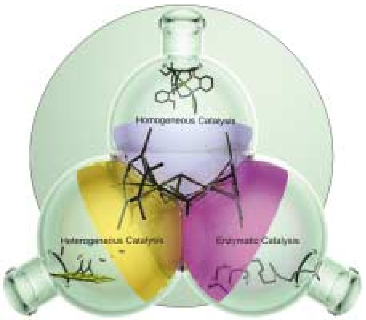
COVER PICTURE



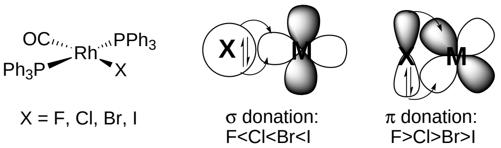
The cover picture shows a representation of supramolecular cluster catalysis, which is commonly regarded as a field lying at the interface of homogeneous and heterogenous catalysis. Homogeneous catalysis is epitomized by Halpern's elucidation of the molecular details of the enantioselective hydrogenation of prochiral alkenes (top flask) catalyzed by a rhodium diphosphane complex. The three-way catalyst is the emblem of heterogeneous catalysis (left flask). The central structure depicts a cluster capable of hydrogenating aromatic substrates under mild biphasic conditions. Most interestingly, the mechanism relies solely on hydrophobic interactions between the catalyst and the substrate. Such weak contacts are reminiscent of enzymatic catalysis as exemplified by triterpene cyclases, which convert squalenes into steroid precursors (right flask). The system described thus lies at the interface of enzymatic, homogeneous, and heterogeneous catalysis. Further details are reported by Süss-Fink et al. on p. 99 ff.

REVIEWS

K. Fagnou, M. Lautens* 26–47

Halide Effects in Transition Metal Catalysis

Tuning catalysts: varying the halide moiety represents a valuable method of tuning the reactivity and selectivity of halide-containing metal complexes. The differences observed are a product of the steric and electronic properties of the halide ligand which has the ability to donate electron density to the metal center in a predictable manner (see picture). This review discusses the physical properties of various halide–metal complexes and the effect of varying the halide in various transition metal promoted processes. An understanding of the changes that can arise leads to the notion that the metal–halide moiety can be used as a tunable functionality in the design of better transition metal catalyzed reactions.



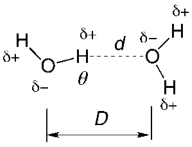
Angew. Chem. **2002**, *114*, 26–49

Keywords: asymmetric synthesis · halogens · homogeneous catalysis · ligand effects · transition metals

T. Steiner* 48–76

The Hydrogen Bond in the Solid State

A difficult dividing line: The hydrogen bond is the most important of all the directional intermolecular interactions (see picture). It is understood from modern bonding concepts as a very broad phenomenon with open borders to other interactions, such as covalent bonding, ionic, cation–π, and van der Waals interactions. There are dozens of different types of $X{-}H\cdots A$ hydrogen bonds (A = acceptor) with dissociation energies that span more than two orders of magnitude. This review brings together the research of the last ten years on hydrogen bonds, particularly in the solid state.



Angew. Chem. **2002**, *114*, 50–80

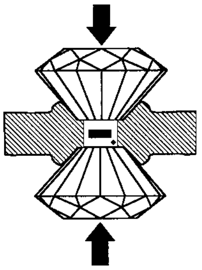
Keywords: donor–acceptor systems · electrostatic interactions · hydrogen bonds · noncovalent interactions · proton transfer

MINIREVIEW

E. Kroke* 77–82

High-Pressure Syntheses of Novel Binary Nitrogen Compounds of Main Group Elements

Putting nitrogen under pressure: The application of high-pressure techniques (for example the depicted diamond anvil cell) allows the synthesis of numerous new materials with useful properties. Recent examples include diazenides, that is, compounds with N_2^{2-} ions (autoclave techniques), γ-P_3N_5, the first compound with tetragonal PN_5 pyramids (multianvil press), as well as spinel-Si_3N_4, a promising hard ceramic material (shock-wave methods).



Angew. Chem. **2002**, *114*, 81–86

Keywords: high-pressure chemistry · main group elements · nitrides · nitrogen · phase transitions

ESSAYS

Chemistry—recipes for success in the kitchen: Molecular gastronomy is the part of food science that investigates culinary processes, such as the formation of the two cheese soufflés shown. It is a multidisciplinary approach involving mainly chemistry and physics. Its five main aims are discussed and recent results are given.

Angew. Chem. **2002**, *114*, 87 – 92

H. This* .... 83 – 88

Molecular Gastronomy

Keywords: culinary processes · every-day chemistry · food science · molecular gastronomy

HIGHLIGHT

Nucleic acids direct chemical reactions. Recent examples of DNA-templated synthesis suggest that DNA can direct various chemical reactions sequence-specifically and independent of distance in a surprisingly general manner.

Angew. Chem. **2002**, *114*, 93 – 95

D. Summerer, A. Marx* .... 89 – 90

DNA-Templated Synthesis: More Versatile than Expected

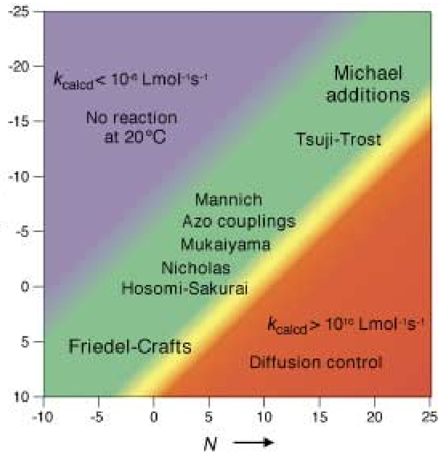
Keywords: chemical ligation · DNA · oligonucleotides · supramolecular chemistry · template synthesis

