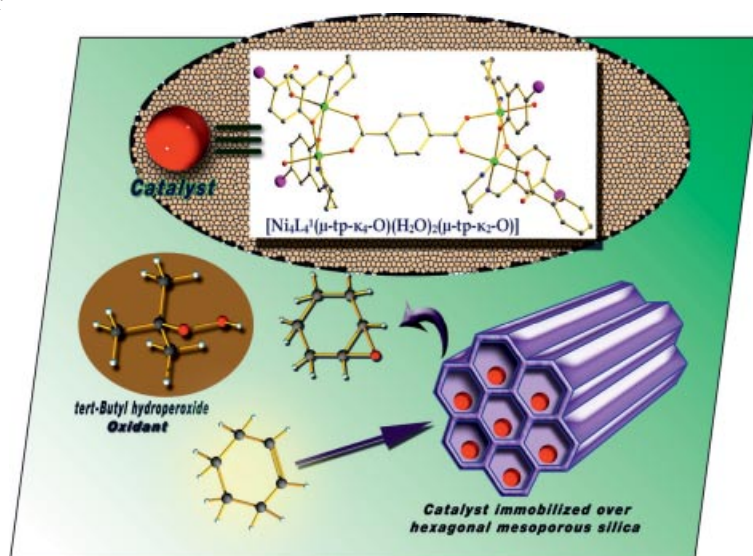


The EUCHEMSOC Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUCHEMSOC Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows how a novel tetranuclear  $\text{Ni}^{\text{II}}$  complex  $[\text{Ni}_4\text{L}_4^1(\mu\text{-tp-}\kappa_4\text{-O})(\text{H}_2\text{O})_2(\mu\text{-tp-}\kappa_2\text{-O})] \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  [ $\text{L}^1 = N\text{-(3-aminopropyl)-5-bromosalicylaldehyde}$ ] acts as an active catalyst for the partial oxidation of cyclohexene into its epoxide product when it is immobilized over a network of hexagonal mesoporous silica. Herein the catalytic sites allow the formation of epoxide over their surfaces. *tert*-Butyl hydroperoxide acts as an oxidant for the partial oxidation process. A dinuclear unit is formed, in which the  $\text{Ni}^{\text{II}}$  is bridged by a phenolato group, and two such units are connected through a terephthalate moiety to form a tetranuclear nickel(II) complex. The tetranuclear units are connected to each other by another terephthalate moiety in its bis(monodentate) mode to form one-dimensional networks. Details are described in the article by P. Banerjee et al. on p. 5033 ff. The artwork was designed by Mr. Jishnunil Chakraborty and Mr. Gopal Das.



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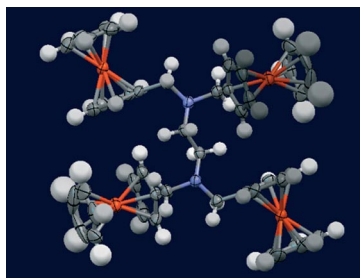
## MICROREVIEW

### Metalloocene-Containing Dendrimers

A. E. Kaifer\* ..... 5015–5027

Electron Transfer and Molecular Recognition in Metallocene-Containing Dendrimers

**Keywords:** Metallocenes / Dendrimers / Electrochemistry / Molecular recognition / Supramolecular chemistry



Dendrimers containing multiple metallocenes on their surface or a single metallocene in their core offer interesting properties in electron-transfer reactions and molecular recognition processes.

## SHORT COMMUNICATION

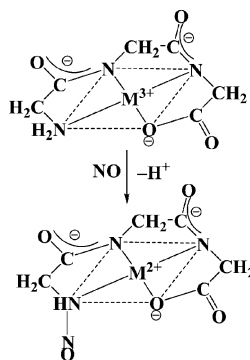
### Reductive Nitrosation

D. Shamir, I. Zilbermann,\* E. Maimon,  
G. Gellerman, H. Cohen,  
D. Meyerstein\* ..... 5029–5031



Reductive Nitrosation of Peptides Ligated to High-Valent Metal Cations

**Keywords:** Nitrosation / Peptides / NO / High-valent transition metals



Reductive *N*-nitrosations occur according to a radical mechanism.

