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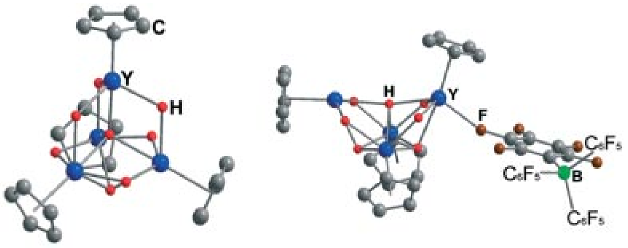
## MICROREVIEWS

### Rare Earth Metal Polyhydrides

**Z. Hou,* M. Nishiura,**
**T. Shima ................................ 2535–2545**

Synthesis and Reactions of Polynuclear Polyhydrido Rare Earth Metal Complexes Containing "$(C_5Me_4SiMe_3)LnH_2$" Units: A New Frontier in Rare Earth Metal Hydride Chemistry

**Keywords:** are earths / Hydride ligands / Cyclopentadienyl ligands / Cluster compounds / Hydrogenation



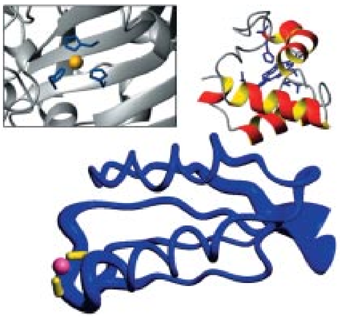
The synthesis, structures, and novel reactions of a series of neutral (left) and cationic (right) polyhydrido rare earth metal complexes are reviewed.

### Metalloproteomes

**I. Bertini*, A. Rosato ............. 2546–2555**

From Genes to Metalloproteins: A Bioinformatic Approach

**Keywords:** Iron / Zinc / Copper / Heme proteins / Metalloproteins / Bioinformatics



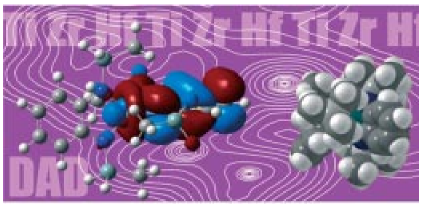
A significant fraction of the proteins that organisms produce and exploit to sustain cellular life require metal ions for their biological function (metalloproteins). Because the experimental characterization of metal requirements at the whole genome level is still not routinely feasible, catalogues of metalloproteins can only be compiled through bioinformatic methods. This review discusses the results of the application of bioinformatics to the identification of various metalloprotein types in selected organisms whose complete genome sequence is available. An overview of the usage of different essential metal ions across domains of life is provided.

### Diimino/Enediamido Complexes

**C. Mealli,* A. Ienco, A. D. Phillips,**
**A. Galindo* .......................... 2556–2568**

A Critical Review of Electronic Effects in Enediamido and α-Diimino Complexes of the Group 4 Metals

**Keywords:** N ligands / Group 4 metals / Metallacycles / Density functional calculations / Electronic structure



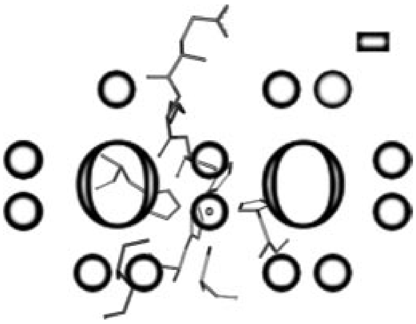
The stereochemical features of the group 4 metal complexes with *noninnocent* α-diimino chelates such as 1,4-diaza-1,3-butadiene (DAD) are systematically reviewed from an electronic point of view with the help of density functional calculations. The Quantum Theory of Atoms in Molecules (QTAIM) approach is also used to interpret the dichotomy of planar/bent metallacycles which is observed in very similar homoleptic $[M(DAD)_2]$ complexes.

### Metalloenzymes

**A. S. Pereira, P. Tavares, F. Folgosa,**
**R. M. Almeida, I. Moura,***
**J. J. G. Moura ....................... 2569–2581**

Superoxide Reductases

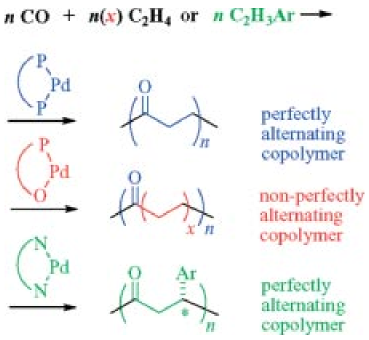
**Keywords:** Bioinorganic chemistry / Nonheme iron centres / Superoxide / Structure-activity relationships



This review aims to describe the structural characteristics of superoxide reductases and the mechanistic aspects of biological superoxide anion reduction. The geometry of the active site, the possible electron donors in vivo and the current hypothesis for the catalytic mechanism are discussed. Some phylogenetic considerations are presented.

### Pd-Catalysed Copolymerisation

Co- and terpolymerisations of carbon monoxide and alkenes are usually catalysed by palladium complexes, and the recent introduction of phosphane-sulfonate ligands has allowed this reactivity to be extended to non-alternating CO/ethene copolymerisation. After a general overview of the topic, selected recent advances in this field are described.



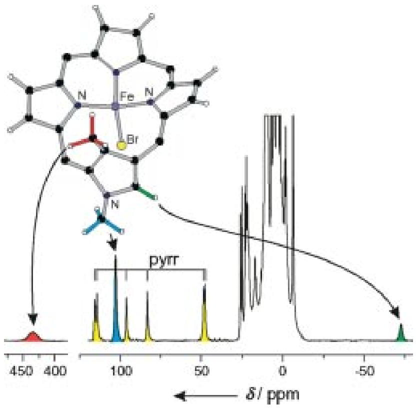
**E. J. García Suárez, C. Godard, A. Ruiz, C. Claver*** ............... 2582–2593

Alternating and Non-Alternating Pd-Catalysed Co- and Terpolymerisation of Carbon Monoxide and Alkenes

**Keywords:** Polymerisation / Polyketones / Palladium / Carbon monoxide / Alkenes

### Metallocarbaporphyrinoids

This microreview presents the general characteristics of paramagnetic metallocarbaporphyrinoids with a focus on NMR studies. NMR spectroscopy of paramagnetic molecules is a powerful probe of several intriguing aspects of their molecular and electronic structures, structural rearrangements, and reactivity, including oxidation and oxygenation.



