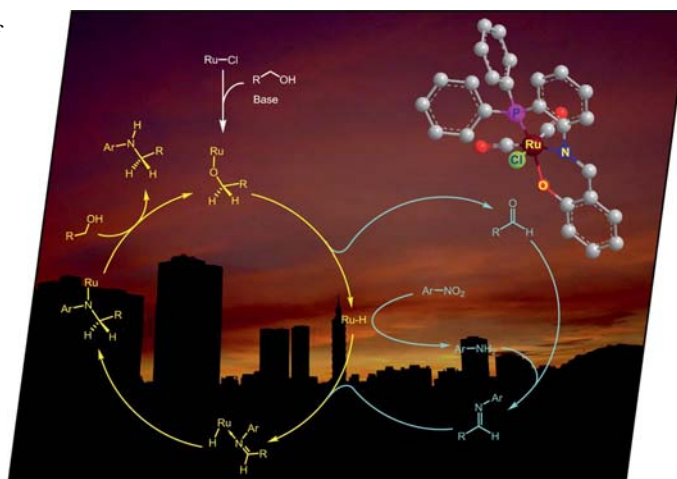


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## COVER PICTURE

The cover picture shows the catalytic conversion of amines or nitroarenes with alcohols into useful amino compounds by [P,N,O]-Ru<sup>II</sup> complexes in a one-pot reaction, which is a sustainable cycle in organic synthesis. The ruthenium(II) complexes serving as catalysts in this work were prepared by complexation of Ru<sup>II</sup> precursors with various [P,N,O] ligands and were characterized by spectroscopic methods and X-ray crystallography. These investigations provided some insight into ligand effects on the metal ions. Details are discussed in the article by C.-C. Lee et al. on p. 4801ff.



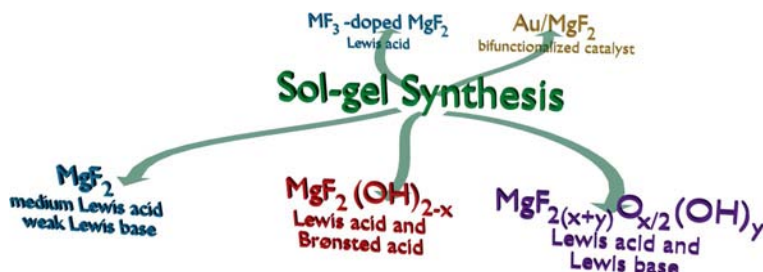
## MICROREVIEW

### Magnesium Fluoride Catalysts

E. Kemnitz,\* S. Wuttke,  
S. M. Coman ..... 4773–4794

Tailor-Made  $\text{MgF}_2$ -Based Catalysts by  
Sol–Gel Synthesis

**Keywords:** Nanoparticles / Magnesium /  
Fluorides / Heterogeneous catalysis / Sol–  
gel processes



Nanosized metal fluorides prepared by the fluorolytic sol–gel method represent an exciting new class of high-surface-area solid acid–base catalysts. A combination of

fluorolytic and hydrolytic sol–gel synthesis provides access to metal hydroxide fluorides or metal oxide fluorides.

## SHORT COMMUNICATION

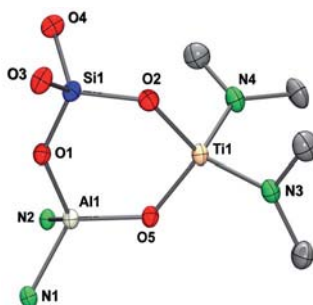
### Molecular Alumosilicates

R. Huerta-Lavorie, F. Rascón-Cruz,  
D. Solís-Ibarra, N. Zavala-Segovia,  
V. Jancik\* ..... 4795–4799



Soluble Alumotitanosilicates and Their  
Zirconium and Hafnium Analogues

**Keywords:** Aluminum / Titanium / Silicates



Unprecedented molecular heterobimetallic alumosilicates with inorganic cores  $\text{O–Al–O–Si–O–M}$  or  $(\text{O–Al–O–Si–O})_2\text{M}$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) have been prepared by reaction of the molecular alumosilicate  $\text{LAl}(\text{OH})(\mu\text{-O})\text{Si}(\text{OH})(\text{O}t\text{Bu})_2$  ( $\text{L} = [\text{HC}\{(\text{Me})\text{N}(\text{Ar})\}_2]^-$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) with group 4 metal amides in different ratios.