VIPs

The following communications are “Very Important Papers” in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Gold – Xenon Complexes	T. Drews, S. Seidel, K. Seppelt*	
Iron-Catalyzed Polyethylene Chain Growth on Zinc: Linear α-Olefins with a Poisson Distribution	G. J. P. Britovsek, S. A. Cohen, V. C. Gibson,* P. J. Maddox, M. van Meurs*	
The Uronium/Guanidinium Peptide Reagents: Finally the True Uronium Salts	L. A. Carpino,* H. Imazumi, A. El-Faham, F. J. Ferrer, C. Zhang, Y. Lee, B. M. Foxman, P. Henklein, C. Hanay, C. Mügge, H. Wenschuh, J. Klose, M. Beyermann, M. Bienert	
Expanding Divalent Organolanthanide Chemistry: The First Organothulium(II) Complex and the In Situ Organodysprosium(II) Reduction of Dinitrogen	W. J. Evans,* N. T. Allen, J. W. Ziller	◆
Nonrelaxable Anisotropic Organization of Organic-Inorganic Hybrid Materials Induced by an Electric Field	G. Cerveau, R. J. P. Corriu,* E. Framery, S. Ghosh, M. Nobili	
Self-Assembled, Deterministic Carbon Nanotube Wiring Networks	M. R. Diehl, S. N. Yaliraki, R. A. Beckman, M. Barahona, J. R. Heath*	◆

A nucleophilicity scale has been developed that covers 30 orders of magnitude from simple arenes to stabilized carbanions (see picture). Amazingly, the addition of an electrophilicity parameter E and a nucleophilicity parameter N is sufficient to predict semiquantitatively the rates of a large variety of organic reactions.



Angew. Chem. **2002**, *114*, 97 – 102

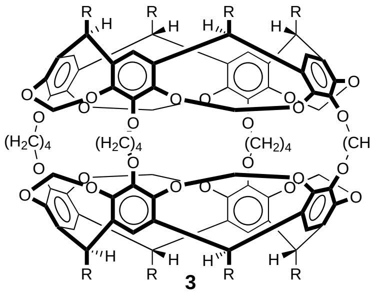
R. Lucius, R. Loos, H. Mayr* . . . 91 – 95

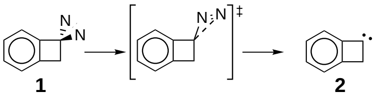
Kinetic Studies of Carbocation – Carbanion Combinations: Key to a General Concept of Polar Organic Reactivity

Keywords: electrophilic addition · linear free-energy relationships · Michael addition · reaction kinetics · substituent effects

---

Incarceration strongly increases the rate of the thermal decomposition of diazirine **1** to yield carbene **2**. The increase of the inner phase rate is rationalized by a stabilization of the transition state through dispersion interactions between the breaking C–N bonds and one of the highly polarizable arene rings of the surrounding host **3**.


3


1 inner phase of **3** **2**

Angew. Chem. **2002**, *114*, 102 – 105

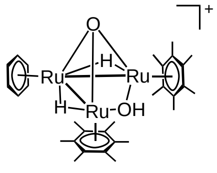
R. Warmuth,* J.-L. Kerdelhué, S. Sánchez Carrera, K. J. Langenwalter, N. Brown . . . . 96 – 99

Rate Acceleration through Dispersion Interactions: Effect of a Hemicarcerand on the Transition State of Inner Phase Decompositions of Diazirines

Keywords: dispersion interactions · hemicarcerands · host – guest systems · molecular container · transition states

---

At the interface of homogeneous, heterogeneous, and enzymatic catalysis is the catalytic hydrogenation of benzene to give cyclohexane by the triruthenium cluster **1**. Experimental evidence and molecular modeling studies strongly support a catalytic mechanism in which the aromatic substrate is hydrogenated in the hydrophobic pocket spanned by the three η^6-bound arene ligands without being coordinated to a Ru center.


1

Angew. Chem. **2002**, *114*, 105 – 108

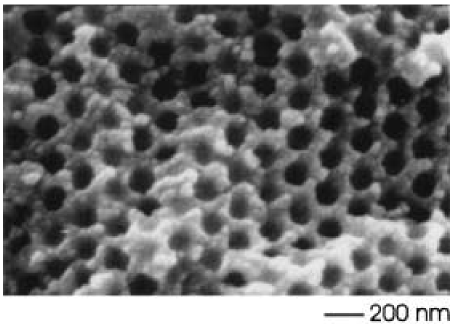
G. Süss-Fink,* M. Faure, T. R. Ward . . . . 99 – 101

Supramolecular Cluster Catalysis: Benzene Hydrogenation Catalyzed by a Cationic Triruthenium Cluster under Biphasic Conditions

Keywords: biphasic catalysis · cluster compounds · host – guest systems · hydrogenation · supramolecular chemistry

---

Mesoporous silver with a three-dimensional periodic structure has been prepared electrochemically (see picture) starting from colloidal crystals immobilized in a hydrogel. In this new process it is possible to tune both the size of the enclosures and the thickness of the walls between the enclosed particles in the mesoscale ordered material.



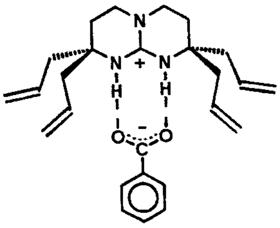
Angew. Chem. **2002**, *114*, 108 – 110

C. Lellig, W. Härtl, J. Wagner, R. Hempelmann* . . . . 102 – 104

Immobilized Highly Charged Colloidal Crystals: A New Route to Three-Dimensional Mesoscale Structured Materials

Keywords: colloids · gels · mesoporous materials · nanostructures · self-assembly

Lock-and-key binding is an inadequate description for the molecular-recognition interaction of guanidinium cations and carboxylates in acetonitrile (see picture) as shown by direct calorimetric determinations in a tailored series of host–guest pairs.



