$ have been analyzed together with those of the corresponding diphosphinic acids. The different conformations adopted by the diphosphiante groups as a result of the alkyl chain elongation account for the remarkably different steric arrangements of the corresponding Cu complexes.

F. Costantino, A. Ienco,* S. Midollini, A. Orlandini, L. Sorace, A. Vacca **3046–3055**

Copper(II) Complexes with Bridging Diphosphinates – The Effect of the Elongation of the Aliphatic Chain on the Structural Arrangements Around the Metal Centres

Keywords: Copper complexes / Diphosphinates / Bridging ligands / Magnetic properties

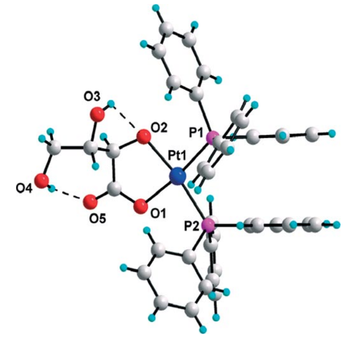
CONTENTS

Platinum Threonate

P. Bergamini,* E. Marchesi, A. Marchi,
V. Bertolasi, M. Fogagnolo,
A. Canella .... 3056−3061

Formation of L-Threonic Acid from L-Ascorbic Acid Oxidative Ring Opening and its Coordination to Pt^{II}: X-ray Crystal Structures of $[Pt(threonato\text{-}O,O')(PPh_3)_2]$ and $[Pt(oxalato)(PPh_3)_2]$

Keywords: Threonic acid / Ascorbic acid / Platinum / Antitumor agents



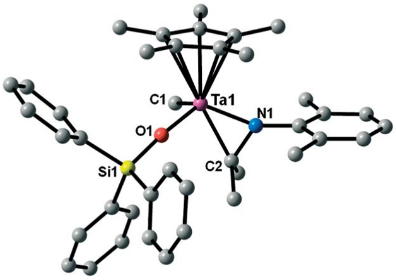
The ring opening induced by atmospheric molecular oxygen in a basic solution of L-ascorbic acid produced oxalic and L-threonic acid. The reactions of these acids with the carbonate complex $[Pt(CO)_3\text{-}(PPh_3)_2]$ yielded $[Pt(oxalato)(PPh_3)_2]$ and the new complex $[Pt(threonato\text{-}O,O')\text{-}(PPh_3)_2]$, respectively. The X-ray crystal structures of both complexes were determined.

Tantalum Siloxides

A. Conde, R. Fandos,* A. Otero,*
A. Rodríguez, P. Terreros .... 3062−3067

Synthesis and Reactivity of Monocyclopentadienyltantalum(V) Siloxide Complexes

Keywords: Cyclopentadienyl ligands / Tantalum / Silicon



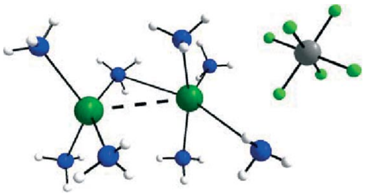
We report the reactivity of tantalum complexes containing a siloxide group as an ancillary ligand with several unsaturated organic molecules such as isocyanides or carbon monoxide.

Reactive Fluoride Route

W. Meng, F. Kraus* .... 3068−3074

Crystal Structures of $Ag_2ZrF_6{\cdot}8NH_3$ and $Ag_2HfF_6{\cdot}8NH_3$ and Their Synthesis by the "Reactive Fluoride Route" in Liquid Ammonia

Keywords: Structure elucidation / Fluorides / Liquid ammonia / Zirconium / Hafnium / Silver / Ammoniates



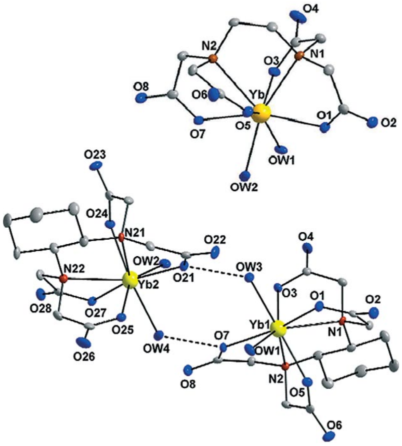
The ionic fluorides $Ag_3M_2F_{14}$ (M = Zr, Hf) react with liquid ammonia. The Ag^{II} ions of the starting materials are reduced to Ag^{I}, and all coordination polyhedra completely rearrange and form the new fluoride ammoniates $Ag_2MF_6{\cdot}8NH_3$ (M = Zr, Hf), which feature argentophilic interactions previously unknown in fluorides. The reduction of Ag^{II} to Ag^{I} and the high solution enthalpy of Ag^{I} enable this reaction.

Structure of Yb^{3+} Complexes

R. Janicki, P. Starynowicz,
A. Mondry* .... 3075−3082

Complexes of Yb^{3+} with EDTA and CDTA − Molecular and Electronic Structure

Keywords: X-ray diffraction / Absorption / Density functional calculations / N,O ligands / Ytterbium



Spectroscopic results revealed high sensitivity of the electronic $4f^{13}$ configuration of Yb^{3+} complexes upon minor changes in the coordination geometry around the Yb centre, and theoretical calculations proved the complicated character of the charge-transfer transition (Yb → ligand and ligand → Yb).

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* Author to whom correspondence should be addressed.

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