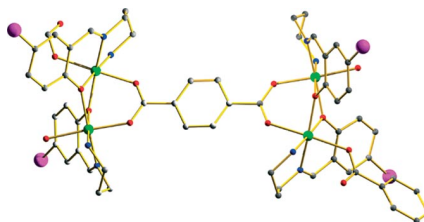
## FULL PAPERS

### Nickel Epoxidation Catalysts

J. Chakraborty, M. Nandi, H. Mayer-Figge,  
W. S. Sheldrick, L. Sorace, A. Bhaumik,  
P. Banerjee\* ..... 5033–5044

Nickel Complexes with N<sub>2</sub>O Donor Ligands: Syntheses, Structures, Catalysis and Magnetic Studies

**Keywords:** Nickel / N<sub>2</sub>O ligands / Epoxidation / Heterogeneous catalysis / Magnetic properties



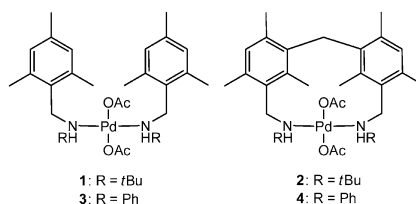
The terephthalato-bridged tetranuclear polymeric Ni<sup>II</sup> complexes [Ni<sub>4</sub>L<sub>4</sub><sup>1</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·2C<sub>2</sub>H<sub>5</sub>OH·CH<sub>3</sub>OH·3H<sub>2</sub>O (**1**) and [Ni<sub>4</sub>L<sub>4</sub><sup>2</sup>(μ-tp-κ<sub>4</sub>-O)(H<sub>2</sub>O)<sub>2</sub>(μ-tp-κ<sub>2</sub>-O)]·3H<sub>2</sub>O (**2**) are synthesized along with the dicyanoargentate-bridged polymeric complexes [Ni<sup>II</sup>(L<sup>1</sup>)(H<sub>2</sub>O){Ag(CN)<sub>2</sub>}]<sub>α</sub> (**3**) and [Ni<sup>II</sup>(L<sup>3</sup>)(MeOH){Ag(CN)<sub>2</sub>}]<sub>α</sub> (**4**). All four complexes are effective catalysts for the epoxidation of alkenes. Variable-temperature magnetic susceptibility measurements of complex **1** show a medium-strength antiferromagnetic coupling between the Ni<sup>II</sup> centers.

## Square-Planar Palladium Complexes

L. Chahen, B. Therrien,  
G. Süß-Fink\* 5045–5051

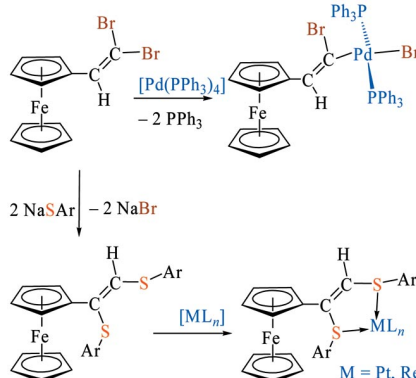
Square-Planar Diacetatopalladium Complexes with *trans*-Configured Secondary Amine Ligands that Avoid Orthometalation: Ligand Synthesis, Coordination, Molecular Structure and Catalytic Potential for Suzuki Cross-Coupling Reactions

**Keywords:** Cross-coupling / Palladium / N ligands / Amines / Homogeneous catalysis



*trans*-Configured square-planar palladium complexes have been synthesized by treating palladium acetate with the amines or diamines. All complexes are found to catalyze Suzuki cross-coupling reactions of deactivated and even sterically hindered arene substrates.

The oxidative addition of (2,2-dibromovinyl)ferrocene to  $[\text{Pd}(\text{PPh}_3)_4]$  yields the  $\sigma$ -alkenyl complex *trans*- $[\text{Pd}(\text{Br})_2(\text{PPh}_3)_2]-\text{C}(\text{Br})=\text{C}(\text{H})-\text{Fc}]$ . Nucleophilic attack of NaSR on  $[\text{Br}_2\text{C}=\text{C}(\text{H})-\text{Fc}]$  produces the  $\pi$ -conjugated dithioether compounds  $[(\text{RS})\text{CH}=\text{C}(\text{SR})-\text{Fc}]$ , which react with  $[\text{Re}(\text{thf})(\text{CO})_3(\mu-\text{Br})_2]$  or  $[\text{PtCl}_2(\text{PhCN})_2]$  to afford heterodinuclear dithioether complexes.