Angew. Chem. **2002**, *114*, 111–114

M. Haj-Zaroubi, N. W. Mitzel,
F. P. Schmidtchen* 104–107

The Rational Design of Anion Host Compounds: An Exercise in Subtle Energetics

Keywords: bond enthalpy · calorimetry · host–guest systems · molecular recognition · nitrogen heterocycles

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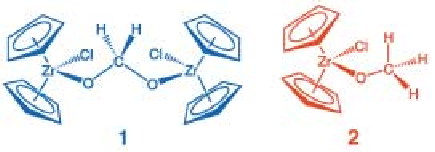
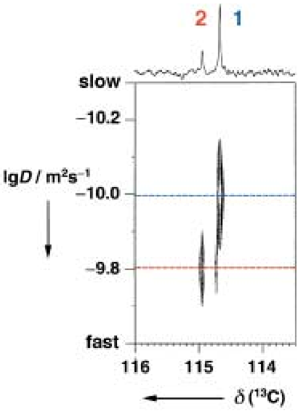
A new tool for the investigation of reaction intermediates: By using DOSY NMR spectroscopy, the presence of a binuclear complex **1** as the key intermediate on the way to **2** (see spectrum) was detected for the first time in the title reaction.





Angew. Chem. **2002**, *114*, 114–116

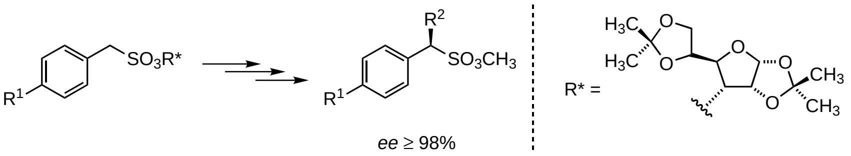
N. E. Schlörer, E. J. Cabrita,
S. Berger* 107–109

Characterization of Reactive Intermediates by Diffusion-Ordered NMR Spectroscopy: A Snapshot of the Reaction of $^{13}CO_2$ with $[Cp_2Zr(Cl)H]$

Keywords: diffusion · intermediates · NMR spectroscopy · organometallic compounds

---

The right choice of sugar auxiliary led to a breakthrough in the first asymmetric α-alkylations of sulfonic acid esters (see scheme). The high asymmetric inductions were reached with 1,2:5,6-di-*O*-isopropyliden-α-D-allofuranose as the auxiliary group, which can be cleaved off again under mild conditions. Enantiopure α-substituted methyl sulfonates are important building blocks and precursors of bioactive compounds.



Angew. Chem. **2002**, *114*, 116–119

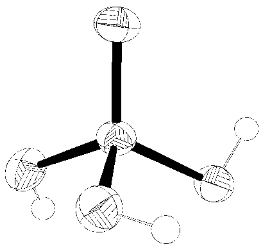
D. Enders,* N. Vignola, O. M. Berner,
J. W. Bats 109–111

The First Highly Efficient Asymmetric Synthesis of α-Substituted Methyl Sulfonates

Keywords: alkylation · asymmetric synthesis · carbohydrates · chiral auxiliaries · metalation · sulfonates

---

The complete protonation of sulfuric acid, one of the strongest acids, can be achieved with the superacid HF/SbF_5. The salt $H_3SO_4^+SbF_6^-$ is isolated at −78 °C from the reaction of the superacid with bis(trimethylsilyl) sulfate (the structure of the $D_3SO_4^+$ ion in the crystal of the analogous deuterium compound is depicted).



Angew. Chem. **2002**, *114*, 119–121

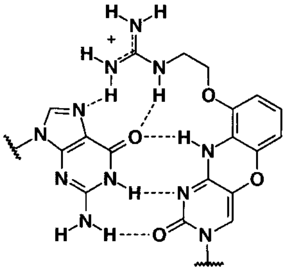
R. Minkwitz,* R. Seelbinder,
R. Schöbel 111–114

Protonated Sulfuric Acid: Preparation of Trihydroxyoxosulfonium Hexafluoroantimonate $H_3SO_4^+SbF_6^-$

Keywords: IR spectroscopy · protonation · sulfuric acid · superacids

Bound and clamped: A novel heterocyclic base modification, the guanidino G-clamp, is designed to allow two Hoogsteen-type hydrogen bonds to form between the amino and imino nitrogen atoms of a tethered guanidinium group to O6 and N7 of guanosine, which results in a total of five hydrogen bonds (broken lines, see picture). Details of a crystal structure at 1.0-Å resolution of a modified DNA decamer containing this guanidino G-clamp analogue demonstrate its mechanism of binding.

Angew. Chem. **2002**, *114*, 123–125



C. J. Wilds, M. A. Maier, V. Tereshko, M. Manoharan,* M. Egli* 115–117

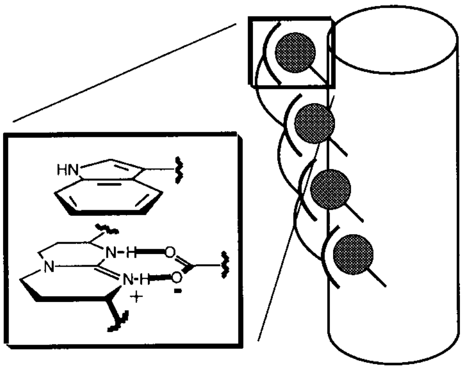
Direct Observation of a Cytosine Analogue that Forms Five Hydrogen Bonds to Guanosine: Guanidino G-Clamp

Keywords: antisense • DNA structures • hydrogen bonds • molecular recognition • X-ray crystallography

---

The relative position of the Asp and Trp residues in a peptide chain is important for recognizing a tetraguanidinium receptor through hydrogen bonding and cation–π interactions. The molecule not only binds with high affinity ($K_a = 1.1 \times 10^8\,\text{M}^{-1}$), it also stabilizes the helical conformation of the peptide (see schematic representation) as demonstrated by NMR and CD spectroscopy.

Angew. Chem. **2002**, *114*, 125–127



B. P. Orner, X. Salvatella, J. Sánchez Quesada, J. de Mendoza, E. Giralt, A. D. Hamilton* 117–119

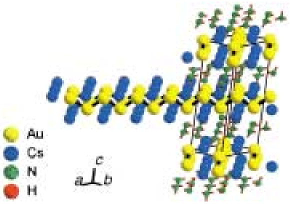
De Novo Protein Surface Design: Use of Cation–π Interactions to Enhance Binding between an α-Helical Peptide and a Cationic Molecule in 50% Aqueous Solution

Keywords: helical structures • host–guest systems • molecular recognition • NMR spectroscopy • noncovalent interactions

---

Treating CsAu with liquid NH_3 yields the deep blue ammoniate $CsAu\cdot NH_3$ (see picture and structure). The unusual electronic structure, as well as the properties, indicate that this unique compound, which behaves like an alkali metal when dissolved in ammonia, may serve as a guide to a more thorough understanding of solvated electrons.