**E. Pacholska-Dudziak, L. Latos-Grażyński*** ............. 2594–2608

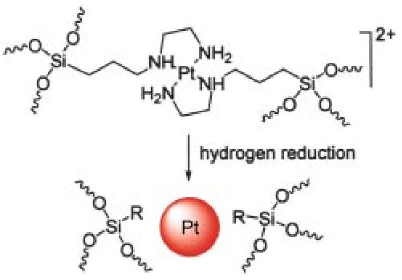
NMR Studies of Paramagnetic Metallocarbaporphyrinoids

**Keywords:** Carbaporphyrinoids / Porphyrinoids / NMR spectroscopy / Organometallic chemistry

## SHORT COMMUNICATION

### Sol-Gel Films

Silica films on glass substrates with homogeneously dispersed platinum, gold or silver nanoparticles were prepared by sol-gel processing of triethoxysilyl-substituted complexes, followed by hydrogen treatment of the films at elevated temperatures.



**M. Malenovska, S. Martinez, M.-A. Neouze, U. Schubert*** ......................... 2609–2611

Growth of Metal Nanoparticles in a Sol-Gel Silica Thin Film

**Keywords:** Thin films / Nanostructures / Inorganic-organic hybrid materials / Nanocomposites

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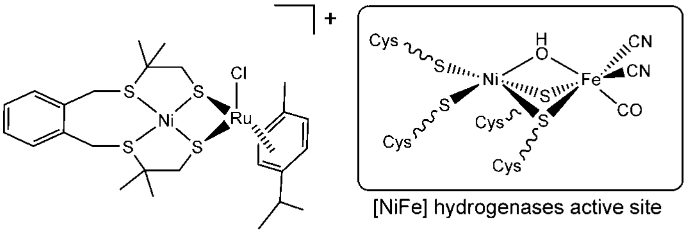
## FULL PAPERS

### Hydrogenase Models

**Y. Oudart, V. Artero,* J. Pécaut, C. Lebrun, M. Fontecave ......................... 2613–2626**

Dinuclear Nickel–Ruthenium Complexes as Functional Bio-Inspired Models of [NiFe] Hydrogenases

**Keywords:** Nickel / Ruthenium / Hydrogen / Electrocatalysis / Biomimetic chemistry / Hydrogenases



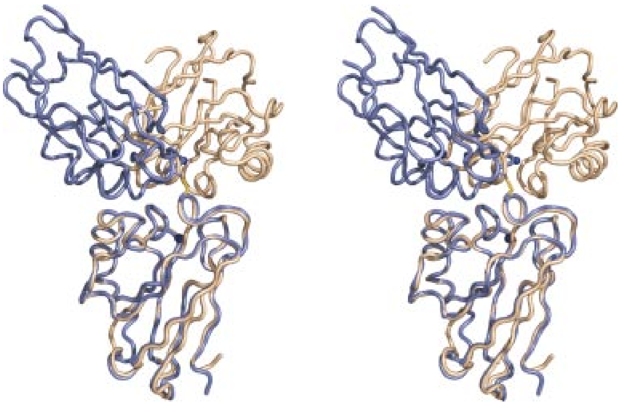
New dinuclear nickel-ruthenium catalysts for $H_2$ production that mimic the active site of [NiFe] hydrogenases are described. The activity of these new complexes is explained by the existence of a cooperative effect between the metal centers and is further related to their electronic properties.

### Biological Charge Transport

**T. E. de Jongh, M. Hoffmann, O. Einsle, D. Cavazzini, G.-L. Rossi, M. Ubbink, G. W. Canters* ..................... 2627–2634**

Inter- and Intramolecular Electron Transfer in Modified Azurin Dimers

**Keywords:** Metalloproteins / Protein structures / Copper protein / Electronic coupling / Hydrophobic patch



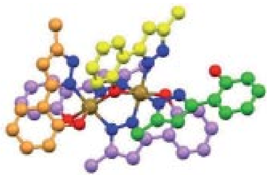
Crystal packing (stereo view) of wild-type azurin (beige) and the disulfide linked dimer of N42C/M64E azurin (blue). The packing has a profound effect on the electron exchange.

### Ligand Versatility

**M. Viciano-Chumillas, S. Tanase, G. Aromí, J. M. M. Smits, R. de Gelder, X. Solans, E. Bouwman, J. Reedijk* ....... 2635–2640**

Coordination Versatility of 5(3)-(2-Hydroxyphenyl)-3(5)-methylpyrazole: Synthesis, Crystal Structure and Properties of Co$^{III}$, Ni$^{II}$ and Cu$^{II}$ Complexes

**Keywords:** Cobalt / Nickel / Copper / Pyrazoles / Phenols / Crystal structures



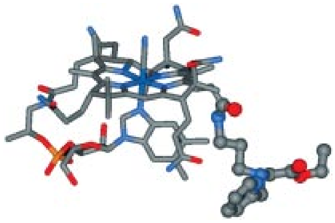
The stabilization of a highly asymmetric dinuclear cobalt(III) complex containing four different coordination modes of the 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole ligand and the synthesis and characterization of two mononuclear complexes of Ni$^{II}$ and Cu$^{II}$ are discussed in detail.

### Vitamin $B_{12}$ Derivatives

**B. Spingler, S. Mundwiler, P. Ruiz-Sánchez, D. R. van Staveren, R. Alberto* ........................... 2641–2647**

Structures of the b- and d-Acid Derivatives of Vitamin $B_{12}$ and Their Complexes with $[M(CO)_3]^+$ (M = $^{99m}$Tc, Re)

**Keywords:** Vitamins / X-ray diffraction / Rhenium / Technetium / Labelling



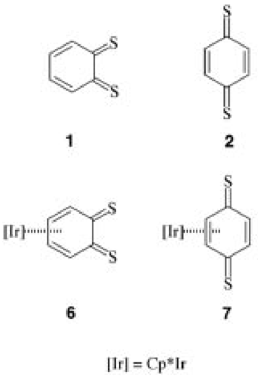
Vitamin $B_{12}$ has been conjugated to tridentate chelators at the b- and d-positions on the corrin periphery. X-ray structure analyses confirmed the corresponding assignments from NMR spectroscopy.