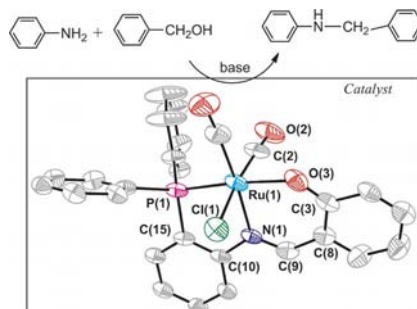
## FULL PAPERS

### Tridentate P,N,O Ligands

C.-C. Lee, W.-Y. Chu, Y.-H. Liu,  
S.-M. Peng, S.-T. Liu\* ..... 4801–4806

Coordination and Catalytic Activity of  
Ruthenium Complexes Containing Tridentate  
P,N,O Ligands

**Keywords:** Ruthenium / Tridentate li-  
gands / Amination / Hydrogen transfer /  
N,P ligands



Ruthenium complexes containing P,N,O ligands have been synthesized and characterized. These  $\text{Ru}^{\text{II}}$  species appear to be good catalysts for the reductive amination of amines or nitrobenzene with alcohols.

[K(15-crown-5)<sub>2</sub>]<sub>2</sub>[Ni<sub>4</sub>(α-tpdt)<sub>6</sub>] was prepared by oxidation of the dianionic [Ni(α-tpdt)<sub>2</sub>]<sup>2-</sup> complex and was characterised by X-ray crystallography. This compound constitutes an unprecedented example of an in-line mixed-valence Ni<sub>4</sub> dithiolene (Ni<sub>4</sub>S<sub>12</sub>) cluster.

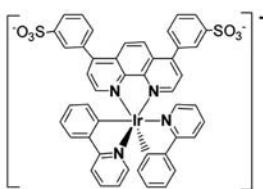
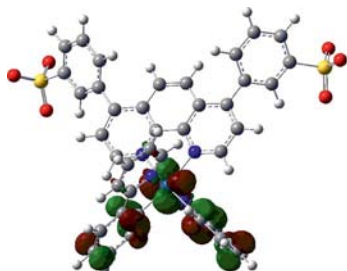


A. I. S. Neves, I. C. Santos,  
L. C. J. Pereira, C. Rovira, E. Ruiz,  
D. Belo,\* M. Almeida\* ..... 4807–4815

Ni-2,3-thiophenedithiolate Anions in New Architectures: An In-Line Mixed-Valence Ni Dithiolene (Ni<sub>4</sub>–S<sub>12</sub>) Cluster

**Keywords:** Nickel / Cluster compounds / Crown compounds / Magnetic properties / S ligands / Sulfur heterocycles

### Luminescent Iridium Complexes



The photophysical and electrochemical properties of water- and organic solvent-soluble phenanthroline-based bis-cyclometallated iridium complexes were investigated. The luminescent and electrochemi-

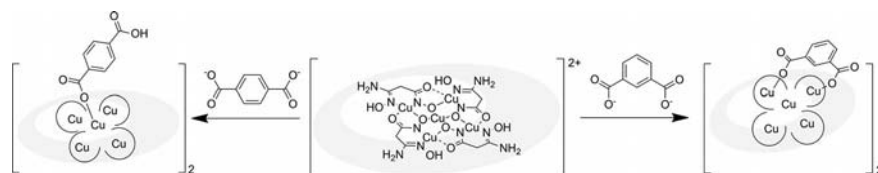
cal characteristics are found to be strongly dependant on the medium, which has implications for sensing and other applications of such materials in aqueous media.

R. V. Kiran, C. F. Hogan,\* B. D. James,  
D. J. D. Wilson ..... 4816–4825

Photophysical and Electrochemical Properties of Phenanthroline-Based Bis-cyclometallated Iridium Complexes in Aqueous and Organic Media

**Keywords:** Iridium / Electrochemistry / Luminescence / Density functional calculations

### Sorption by Complexes



Three complexes were obtained starting from a pentacopper 12-metallacrown-4 and isomeric benzenedicarboxylates. The structures of the complexes determined by XRD

may be considered as models of intermediates that form during the interaction of these non-rigid sorbents with alcohols.