Angew. Chem. **2002**, *114*, 128–132

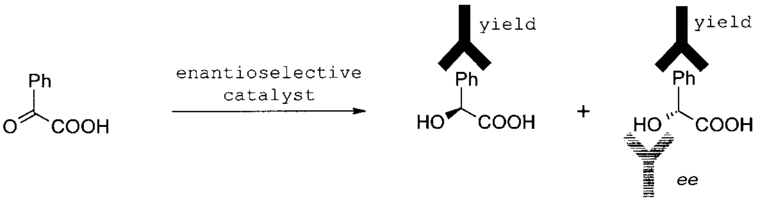


A.-V. Mudring, M. Jansen,* J. Daniels, S. Krämer, M. Mehring, J. P. Prates Ramalho, A. H. Romero, M. Parrinello 120–124

Cesiumauride Ammonia (1/1), $CsAu\cdot NH_3$: A Crystalline Analogue to Alkali Metals Dissolved in Ammonia?

Keywords: ammonia • cesium • gold • solvated electrons

More than 1000 yields and *ee* determinations are possible per day using an immunoassay. This highly efficient screening method is based on the remarkable binding specificity of antibodies. It has been employed in the development of straightforward procedures for the direct conversion of α-keto acids into chiral α-hydroxy acids, for which the enantioselective reduction of benzoyl formic acid to mandelic acid serves as a model reaction (see scheme).



Angew. Chem. **2002**, *114*, 132–135

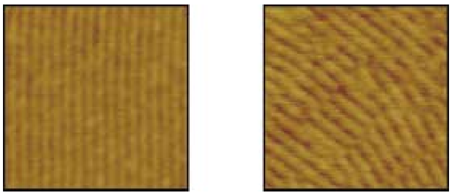
F. Taran, C. Gauchet, B. Mohar, S. Meunier, A. Valleix, P. Y. Renard, C. Créminon, J. Grassi, A. Wagner,* C. Mioskowski* 124–127

High-Throughput Screening of Enantioselective Catalysts by Immunoassay

Keywords: antibodies • asymmetric catalysis • combinatorial chemistry • high-throughput screening • reduction

1433-7851/02/4101-0009 $ 17.50+.50/0

Peptide length affects the size of the ridges observed in the atomic force microscopy (AFM) images of the Langmuir–Blodgett films of amphiphilic peptides: Well-ordered LB films can be prepared from a 14-residue amphiphilic peptide (left), while ordered LB films with a wider lattice (right) are obtained from an 18-residue peptide. The 100 nm × 100 nm images pictured were obtained by AFM using carbon nanotube tips.



Angew. Chem. **2002**, *114*, 135–138

E. T. Powers, S. I. Yang, C. M. Lieber,*
J. W. Kelly* 127–130

Ordered Langmuir–Blodgett Films of Amphiphilic β-Hairpin Peptides Imaged by Atomic Force Microscopy

Keywords: nanostructures · peptides · scanning probe microscopy · self-assembly · thin films

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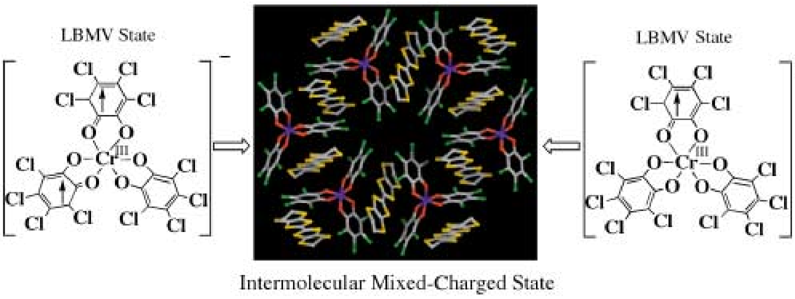
Coexistence of two kinds of ligand-based mixed-valence (LBMV) isomers is observed for the first time in the title compound (see scheme). Together with its mixed-charged state, the compound shows semiconducting behavior with an intermolecular ferromagnetic interaction, which is attributable to the association of five paramagnetic components in the crystal phase.



Angew. Chem. **2002**, *114*, 138–141

H.-C. Chang, S. Kitagawa* 130–133

An Unprecedented Mixed-Charged State in a Supramolecular Assembly of Ligand-Based Mixed-Valence Redox Isomers $(ET^{\bullet+})_3[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$

Keywords: chromium · donor–acceptor systems · magnetic properties · mixed-valent compounds · O ligands

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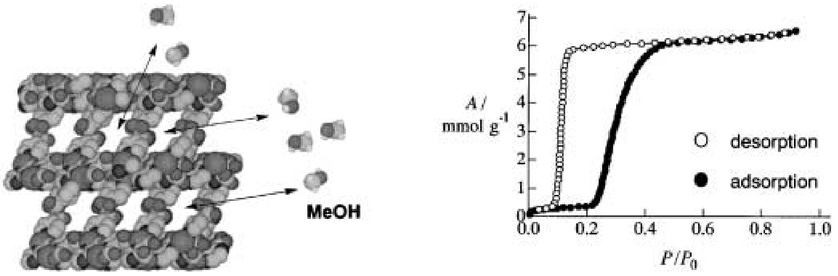
A hysteretic adsorption and desorption profile (right) accompanied by a transformation of the crystal structure is observed for the title coordination polymer, which possesses a pillared-layer structure (left), on exposure to H_2O or MeOH vapor under pressure.