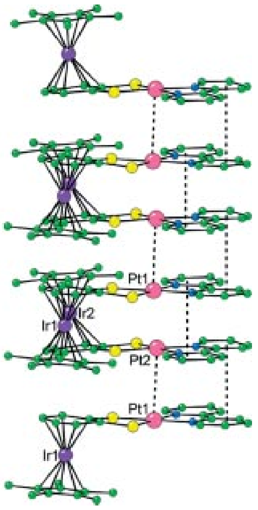
## Dithiobenzoquinone Complexes

**J. Moussa, M. N. Rager, K. Boubekeur, H. Amouri* .......................... 2648–2653**

*ortho-* and *para*-Thioquinonoid π-Complexes: First Synthesis, Reactivity, and Crystal Structure Determination

**Keywords:** Reactive intermediates / Coordination modes / Sulfur / Thioquinones / Iridium





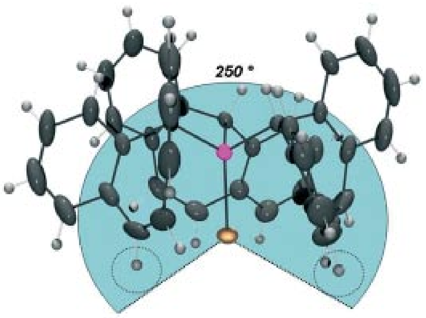
Overcoming a long-standing challenge, the *o-* and *p*-dithiobenzoquinone iridium complexes **6** and **7** were synthesized for the first time, and the X-ray molecular structure of [Cp*Ir-*p*-($\eta^4$-$C_6H_4S_2$)] (**7**) is reported. The organometallic linker **6** reacts with "Pt(bpy)" subunits to give the complex [Pt(bpy){Cp*Ir-*o*-($\eta^4$-$C_6H_4S_2$)}][OTf]$_2$ (**10**), which forms a supramolecular chain through π–π/Pt···Pt interactions.

## Coordination Polymorphism

**U. Fischbach, H. Rüegger, H. Grützmacher* .................. 2654–2667**

Tris(dibenzo[*a*,*d*]cycloheptenyl)phosphane: A Bulky Monodentate or Tetrapodal Ligand

**Keywords:** Alkene ligands / Gold / Iridium / Palladium / Phosphane ligands / Rhodium / Silver / Tetradentate ligands / Solid-state NMR spectroscopy



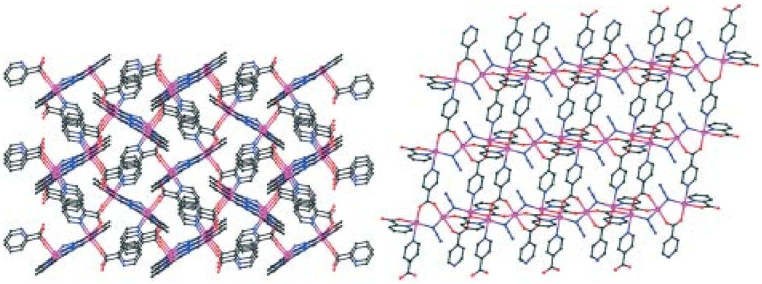
Either a very bulky monodenate phosphane ligand (cone angle about 250°) or a tetradentate $\kappa^1$:$\eta^6$ ligand. These are the coordination modes of the highly rigid tris(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)phosphane (trop$_3$P) in d$^{10}$ [Ag$^I$, Au$^I$] and d$^8$ [Rh$^I$, Ir$^I$, Pd$^{II}$] valence configured metal complexes.

## Coordination Polymers

**L. Cheng, W.-X. Zhang, B.-H. Ye,* J.-B. Lin, X.-M. Chen* ......... 2668–2676**

Spin Canting and Topological Ferrimagnetism in Two Manganese(II) Coordination Polymers Generated by In Situ Solvothermal Ligand Reactions

**Keywords:** Solvothermal ligand reaction / Coordination polymers / Spin canting / Topological ferrimagnetism



Two Mn$^{II}$ coordination polymers, [Mn$_2$(bpt)(pa)$_2$(N$_3$)]$_n$ [**1**; Hpa = picolinic acid, Hbpt = 3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole] and [Mn$_3$(ina)$_2$(pa)$_2$(N$_3$)$_2$]$_n$ (**2**; Hina = isonicotinic acid), containing in situ generated bpt and pa ligands have been synthesized under solvothermal conditions. They exhibit spin-canting magnetism and topological ferrimagnetism with an AF-AF-F sequence, respectively.

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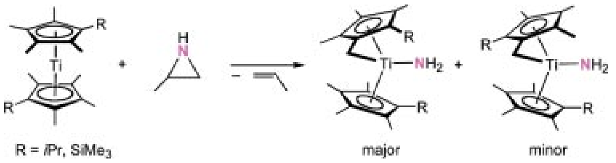
## Titanium Chemistry

**T. E. Hanna, E. Lobkovsky,**
**P. J. Chirik* .......................... 2677−2685**

N−H Group Transfer and Oxidative Addition Chemistry Promoted by Isolable Bis(cyclopentadienyl)titanium Sandwich Complexes

**Keywords:** Titanium / Oxidative addition / Cyclopentadienyl / Group transfer / Nitrogen



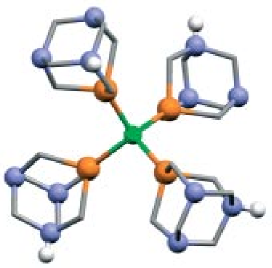
Addition of propylenimine to isolable titanocene complexes has resulted in [NH] group transfer which is followed by rapid cyclometalation. This reactivity contrasts [O] atom transfer where isolable titanocene oxides were obtained.

## Phosphane Complexes

**A. M. Kirillov, P. Smoleński,**
**M. F. C. Guedes da Silva,**
**A. J. L. Pombeiro* ................ 2686−2692**

The First Copper Complexes Bearing the 1,3,5-Triaza-7-phosphaadamantane (PTA) Ligand

**Keywords:** Copper / N,P ligands / Structure elucidation / Phosphane ligands



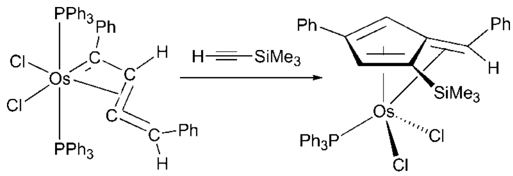
The water-soluble Cu$^I$ compounds [Cu(PTAH)$_4$](NO$_3$)$_5$ and [Cu(PTA)$_4$](NO$_3$) were easily prepared and fully characterized, providing the first examples of Cu complexes bearing PTA or any derived ligand with a cagelike PTA core.

## Alkyne Oligomerization

**T. B. Wen, W. Y. Hung,**
**H. H.-Y. Sung, Z. Zhou, I. D. Williams,**
**G. Jia* ................................ 2693−2701**

Coupling Reactions of an Allenylcarbene Complex with Alkynes and Styrene

**Keywords:** Osmium / Fulvenes / Carbenes / Alkynes / Alkenes



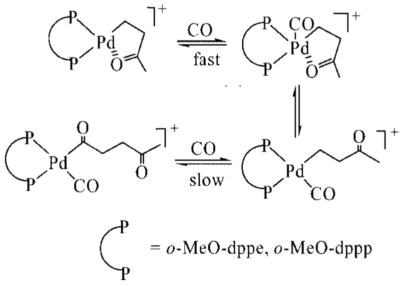
The allenylcarbene complex [OsCl$_2${=CPh-(η$^2$-CH=C=CHPh)}(PPh$_3$)$_2$] undergoes coupling reactions with alkynes to produce fulvene complexes. A similar coupling reaction also occurs between this complex and styrene.