## Heterodinuclear Ferrocene Complexes

S. Clément, L. Guyard, M. Knorr,\*  
F. Villafañe, C. Strohmann,  
M. M. Kubicki ..... 5052–5061

(2,2-Dibromovinyl)ferrocene as a Building Block for the Assembly of Heterodinuclear Complexes – Preparation of an  $\sigma$ -Alkenyl-palladium Complex and Dimetallic Dithioether Complexes

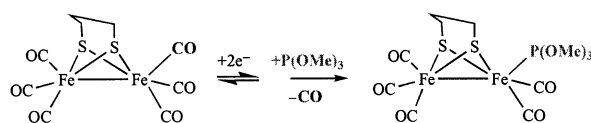
**Keywords:** Oxidative addition / Thioether ligands / Platinum / Rhenium / Palladium / Electrochemistry

## Iron-Only Hydrogenase Models

D. Morvan, J.-F. Capon,  
F. Gloaguen,\* P. Schollhammer,  
J. Talarmin ..... 5062–5068

Electrochemical Synthesis of Mono- and Disubstituted Diiron Dithiolate Complexes as Models for the Active Site of Iron-Only Hydrogenases

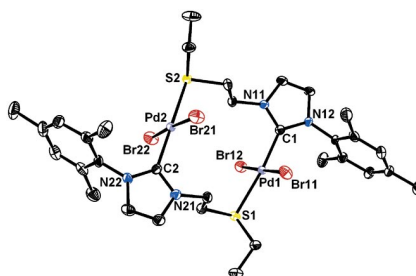
**Keywords:** Biomimetic catalysis / Iron-only hydrogenases / Diiron dithiolate / CO substitution / Electrochemistry / Proton reduction



$[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_5\{\text{P}(\text{OMe})_3\}]$  (2) and  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4\{\text{P}(\text{OMe})_3\}_2]$  (3) were prepared by the electrochemical reduction of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_6]$  (1) in the presence of trimethyl phosphite. Electrochemical

data indicate a CO-displacement reaction catalyzed by electron transfer. These compounds serve as models for the active site of iron-only hydrogenases.

A series of new, bifunctional imidazolium–thioether ligands have been synthesised using a general method and used as N-heterocyclic carbene (NHC) precursors for complexation studies on various transition metals ( $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$  and  $\text{Rh}^{\text{I}}$ ).  $\text{Rh}^{\text{I}}$  complexes showed a good activity for the hydrosilylation of ketones.



J. Wolf, A. Labande,\* J.-C. Daran,  
R. Poli ..... 5069–5079

Nickel(II), Palladium(II) and Rhodium(I) Complexes of New NHC-Thioether Ligands: Efficient Ketone Hydrosilylation Catalysis by a Cationic Rh Complex

**Keywords:** N-Heterocyclic carbenes / S ligands / Nickel / Palladium / Rhodium

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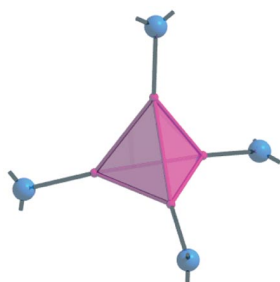
## Cluster Chemistry

A. Seifert, G. Linti\* ..... 5080–5086



Synthesis and Structure of Tetrameric Gallium(I) Amides

**Keywords:** Gallium / Amides / Cluster compounds / X-ray structures / Density functional calculations



The gallium(I) amides  $\text{GaNR}_2$  [ $\text{NR}_2 = \text{tmp}, \text{N}(\text{SiMe}_3)\text{dipp}$ ] were prepared from “GaI”. They form distorted tetrahedral tetramers in the solid state.