Angew. Chem. **2002**, *114*, 141–143

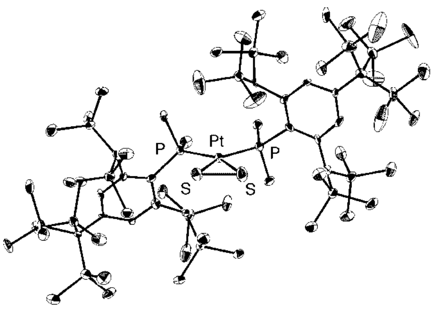
R. Kitaura, K. Fujimoto, S.-i. Noro,
M. Kondo, S. Kitagawa* 133–135

A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: $[Cu_2(pzdc)_2(dpyg)]_n$ (pzdc = Pyrazine-2,3-dicarboxylate; dpyg = 1,2-Di-(4-pyridyl)glycol)

Keywords: copper · crystal engineering · host–guest systems · hydrogen bonds · inclusion compounds · microporosity

---

Rings with platinum: The first platinum disulfur and diselenium complexes have been synthesized by taking advantage of new phosphane ligands bearing an extremely bulky substituent (see structure). The molecular structures of the disulfur and diselenium complexes are very similar, and these complexes, as well as an analogous dioxygen complex $[(PPh_3)_2PtO_2]$, have a square-planar geometry and a three-membered PtE_2 (E = S, Se) ring.



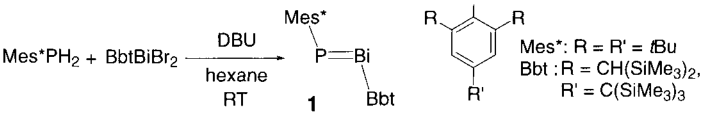
Angew. Chem. **2002**, *114*, 144–146

K. Nagata, N. Takeda,
N. Tokitoh* 136–138

The First Disulfur and Diselenium Complexes of Platinum: Syntheses and Crystal Structures

Keywords: metallacycles · platinum · P ligands · selenium · sulfur

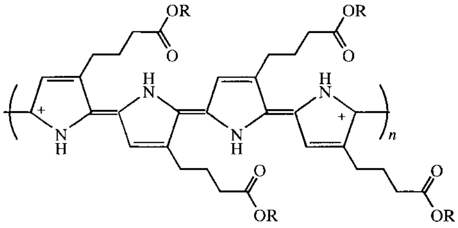
The exceedingly different size of p orbitals is overcome in the novel doubly bonded system between phosphorus and bismuth atoms that occurs in the first stable phosphabismuthene **1**. Compound **1** was obtained from the condensation reaction of Mes*PH_2 with an overcrowded dibromobismuthane by using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base (see scheme).



Angew. Chem. **2002**, *114*, 147–149

Keywords: bismuth • multiple bonds • phosphorus

Conducting films and pellets formed from *β*-substituted polypyrroles (see picture; R = H, CH_3) erode under aqueous conditions in a pH-dependent manner, which allows erosion rates to be tailored through differences in polymer side-chain structure. These conducting materials support the attachment, proliferation, and differentiation of primary human cells, and could lead to the use of conducting polymers in a variety of new biomedical applications.



Angew. Chem. **2002**, *114*, 149–152

Keywords: biomaterials • cell differentiation • conducting materials • polymers • polypyrroles

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Methylidyne, vinylidene, and ethylidyne on a surface: Inelastic neutron scattering (INS) vibrational spectroscopy is used to investigate the surface intermediate species formed during the decomposition of methane on Ru/Al_2O_3 and Ni/SiO_2 catalysts. The findings are compared to previous work on idealized single-crystal model catalysts and begin to bridge the gap between surface science and real-world catalysts in terms of the type of material and pressure used.

Angew. Chem. **2002**, *114*, 152–154

Keywords: heterogeneous catalysis • methane • nickel • reaction mechanisms • ruthenium • surface analysis

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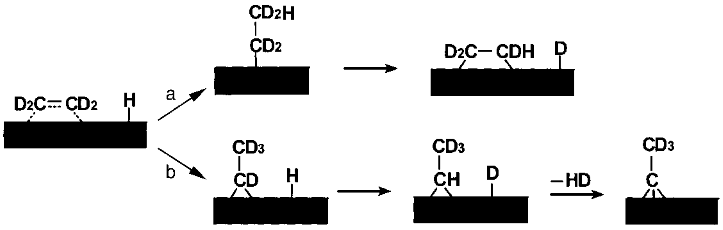
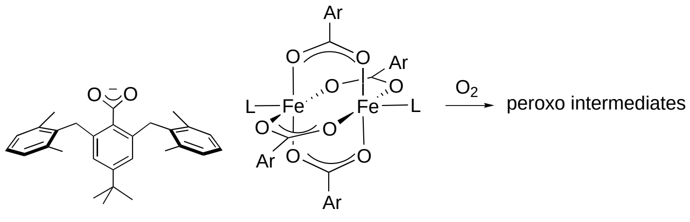
Ethylene on a surface: $C_2D_{4-x}H_x$ ($x = 0-4$) species that result from H/D exchange reactions on a Pt(111) surface are quantitatively identified by using a Cs^+ reactive ion scattering method (RIS). Two temperature-dependent pathways are identified for the exchange process (see scheme; a: $T < 265$ K; b: $T > 265$ K).



Angew. Chem. **2002**, *114*, 154–156

Keywords: H/D exchange • heterogeneous catalysis • platinum • reaction mechanisms • surface analysis

The structural influences of the supporting carboxylate ligand on biologically relevant Fe/O_2 chemistry are emphasized by the unusual Raman and Mössbauer spectroscopic properties of the intermediate derived from **1** relative to those of known (peroxo)diferric species. These (peroxo)diferric intermediates were generated from paddlewheel complexes (L = py, MeIm, and thf) of the new carboxylate $ArCO_2^-$ ligand on reaction with O_2. MeIm = 1-methylimidazole, py = pyridine.