## CO/Ethene Copolymerization

**C. Bianchini,* A. Meli, W. Oberhauser,***
**C. Claver,**
**E. J. Garcia Suarez ............... 2702−2710**

Unraveling the *o*-Methoxy Effect in the CO/Ethene Copolymerization Reaction by Diphosphanepalladium(II) Catalysis

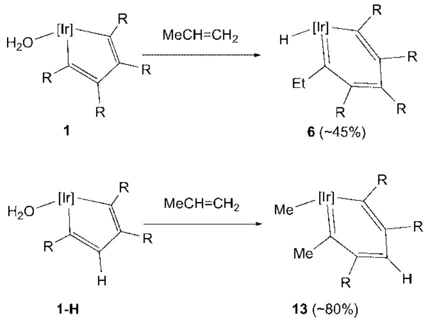
**Keywords:** Polyketones / Palladium / Diphosphane ligands / Catalysis / Copolymerization / Kinetics



*o*-MeO substituents on the phosphorus aryl rings of chelating diphosphane ligands increase the activity of Pd$^{II}$ catalysts for the alternating CO/ethene copolymerization in either protic or aprotic solvents. In particular, the presence of *o*-MeO substituents affects the kinetics of the copolymerization process that becomes independent of the CO pressure. In situ high-pressure NMR experiments have provided valuable information on relevant steps of the copolymerization process.

## Iridabenzenes

A new synthesis of iridabenzene species is described. Surprisingly, the coupling of the iridacyclopentadienes **1** and **1-H** with propene is highly dependent on the nature of the substituents in the starting metallacycle.

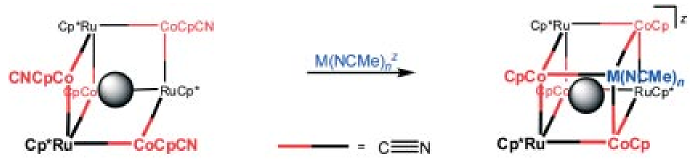


**M. Paneque,* M. L. Poveda,* N. Rendón, E. Álvarez, E. Carmona** .......................... 2711–2720

The Synthesis of Iridabenzenes by the Coupling of Iridacyclopentadienes and Olefins

**Keywords:** Metallacycles / Olefins / Insertion / Isomerisation / Alkylidenes

## Supramolecular Cages



The coordination chemistry of the unusual metallo-ligand $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ ($Cs\subset Co_4Ru_3$) is described with attention to the behavior of the ligand itself, its binding to Lewis-acidic metal cations, and its ability to stabilize catalytically relevant $Ru-PPh_3$ fragments.

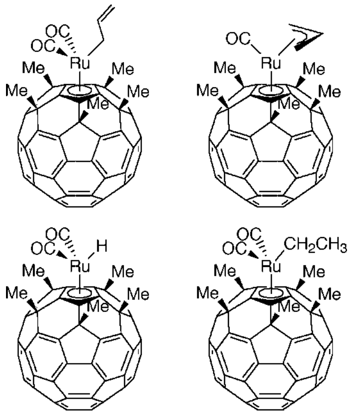
**J. L. Boyer, H. Yao, M. L. Kuhlman, T. B. Rauchfuss,* S. Wilson** ... 2721–2728

Cyanometalate Cages with Exchangeable Terminal Ligands

**Keywords:** Cyanide / Ruthenium / Hydrogen bonds / Cage compounds / Heterometallic complexes

## Metal–Fullerene Complexes

$\eta^1$-Allyl and $\eta^3$-allyl, ethyl, and hydrido ruthenium complexes of pentamethyl[60]fullerene, $Ru(\eta^5\text{-}C_{60}Me_5)R(CO)_2$ (R = $\eta^1$-allyl, Et, H) and $Ru(\eta^5\text{-}C_{60}Me_5)(\eta^3\text{-allyl})(CO)$, were prepared. Conversion of the $\eta^1$-allyl complex to the $\eta^3$-allyl complex and catalytic performance of the hydrido complex in the isomerization of 1-decene to internal decenes are described.



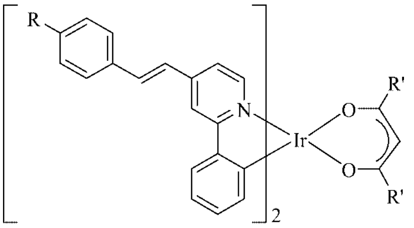
**Y. Matsuo, T. Uematsu, E. Nakamura*** ....................... 2729–2733

Synthesis and Catalytic Activity of $\eta^1$-Allyl and $\eta^3$-Allyl, Ethyl, and Hydrido Complexes of Ruthenium–Pentamethyl[60]fullerene

**Keywords:** Ruthenium / Fullerenes / Allyl complexes / Hydrido complexes / Isomerization

## Coordination Chemistry

Large bathochromic shifts in emission energy at 77 K can be achieved by adding a conjugated styryl group to the ppy ligand of the $[Ir(C^{\wedge}N\text{-ppy})_2(acac)]$ complex and by introducing either a strong electron-donating (dialkylamino, $\lambda_{em}$ = 651 nm) or -withdrawing (nitro, $\lambda_{em}$ = 647 nm) group.



R' = $CH_3$; R = OMe, $NEt_2$, H, $NO_2$
R' = *t*Bu; R = OMe, $NEt_2$

**M. Lepeltier, T. K.-M. Lee, K. K.-W. Lo,* L. Toupet, H. Le Bozec, V. Guerchais*** ........................ 2734–2747

Synthesis and Photophysical Properties of Bis-Cyclometallated Iridium(III)–Styryl Complexes and Their Saturated Analogues

**Keywords:** Iridium / Luminescence / Biscyclometallated complexes

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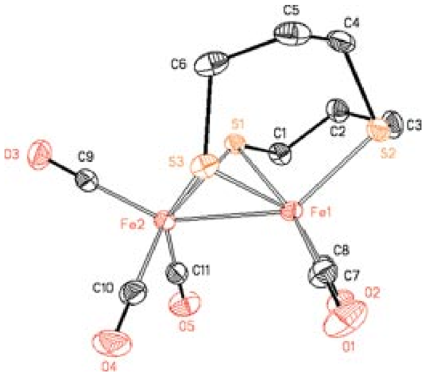
## [Fe-only]-Hydrogenase Models