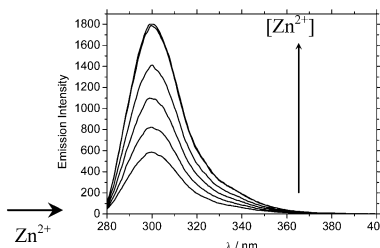
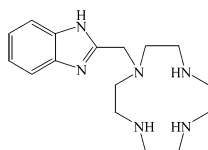
## Fluorescent Probes

A. El Majzoub, C. Cadiou,  
I. Déchamps-Olivier, F. Chuburu,\*  
M. Aplincourt ..... 5087–5097



(Benzimidazolymethyl)cyclen: A Potential Sensitive Fluorescent PET Chemosensor for Zinc

**Keywords:** Zinc / Macrocyclic ligands / X-ray diffraction / UV/Vis spectroscopy / Fluorescent probes / Fluorimetric titrations



A new fluorescent probe for  $\text{Zn}^{2+}$ , namely (benzimidazolymethyl)cyclen [LH], was designed and synthesised. On addition of

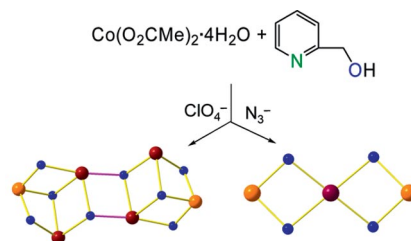
successive amounts of  $\text{Zn}^{2+}$ , the fluorescence emission of LH increases linearly by a factor of 3.

## Mixed-Valence $\text{Co}^{\text{II/III}}$ Complexes

T. C. Stamatatos, A. K. Boudalis,  
K. V. Pringouri, C. P. Raptopoulou,  
A. Terzis, J. Wolowska, E. J. L. McInnes,\*  
S. P. Perlepes\* ..... 5098–5104

Mixed-Valence Cobalt(II/III) Carboxylate Clusters:  $\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2$  and  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2$  Complexes from the Use of 2-(Hydroxymethyl)pyridine

**Keywords:** Mixed-valence cobalt complexes / [2-(Hydroxymethyl)pyridine]metal complexes / Linear trinuclear cobalt complexes / Hexanuclear cobalt clusters / Q-band electron paramagnetic resonance



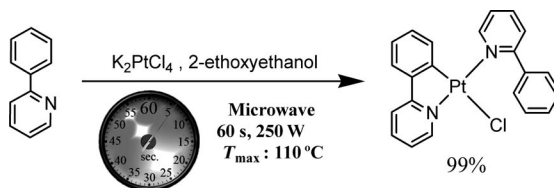
The shown reaction scheme gives a hexanuclear, mixed-valence cationic cluster containing the unprecedented  $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2(\mu_3\text{-OR}')_4(\mu\text{-OR}')_4]^{6+}$  core (the benzoate analogue has a similar structure) and a linear  $\text{Co}^{\text{III}}\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  neutral complex containing the  $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\mu\text{-OR}')_4]^{4+}$  core, depending on the inorganic anion present; the  $\text{Co}^{\text{II}}$  ions in the hexanuclear clusters are antiferromagnetically coupled.

## Microwave-Assisted Cycloplatination

N. Godbert, T. Pugliese, I. Aiello,  
A. Bellusci, A. Crispini,  
M. Ghedini\* ..... 5105–5111

Efficient, Ultrafast, Microwave-Assisted Syntheses of Cycloplatinated Complexes

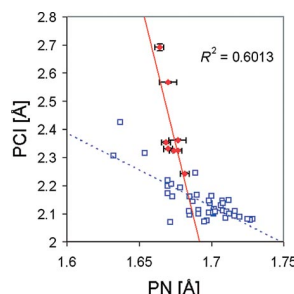
**Keywords:** Cycloplatination / Microwave synthesis / Platinum / Antitumor agents / X-ray diffraction



Mononuclear cycloplatinated chlorido complexes containing neutral ligands are synthesised by two different methods, namely conventional and microwave-assisted

synthesis. All new complexes have been fully characterised and their crystal structures determined.

A series of N-heterocyclic chlorophosphanes and 1,3,2-diazaphospholenium salts with different substitution patterns is prepared and characterised by single-crystal X-ray diffraction studies. An analysis of trends in the structural parameters supports the view that the unusual P–Cl bond lengthening is attributable to  $n(\text{N})/\sigma^*(\text{P}-\text{Cl})$  hyperconjugation.