$ArCO_2^-$

Angew. Chem. **2002**, *114*, 157–160

F. A. Chavez, R. Y. N. Ho, M. Pink,
V. G. Young, Jr., S. V. Kryatov,
E. V. Rybak-Akimova,* H. Andres,
E. Münck,* L. Que, Jr.,*
W. B. Tolman* 149–152

Unusual Peroxo Intermediates in the Reaction of Dioxygen with Carboxylate-Bridged Diiron(II,II) Paddlewheel Complexes

Keywords: bioinorganic chemistry · carboxylate ligands · iron · oxygen

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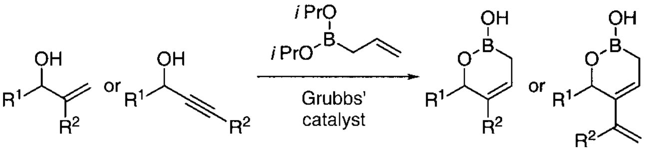
In only one to four steps, complex structures containing multiple rings, stereocenters, and unsaturated units have been prepared by employing a new annulation reaction of unsaturated boronic esters with allylic and propargylic alcohols (see scheme).



Angew. Chem. **2002**, *114*, 160–162

G. C. Micalizio,
S. L. Schreiber* 152–154

A Boronic Ester Annulation Strategy for Diversity-Oriented Organic Synthesis

Keywords: annulation · boronic esters · diversity-oriented synthesis · domino reactions · metathesis

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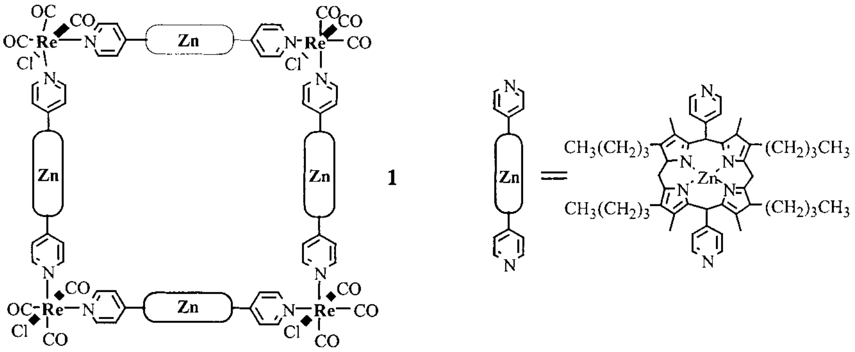
Micropatterned thin films of tailorable molecular materials with uniform, nanoscale cavities, such as **1**, were prepared by soft lithographic methods. In this form the materials readily diffract visible light, and because the efficiency of diffraction is enhanced by sorption of guest molecules, the diffraction response can be used for signal transduction in chemical-sensing applications.



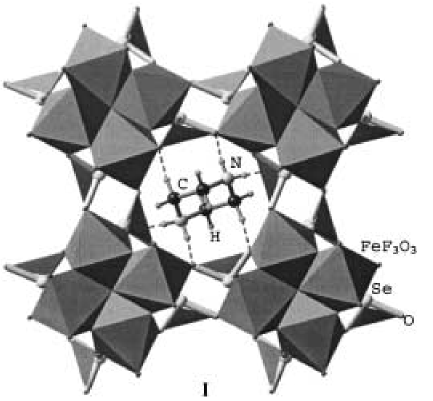
Angew. Chem. **2002**, *114*, 162–165

G. A. Mines, B.-C. Tzeng,
K. J. Stevenson, J. Li,
J. T. Hupp* 154–157

Microporous Supramolecular Coordination Compounds as Chemosensory Photonic Lattices

Keywords: microporous materials · patterning · sensors · supramolecular chemistry · thin films

One dimensional channels are formed in the three-dimensional open-framework iron selenite $[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$ (**I**), which was synthesized hydrothermally from $FeCl_3 \cdot 6H_2O$, HF, and SeO_2 in the presence of the organic amine piperazine. The same inorganic framework was also obtained with the amines diethylenetetramine, 1,3-diaminopropane, and ethylenediamine. Compound **I** displays unusual magnetic frustration behavior that is attributed to the tetrahedral geometry.



I

Angew. Chem. **2002**, *114*, 166–169

A. Choudhury, U. Kumar D,
C. N. R. Rao* 158–161

Three-Dimensional Organically Templated Open-Framework Transition Metal Selenites

Keywords: crystal growth · iron · magnetic properties · mesoporous materials · selenium

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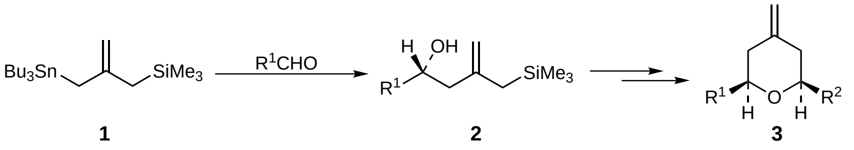
Useful tetrahydropyran units such as **3** can be prepared with high diastereoselectivity (d.r. > 30:1). A key step is the catalytic asymmetric allyl-transfer reaction from **1** to achiral aldehydes catalyzed by $[\{(R)\text{-binol}\}Ti^{IV}\{OCH(CF_3)_2\}_2]$ to give **2** (90–97% *ee*). A second allyl-transfer reaction from **2** to a carbonyl compound leads to **3**. binol = 2,2′-binaphthol.



Angew. Chem. **2002**, *114*, 169–171

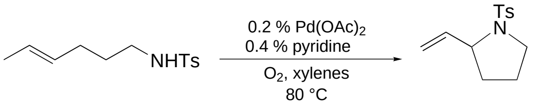
C.-M. Yu,* J.-Y. Lee, B. So,
J. Hong 161–163

Sequential Catalytic Asymmetric Allylic Transfer Reaction: Enantioselective and Diastereoselective Construction of Tetrahydropyran Units

Keywords: aldehydes · asymmetric catalysis · chirality · Lewis acids · titanium

---

Facile and efficient: a palladium-catalyzed intramolecular oxidative amination reaction [Eq. (1)] that uses molecular oxygen as a stoichiometric oxidant. These reactions require no cocatalyst for efficient reoxidation of the palladium, they operate in solvents ranging from heptane to dimethylsulfoxide, and achieve up to 250 turnovers (TO) and rates of 70 TO h^{-1}.