**J. Windhager, M. Rudolph,* S. Bräutigam, H. Görls, W. Weigand* .......... 2748–2760**

Reactions of 1,2,4-Trithiolane, 1,2,5-Trithiepane, 1,2,5-Trithiocane and 1,2,6-Trithionane with Nonacarbonyldiiron: Structural Determination and Electrochemical Investigation

**Keywords:** Iron / Cluster compounds / S ligands / Hydrogenase / Electrocatalysis / Dihydrogen



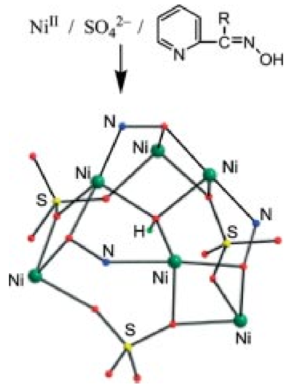
The syntheses of novel [Fe-only]-hydrogenase models starting from 1,2,4-trithiolane, 1,2,5-trithiepane, 1,2,5-trithiocane and 1,2,6-trithionane are described. The products were characterised by spectroscopic methods and X-ray structure analyses. The electrochemical behaviour of one representative complex is described in detail.

## Nickel Cluster Chemistry

**C. Papatriantafyllopoulou, G. Aromi, A. J. Tasiopoulos, V. Nastopoulos, C. P. Raptopoulou, S. J. Teat,* A. Escuer,* S. P. Perlepes* ....................... 2761–2774**

Use of the Sulfato Ligand in 3d-Metal Cluster Chemistry: A Family of Hexanuclear Nickel(II) Complexes with 2-Pyridyl-Substituted Oxime Ligands

**Keywords:** Nickel(II) clusters / Magnetic properties / Sulfato complexes / Oxime complexes



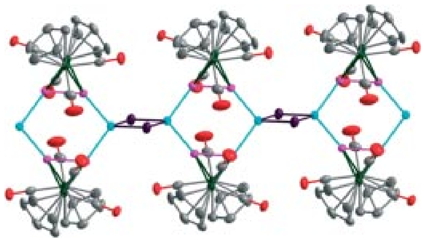
The shown general reaction scheme (R = Me, Ph) gives a family of hexanuclear nickel(II) clusters containing the $[Ni_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)_3(\mu_3\text{-}ONR')_3]^{2+}$ core. The complexes exhibit an overall antiferromagnetic behavior, with a simple 2-*J* model adequately describing the thermal variation of the molar magnetic susceptibility.

## Coordination Polymers

**M. Scheer,* L. J. Gregoriades, M. Zabel, M. Sierka, L. Zhang, H. Eckert* ............................ 2775–2782**

Conformational Analysis of One-Dimensional Coordination Polymers Based on $[Cp_2Cr_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ by Solid-State Multinuclear NMR Spectroscopy and Density Functional Calculations

**Keywords:** Chromium / Copper / Halides / Density functional calculations / NMR spectroscopy / Phosphorus



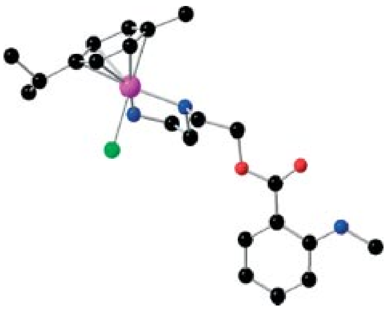
The complex $[Cp_2Cr_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ reacts with copper(I) halides to yield new 1D coordination polymers (iodide derivative shown). Solid-state multinuclear NMR spectroscopy demonstrates the extreme sensitivity of the chemical shift to apparently minor structural variations, and density functional calculations corroborate the conclusions deduced from the experimental evidence.

## Fluorescent (Arene)Ru$^{II}$ Complexes

**F. Zobi, B. B. Mood, P. A. Wood, F. P. A. Fabbiani, S. Parsons, P. J. Sadler* .......................... 2783–2796**

Tagging (Arene)ruthenium(II) Anticancer Complexes with Fluorescent Labels

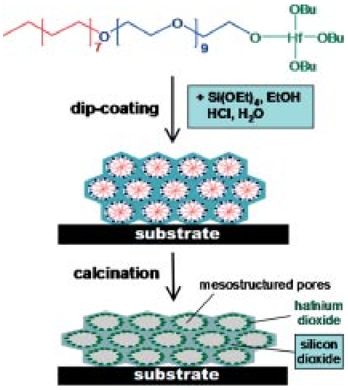
**Keywords:** Anticancer agents / Organometallic compounds / Fluorescence / Ruthenium / Hydrolysis



Fluorescent (arene)ruthenium(II) complexes, obtained from the reaction of the $[(p\text{-cymene})RuCl_2]_2$ dimer with isatoic acid based ligands, were structurally characterized and their solution and fluorescence properties investigated. When the fluorogenic reporter is tagged onto the complex through an ester bond, the resulting compound is a substrate for cytosolic esterases. Compounds bearing an ester bond may be models for esterase-activated Ru-based prodrug delivery systems.

## Doped Silica Films

A surfactant–hafnium alkoxide complex was used as a template in a sol–gel dip-coating process to produce hafnium oxide doped silica films with ratios between 1:60 and 1:6. The influence of subsequent heat treatment was studied by GISAXS and TEM. The surface and in-depth molecular composition of the films was studied by XPS.



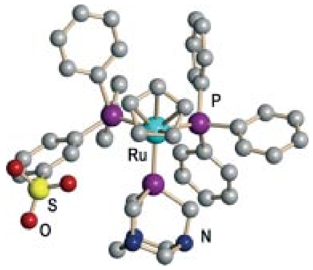
**R. Supplit, N. Hüsing,* S. Gross,
S. Bernstorff, M. Puchberger ... 2797–2802**

Hafnium Oxide Doped Mesostructured Silica Films

**Keywords:** Mesostructured films / Ligand-assisted templating / Self-assembly / Surfactants

## Water-Soluble Ru Complexes

Water-soluble ruthenium(II) complexes have been synthesized and characterised. The crystal structure of [RuCp(mTPPMS)(PPh$_3$)(PTA)]·2H$_2$O, which is the first half-sandwich ruthenium complex to contain three different phosphanes, has been determined. The binding properties of the complexes obtained and of the ligand mTPPMS towards DNA have been studied using the mobility shift assay.