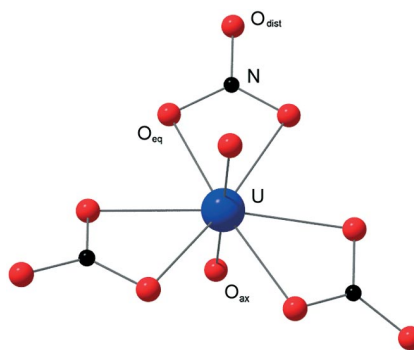
S. Burck, D. Gudat,\* K. Nättinen,  
M. Nieger, M. Niemeyer,  
D. Schmid ..... 5112–5119

2-Chloro-1,3,2-diazaphospholenes – A  
Crystal Structural Study

**Keywords:** Phosphanes / Halides / X-ray  
diffraction / Substituent effects / Structure  
correlation

### Speciation of Uranyl Nitrate

Complex formation between the uranyl ion and nitrate ions is investigated in acetonitrile and the ionic liquid  $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$  at room temperature by optical absorption, magnetic circular dichroism and EXAFS spectroscopy. The sharp peaks in the absorption spectrum are characteristic of a  $[\text{UO}_2(\text{NO}_3)_3]^-$  species with  $D_{3h}$  coordination symmetry. No evidence is found for the formation of uranyl nitrate complexes in aqueous solution.



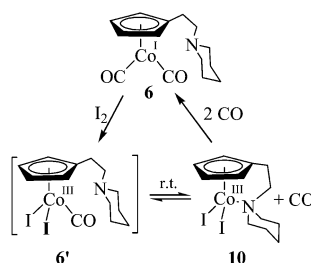
K. Servaes, C. Hennig,\* I. Billard,  
C. Gaillard, K. Binnemans,  
C. Görller-Walrand,  
R. Van Deun\* ..... 5120–5126

Speciation of Uranyl Nitrate Complexes in  
Acetonitrile and in the Ionic Liquid 1-  
Butyl-3-methylimidazolium Bis(trifluoro-  
methylsulfonyl)imide

**Keywords:** EXAFS spectroscopy / Ionic  
liquids / Uranium / UV/Vis spectroscopy /  
X-ray absorption spectroscopy

### Cyclopentadienylcobalt Complexes

Chelation by the amino-functionalised side chain occurred when the Cp'-cobalt(I) dicarbonyl complexes were oxidised by iodine, resulting in the corresponding Cp'-cobalt(III) chelates via diiodocarbonyl intermediates. The stabilities of the intermediates were found to correlate with the I–Co–I angles and the repulsive force from the amino-functionalised groups in the chelates. Complex **6'** was reduced to **6** by the CO released upon chelation. Its  $\text{PPh}_3$ -substituted  $\text{CH}_2\text{CH}_2$  solvate shows a strong  $\text{N}-\text{H}\cdots\text{I}$  hydrogen bond.



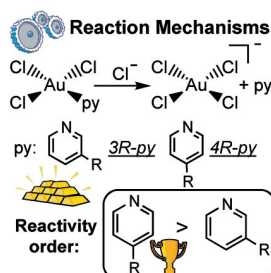
L. Li, S. Han, Q. Li, Z. Chen,  
Z. Pang\* ..... 5127–5137

Synthesis and Reactivity of Cobalt Com-  
plexes with Pendant Nitrogen Functional  
Groups

**Keywords:** Cyclopentadienylcobalt com-  
plexes / Carbonylcobalt complexes

### Inorganic Reaction Mechanisms

The process  $\text{AuCl}_3(3\text{R-py}) + \text{Cl}^- \rightarrow \text{AuCl}_4^- + 3\text{R-py}$  ( $3\text{R-py}$  = *meta*-substituted pyridines) was studied in methanol at 25 °C and the data were compared with those found for *para*-substituted pyridines ( $4\text{R-py}$ ). Until now the two groups of bases have been considered to behave in the same manner in their displacement reactions but, on the contrary, the reactivity of the two classes of N donors is slightly different and follows the order:  $4\text{R-py} > 3\text{R-py}$ . This kinetic result is explained on the basis of an energetic difference between the frontier orbitals of the  $\text{AuCl}_3(3\text{R-py})$  and  $\text{AuCl}_3(4\text{R-py})$  derivatives.



B. Pitteri,\* M. Bortoluzzi ..... 5138–5143

Displacement of Neutral Nitrogen Donors  
by Chloride in  $\text{AuCl}_3(3\text{R-py})$  ( $3\text{R-py}$  =  
*meta*-Substituted Pyridine): Comparison  
between *meta*- and *para*-Substituted Pyr-  
idines by Kinetics and DFT Calculations

**Keywords:** Gold / Kinetics / Nitrogen  
donors / Reaction Mechanism / DFT