(1)

Angew. Chem. **2002**, *114*, 172–174

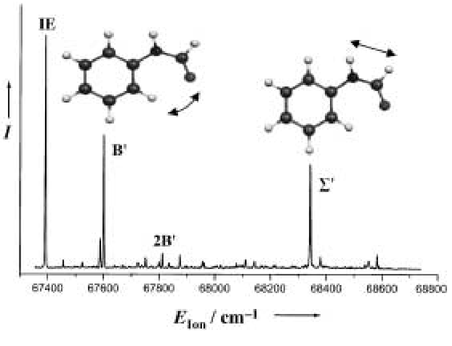
S. R. Fix, J. L. Brice,
S. S. Stahl* 164–166

Efficient Intramolecular Oxidative Amination of Olefins through Direct Dioxygen-Coupled Palladium Catalysis

Keywords: amination · homogeneous catalysis · oxidation · palladium · synthetic methods

---

Spectroscopic characterization of cationic amides: ZEKE photoelectron spectroscopy has been successfully applied to isomers of the model peptide formanilide. The spectra indicate that significant charge delocalization occurs from the aromatic ring to the side chain in the ion. The picture shows the spectrum of the *trans* isomer together with the side-chain in-plane bending and amide stretching modes that are associated with the B′ and Σ′ bands. IE = ionization energy.



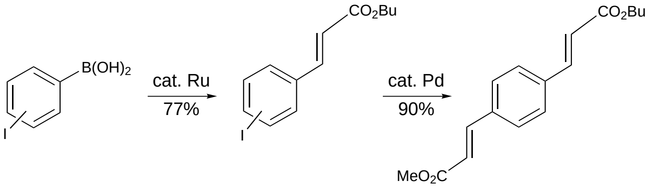
Angew. Chem. **2002**, *114*, 174–176

S. Ullrich, G. Tarczay, X. Tong,
C. E. H. Dessent,
K. Müller-Dethlefs* 166–168

ZEKE Photoelectron Spectroscopy of the *cis* and *trans* Isomers of Formanilide

Keywords: amides · cations · laser spectroscopy · photoelectron spectroscopy · ZEKE spectroscopy

Aryl boronic acids can undergo a Heck-type reaction catalyzed by Ru^{II} in the presence of Cu^{II}, which serves as a reoxidant in each cycle (see scheme, step 1). Compatibility with halide substituents offers attractive synthetic potential (step 2).



Angew. Chem. **2002**, *114*, 177–179

E. J. Farrington, J. M. Brown,*
C. F. J. Barnard, E. Rowsell ... 169–171

Ruthenium-Catalyzed Oxidative Heck Reactions

Keywords: boronic acids • Heck reaction • palladium • ruthenium • synthetic methods

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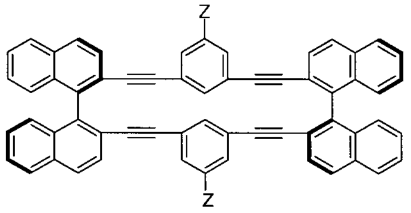
The "commercially available chirality" of the binaphthyl units and the efficiency of the coupling reactions were crucial to the synthesis of double-helical alkynyl cyclophanes **1** in enantiopure form. The unique properties of these molecules have been unambiguously confirmed by single-crystal X-ray structure analysis and CD spectroscopy.



1 Z = H, NO_2

Angew. Chem. **2002**, *114*, 179–181

D. L. An, T. Nakano, A. Orita,
J. Otera* 171–173

Enantiopure Double-Helical Alkynyl Cyclophanes

Keywords: alkynes • chirality • circular dichroism • cyclophanes • helical structures

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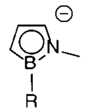
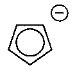
The substituent on boron allows the electronic nature of the heterocycle of *B*-heteroatom-substituted (R = H, O, S, N, P, and F) 1,2-azaborolyl complexes to be modulated. Given that 1,2-azaborolyl is isoelectronic with cyclopentadienyl (see scheme), one of the most widely used ligands in organometallic chemistry, it seems likely that the diverse array of compounds synthesized in this study will stimulate the development of applications of η^5-(1,2-azaborolyl) ligands in metal-catalyzed processes.



1,2-azaborolyl



cyclopentadienyl

Angew. Chem. **2002**, *114*, 182–184

S.-Y. Liu, M. M.-C. Lo,*
G. C. Fu* 174–176

1,2-Azaborolyls, Isoelectronic Analogues of the Ubiquitous Cyclopentadienyl Ligand: Synthesis of *B*-Heteroatom-Substituted 1,2-Azaborolyl Complexes and an Assessment of Their Electronic Features

Keywords: boron • cyclopentadienyl ligands • heterocycles • N ligands

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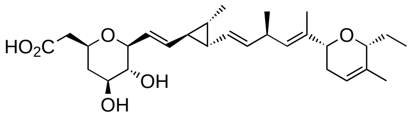
Highly stereoselective radical cyclization and olefin metathesis reactions for the construction of oxacyclic building blocks were key steps in the convergent total synthesis of the orally active antifungal agent ambruticin (**1**).



1 (+)-ambruticin

Angew. Chem. **2002**, *114*, 184–186

E. Lee,* S. J. Choi, H. Kim, H. O. Han,
Y. K. Kim, S. J. Min, S. H. Son, S. M. Lim,
W. S. Jang 176–178

Total Synthesis of Ambruticin

Keywords: antifungal agents • metathesis • natural products • radical reactions • total synthesis

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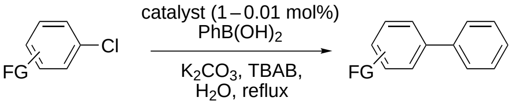
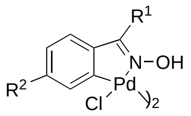
Refluxing water is a good solvent for the coupling reactions of aryl and heteroaryl chlorides with phenylboronic acid (see scheme; FG = functional group). The reactions use oxime-derived palladacycles **1** as thermally stable catalysts, potassium carbonate as base, and tetrabutylammonium bromide (TBAB), and can be carried out in the presence of air.