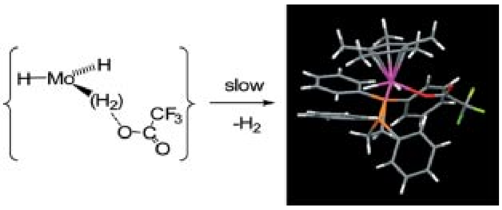


**A. Romerosa,* M. Saoud,
T. Campos-Malpartida, C. Lidrissi,
M. Serrano-Ruiz, M. Peruzzini,
J. A. Garrido,
F. García-Maroto .................. 2803–2812**

DNA Interactions Mediated by Cyclopentadienidoruthenium(II) Complexes Containing Water-Soluble Phosphanes

**Keywords:** Ruthenium / Cyclopentadienyl ligands / Phosphanes / DNA / Bioinorganic chemistry

## Hydride Protonation



The outcome of proton transfer from CF$_3$COOH to [Cp*Mo(dppe)H$_3$] is highly solvent-dependent: either formation of separated [Cp*Mo(dppe)H$_4$]$^+$ and trifluoroacetate ions or H$_2$ evolution with formation of the new [Cp*Mo(dppe)H$_2$(O$_2$CCF$_3$)] complex is observed.

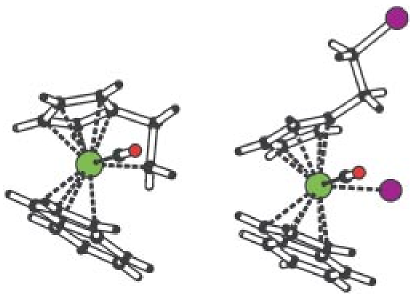
**P. A. Dub, M. Baya, J. Houghton,
N. V. Belkova, J.-C. Daran, R. Poli,*
L. M. Epstein,
E. S. Shubina* ...................... 2813–2826**

Solvent Control in the Protonation of [Cp*Mo(dppe)H$_3$] by CF$_3$COOH

**Keywords:** Molybdenum / Hydrido ligand / Trifluoroacetato ligand / Proton transfer / Dihydrogen bonding

## Functionalized Molybdenocenes

[Mo(CO)$_2$(NCCH$_3$)$_2$(Cp′)][BF$_4$] (Cp′ = Cp, Ind) react with spiro[2.4]hepta-4,6-diene and spiro[4.4]nona-1,3-diene to give $\eta^4$-compounds or products of a ring-opening reaction. The *ansa* compound [Mo($\eta^5$-C$_5$H$_4$CH$_2$-$\eta^1$-CH$_2$)(CO)(Ind)][BF$_4$] was found to be a suitable precursor for the synthesis of ring-functionalized molybdenocenes.



**J. Honzíček, F. A. Almeida Paz,
C. C. Romão* ...................... 2827–2838**

Synthesis, Characterization and Stability of Spirodiene Complexes of Molybdenum(II): New Route to *ansa*-Molybdenocene and Ring-Functionalized Molybdenocene Compounds

**Keywords:** Metallocenes / Molybdenum / Spiro compounds / Functionalized cyclopentadienes / X-ray diffraction

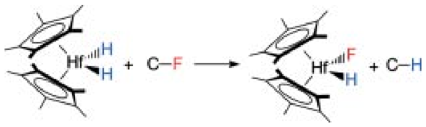
# CONTENTS

## C–F Bond Activation

**R. D. Rieth, W. W. Brennessel,**
**W. D. Jones* .......................... 2839–2847**

Activation of Aromatic, Aliphatic, and Olefinic Carbon–Fluorine Bonds Using Cp*$_2$HfH$_2$

**Keywords:** Metallocenes / Hydrides / Reduction / Fluorocarbons



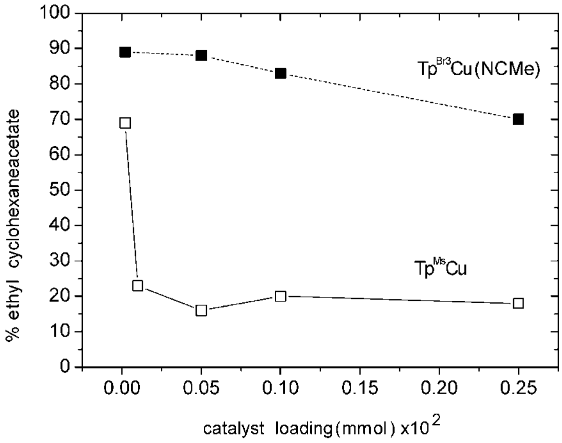
The hafnium metallocene complex Cp*$_2$HfH$_2$ has been shown to react with a variety of carbon–fluorine bonds in aromatic, vinylic, and aliphatic organic substrates. The mechanism(s) of reaction are discussed and compared with the zirconium analog.

## Catalyst-Loading Effects

**A. Caballero, M. M. Díaz-Requejo,**
**S. Trofimenko, T. R. Belderraín,***
**P. J. Pérez* .......................... 2848–2852**

The Effect of Catalyst Loading in Copper-Catalyzed Cyclohexane Functionalization by Carbene Insertion

**Keywords:** Copper / C–H activation / Homogeneous catalysis / Carbenes / N ligands



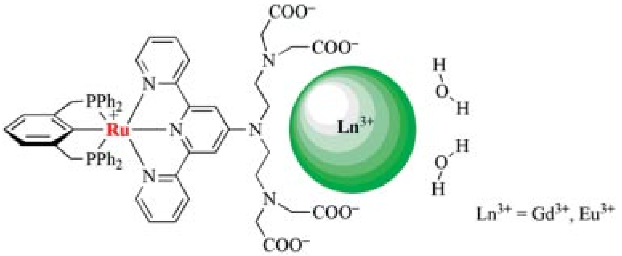
A study of the insertion of the :CHCO$_2$Et group into the C–H bonds of cyclohexane in the presence of a Tp*x*Cu complex as catalyst has demonstrated an anomalous effect of the catalyst loading, namely that the use of low concentrations of catalyst produces an increase in the yield of the C–H activation product.

## Luminescent Lanthanides

**M. Gagliardo, F. Rizzo, M. Lutz,**
**A. L. Spek, G. P. M. van Klink,**
**A. E. Merbach, L. De Cola,**
**G. van Koten* ........................ 2853–2861**

A PCP-Pincer Ru$^{II}$–Terpyridine Building Block as a Potential "Antenna Unit" for Intramolecular Sensitization

**Keywords:** Ruthenium / Lanthanides / Pincer ligands / Luminescence



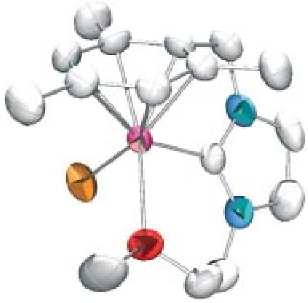
Through application of the "complex as ligand" approach, the heterodinuclear complexes [Ru(PCP)(tpy-DTTA)Ln(H$_2$O)$_2$] were prepared by coordination of Gd$^{III}$ and Eu$^{III}$ ions to the chromophoric moiety of [Ru(PCP)(tpy-DTTANa$_4$)]Cl. Weak d→f energy transfer occurs in the complex [Ru(PCP)(tpy-DTTA)Eu(H$_2$O)$_2$], which results in sensitized luminescence from the Eu$^{III}$ ion.

## Ruthenium–NHC Chelates

**I. Özdemir,* S. Demir, B. Çetinkaya,**
**L. Toupet, R. Castarlenas, C. Fischmeister,**
**P. H. Dixneuf* ...................... 2862–2869**

Chelating η$^6$-Arene-η$^1$-carbene Ligands in Ruthenium Complexes

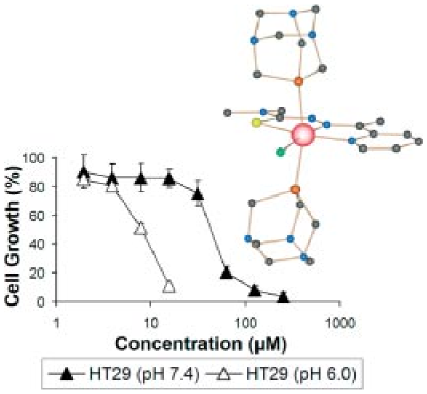
**Keywords:** Ruthenium–arene / NHCs / Imidazolinylidene / Metathesis / ROMP / Polymerization



A series of ruthenium complexes bearing di- or tridentate ligands incorporating an N-heterocyclic carbene (NHC) is reported. X-ray structures are provided, and the catalytic activity for the ring opening metathesis polymerization (ROMP) of norbornene is investigated.

## Antitumour Agents

The first water-soluble ruthenium(II) complex with mixed thiosemicarbazone/PTA ligands has been prepared and characterised by X-ray crystallography and spectroscopic methods. The complex shows pH-dependent antiproliferative activity in vitro in micromolar concentrations.

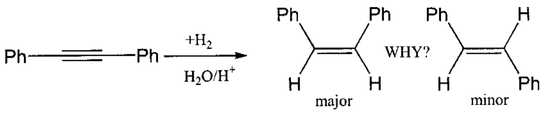


**S. Grguric-Sipka, C. R. Kowol, S.-M. Valiahdi, R. Eichinger, M. A. Jakupec, A. Roller, S. Shova, V. B. Arion,* B. K. Keppler* .... 2870–2878**

Ruthenium(II) Complexes of Thiosemicarbazones: The First Water-Soluble Complex with pH-Dependent Antiproliferative Activity

**Keywords:** Antitumour agents / Ruthenium / N,S ligands / X-ray diffraction

## Aqueous Alkyne Semihydrogenation



Density functional theory was applied to describe the reaction mechanism of the stereoselective hydrogenation of phenyl-substituted alkynes with the water-soluble ruthenium complex [{$RuCl_2$(*m*tppms)$_2$}$_2$] in acidic aqueous solution.

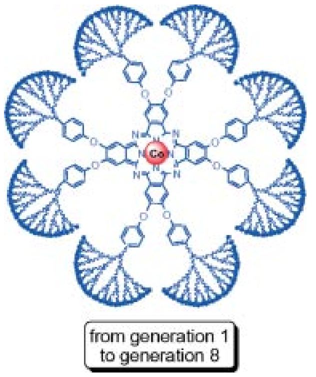
**G. Kovács, G. Ujaque, A. Lledós,* F. Joó* ................................. 2879–2889**

The Role of Water in the Stereoselective Hydrogenation of 1,2-Diphenylacetylene Catalyzed by the Water-Soluble [{$RuCl_2$(*m*tppms)$_2$}$_2$]

**Keywords:** Alkynes / Biphasic catalysis / Density functional calculations / Hydrogenation / Reaction mechanisms

## Dendritic Phthalocyanine Complexes

The first generation of a phosphorus-containing dendrimer possessing a metal-free phthalocyanine as its core is used to complex cobalt, and then the synthesis of the dendrimer is pursued up to the eighth generation. The progressive influence of the branches upon the core is studied by UV/Vis spectroscopy.



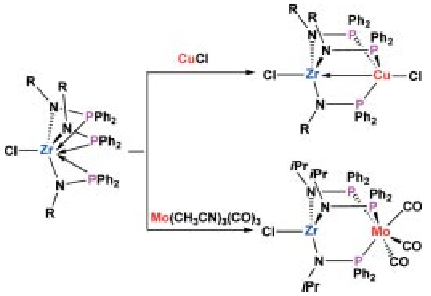
**J. Leclaire, R. Dagiral, A. Pla-Quintana, A.-M. Caminade,* J.-P. Majoral* ...................... 2890–2896**

Metallated Phthalocyanines as the Core of Dendrimers – Synthesis and Spectroscopic Studies

**Keywords:** Dendrimers / Phthalocyanine / Phosphorus / UV/Vis spectroscopy / Cobalt

## Early–Late Dimetallic Complexes

Tris(phosphinoamide)zirconium complexes, $(PPh_2NR)_3ZrCl$ [R = *t*Bu (**1a**), *i*Pr (**1b**)], are synthesized by the reaction of 3 equiv. of $Li(PPh_2NR)$ with $ZrCl_4$. Treatment of CuCl or $Mo(CO)_3(CH_3CN)_3$ with **1a**,**b** afforded the novel heterodimetallic complexes $ClCu(Ph_2PNR)_3ZrCl$ [R = *t*Bu (**2a**), *i*Pr (**2b**)] and $(CO)_3Mo(Ph_2PNiPr)_3$-ZrCl (**3**).



**T. Sue, Y. Sunada, H. Nagashima* .................... 2897–2908**

Zirconium(IV) Tris(phosphinoamide) Complexes as a Tripodal-Type Metalloligand: A Route to Zr–M (M = Cu, Mo, Pt) Heterodimetallic Complexes

**Keywords:** Phosphinoamide / Heterodimetallic / Tripodal ligands

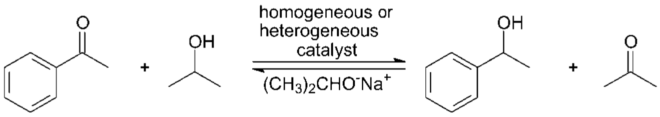
# CONTENTS

## Transfer Hydrogenation

**A. Del Zotto,* C. Greco, W. Baratta, K. Siega, P. Rigo .................. 2909–2916**

Transfer Hydrogenation Reactions Catalyzed by Free or Silica-Immobilized [$RuCl_2$(ampy){$RN(CH_2PPh_2)_2$}] Complexes

**Keywords:** Ruthenium / Transfer hydrogenation / Heterogeneous catalysis / Silica / Ketones



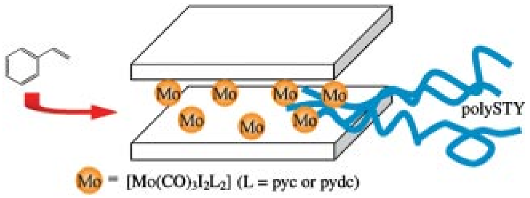
Ruthenium(II) complexes bearing ampy and diphosphane ligands with a C–N–C backbone show very high activity in the homogeneous transfer hydrogenation of ketones. When the catalysts are immobilized on silica supports, the activity is still good but a decrease in the catalytic efficiency is generally observed on recycling.