1

Angew. Chem. **2002**, *114*, 187–189

L. Botella, C. Nájera* 179–181

A Convenient Oxime-Carbapalladacycle-Catalyzed Suzuki Cross-Coupling of Aryl Chlorides in Water

Keywords: biaryls • C–C-coupling • cross-coupling • palladium • phase-transfer catalysis

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

* Author to whom correspondence should be addressed

The cover picture was generated by Thomas Ward and Christophe Thomas with the Pov-Ray program.

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Issue 24, 2001 was published online on December 18

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CORRIGENDUM

M. Nevalainen and A. M. P. Koskinen wish to point out that in their Communication in Issue 21, pp. 4060–4062, only compound **1** and not **2** is a naturally occurring sequiterpene. Furthermore, **2** should not be named as a germacradiene derivative but as a norgermacradiene derivative, because of the missing methyl group.

In the Communication of **Y. Tobe et al.** in Issue 21, pp. 4072–4074, trace g is missing from Figure 1, a mistake for which the editorial team apologizes. The correct figure is shown below. In addition, the authors wish to point out that the fullerene structure of C_{20} is purely speculative and has to date not been proven.

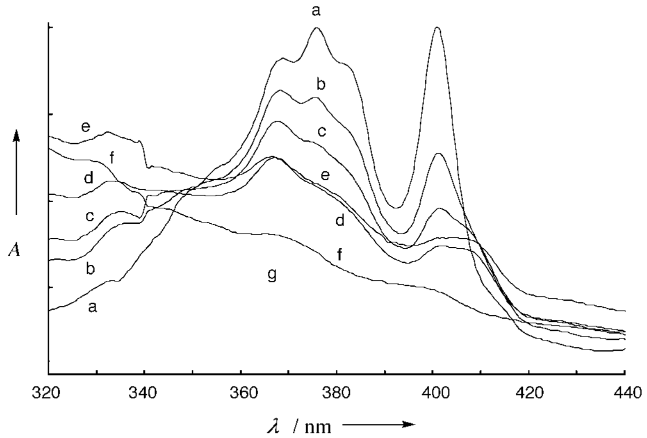
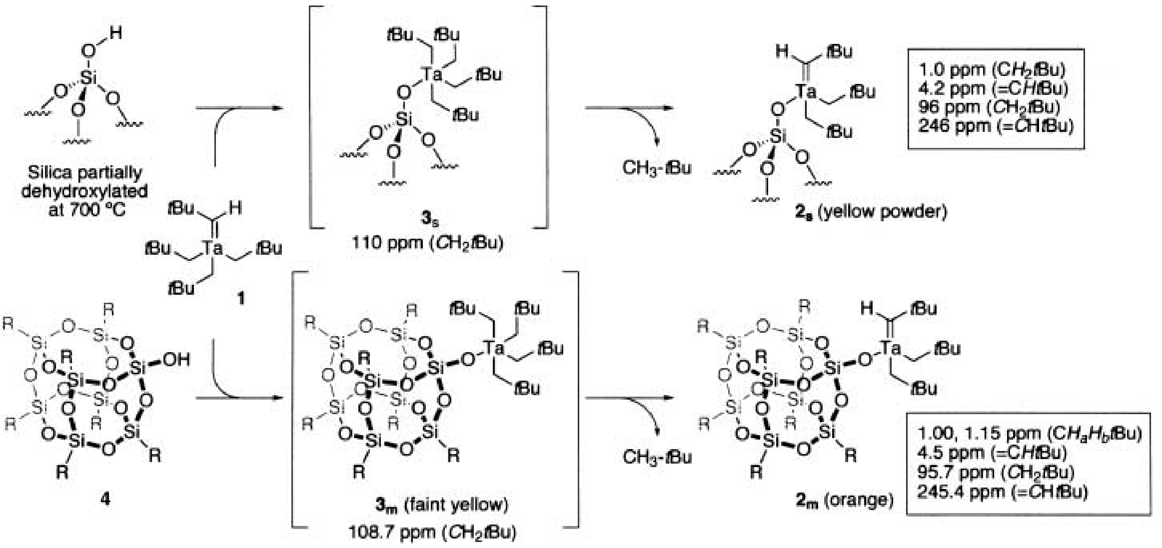


Figure 1. UV/Vis spectral changes for **1a** in a 2-methyltetrahydrofuran/ethanol (6:1) matrix at 77 K by irradiation with a low-pressure mercury lamp. a) before irradiation; b–e) after irradiation for 1, 3, 13, and 24 h, respectively; f) after irradiation for 24 h followed by thaw and refreeze; g) subtraction of line f from line e.

In the Communication of **K. Hegetschweiler and co-workers** in Issue 22, pp. 4179–4182, two important relevant papers were not quoted, for which the authors apologize: R. Schwesinger, K. Piontek, W. Littke, O. Schweikert, H. Prinzbach, C. Krüger, Y.-H. Tsay, *Tetrahedron Lett.* **1982**, *23*, 2427–2430; b) R. Schwesinger, K. Piontek, W. Littke, H. Prinzbach, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 318–319. The authors apologize for this omission. In particular, ref. a describes complex formation of Ba^{2+} with *cis*-benzenetrioxide, a tridentate, tripodal oxygen donor. The resulting complex has icosahedral structures with approximate *T* symmetry, analogous to the complex described by Hegetschweiler and co-workers. Unfortunately, crystallographic data of this Ba complex are not available in the database of the Cambridge Crystallographic Data Centre. The authors thank Professor Prinzbach, Freiburg, for his advice.

In the Communication of **C. Copéret**, **J.-M. Basset**, **and L. Emsley et al.** in Issue 23, 2001, pp. 4493–4496, a printing error caused the inadvertent omission of some parts of the structures in Scheme 1. The correct scheme is shown below. The editorial team apologizes for this error.



Scheme 1. Comparison of the reaction of silica partially dehydroxylated at 700 °C ($SiO_{2(-700)}$) versus (c-C_5H_9)$_7Si_7O_{12}SiOH$.