## LDH Polymerization Catalysts

**M. Vasconcellos-Dias, C. D. Nunes,* P. D. Vaz, P. Ferreira, M. J. Calhorda* .................... 2917–2925**

Pyridine Carboxylate Complexes of $Mo^{II}$ as Active Catalysts in Homogeneous and Heterogeneous Polymerization

**Keywords:** Molybdenum / Lamellar materials / Polymerization / Heptacoordination / Catalysis



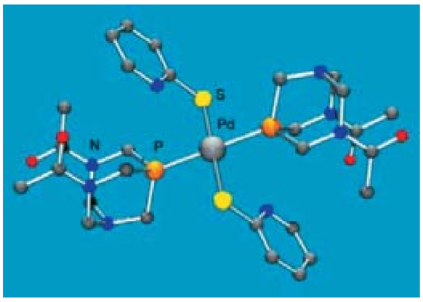
Hydrotalcite–molybdenum hybrid materials: New lamellar materials intercalated with molybdenum(II) organometallic complexes were prepared by a stepwise procedure with pyridine carboxylate derivatives as ligands. Their activity as catalysts in olefin polymerization was determined and compared with that of analogous homogeneous systems.

## Liquid Metals

**E. Vergara, S. Miranda, F. Mohr, E. Cerrada, E. R. T. Tiekink, P. Romero, A. Mendía,* M. Laguna* ..... 2926–2933**

Gold(I) and Palladium(II) Thiolato Complexes Containing Water-Soluble Phosphane Ligands

**Keywords:** Phosphane ligands / Palladium / Gold / Thiolato complexes



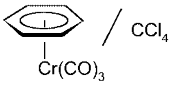
Water-soluble gold(I) and palladium(II) complexes containing different thiolates and the phosphane ligands 1,3,5-triaza-7-phosphaadamantane (PTA) and 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]-nonane (DAPTA) are described and were characterised by spectroscopic techniques and X-ray crystallography.

## Unimolecular Photoinitiators

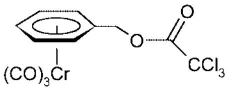
**E. P. Kündig,* L.-H. Xu, M. Kondratenko, A. F. Cunningham Jr.,* M. Kunz ................................ 2934–2943**

Photoinitiation of Acrylate Polymerization with (Arene)chromium Complexes

**Keywords:** Acrylate polymerization / Photoinitiators / Arene complexes / Chromium / Radiation curing



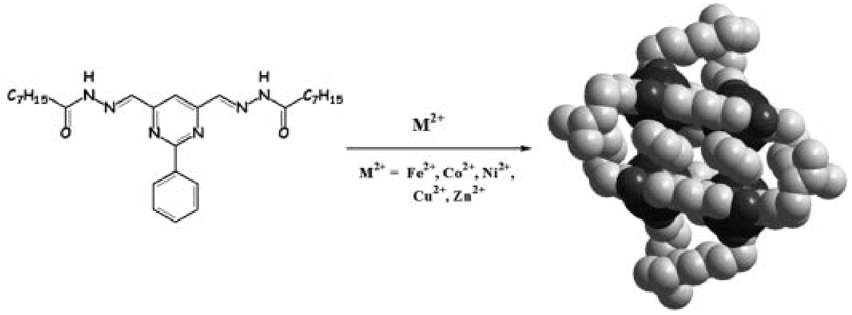
**1**



**17a**

It is known that the couple **1**/$CCl_4$ can induce photoinitiated polymerization (radiation curing) of acrylates. A new investigation into the mechanism of this process shows that photolytic CO/acrylate exchange leads to a complex in which the arene–metal bond is labilized. This then creates a highly reactive metal center that initiates $CCl_3$ radical formation. The proximity of the $COCCl_3$ group makes **17a** a much more active catalyst than **1**/$CCl_4$.

## Metallosupramolecular Chemistry

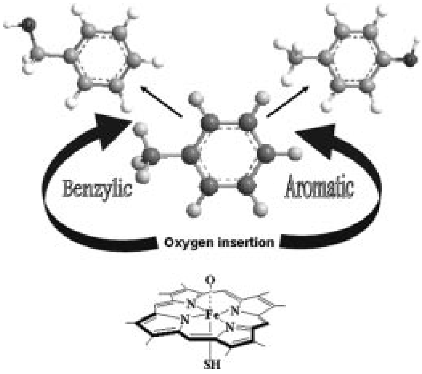


Acylhydrazones formed from 2-phenylpyrimidine-4,6-dicarbaldehyde generate [2×2] grids with a variety of transition metals. The acyl groups provide lateral functionality in these structures.

**Keywords:** Grids / Ditopic acylhydrazones / Component assembly / Crystal structures

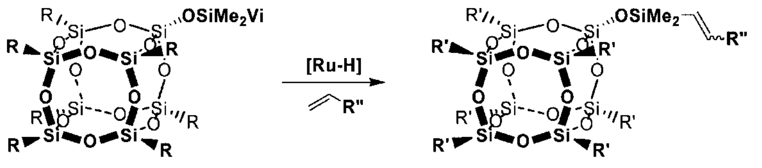
## Cytochrome P450 Models

Density functional calculations on the mechanism of toluene hydroxylation leading to benzyl alcohol and *p*-cresol products are performed. In an enzyme-mimicked environment with all hydrogen atoms of toluene replaced by deuterium atoms the two processes are competitive.



**Keywords:** Density functional calculations / Enzyme catalysis / Enzyme models / Isotope effects / Metalloenzymes

## Silsesquioxanes



R = *i*Bu (**1**), ViMe$_2$SiO (**2**)

R' = *i*Bu (**3–8**), OSiMe$_2$CH=CHR" (**10–15**)

Highly effective synthesis of β-functionalized vinylspherosilicates **1** and **2** by Ru(H)(Cl)(CO)(PCy$_3$)$_2$-catalyzed silylative coupling with α olefins is reported.

**Keywords:** Spherosilicate / Silsesquioxane / Cross-coupling / Ruthenium / Hydrides