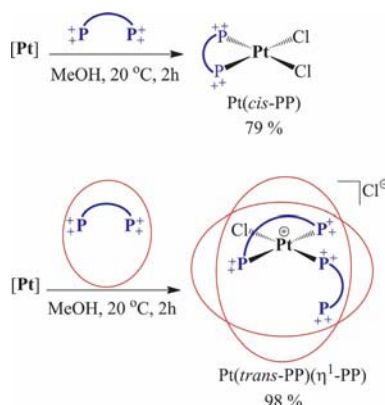
A. V. Pavlishchuk, S. V. Kolotilov,\*  
M. Zeller, O. V. Shvets, I. O. Fritsky,  
S. E. Lofland, A. W. Addison,\*  
A. D. Hunter ..... 4826–4836

Magnetic and Sorption Properties of Supramolecular Systems Based on Pentanuclear Copper(II) 12-Metallacrown-4 Complexes and Isomeric Phthalates: Structural Modeling of the Different Stages of Alcohol Sorption

**Keywords:** Metallacrown compounds / Copper / Sorption / Magnetic properties

### Supramolecular Pt Capsules

Metal in the box! A new supramolecular strategy for controlling the coordination chemistry of transition metal complexes is reported, which involves the encapsulation of metal complexes by mixing functionalized calixarenes and bisphosphane ligated complexes.



T. S. Koblenz, H. L. Dekker,  
C. G. de Koster, P. W. N. M. van Leeuwen,  
J. N. H. Reek\* ..... 4837–4845

Control of the Coordination Geometry Around Platinum by a Supramolecular Capsule

**Keywords:** Supramolecular chemistry / Supramolecular capsules / Platinum / Calixarenes / Ionic interactions / Phosphane ligands

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## Catalytic Activity

M. R. Maurya,\* P. Saini, A. Kumar,  
J. Costa Pessoa\* ..... 4846–4861



Oxidovanadium(IV) Complexes of Tetradentate Ligands Encapsulated in Zeolite-Y as Catalysts for the Oxidation of Styrene, Cyclohexene and Methyl Phenyl Sulfide

**Keywords:** Heterogeneous catalysis / Vanadium / Oxidation / EPR spectroscopy



Complexes  $[V^{IV}O(pydx-en)]$  (1),  $[V^{IV}O(pydx-1,3-pn)]$  (2) and  $[V^{IV}O(pydx-1,2-pn)]$  (3) are reported as well as their encapsu-

lation in the cavity of zeolite-Y and their catalytic activity for the oxidation of styrene, cyclohexene and methyl phenyl sulfide.

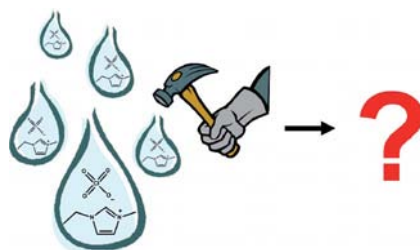
## Ionic Liquids

M. Schmeisser, P. Keil, J. Stierstorfer,  
A. König, T. M. Klapötke,  
R. van Eldik\* ..... 4862–4868



An Ionic Liquid Designed for Coordination Chemistry Revisited: Synthetic Routes and Safety Tests for 1-Ethyl-3-methylimidazolium Perchlorate ([emim][ClO<sub>4</sub>])

**Keywords:** Ionic liquids / Metathesis / Thermal stability / Impact and friction sensitivity



Unlike the conventional synthesis procedure that uses silver perchlorate and 1-ethyl-3-methylimidazolium [emim] halides, we present two alternative methods to synthesize the room-temperature ionic liquid [emim][ClO<sub>4</sub>]. We additionally determined some physicochemical parameters and tested its thermal stability and impact and friction sensitivity.

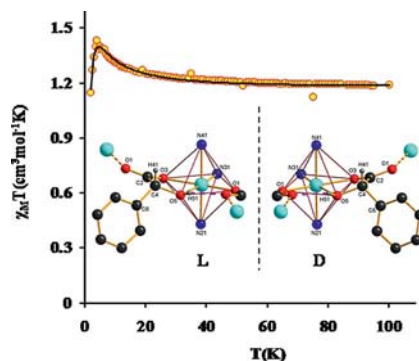
## Chiral Coordination Polymers

G. Novitchi, G. Pilet,  
D. Luneau\* ..... 4869–4877



1D Co<sup>II</sup> and Ni<sup>II</sup> Chiral Polymers That Exhibit Ferromagnetic Interactions

**Keywords:** Crystal engineering / Chain structures / Cobalt / Nickel / Carboxylate ligands



Four 1D chiral coordination polymers of Ni<sup>II</sup> and Co<sup>II</sup> with D- and L-mandelic acid (*Hmand*) were structurally and magnetically characterized. Magnetic studies reveal the presence of ferromagnetic interactions along the chains.

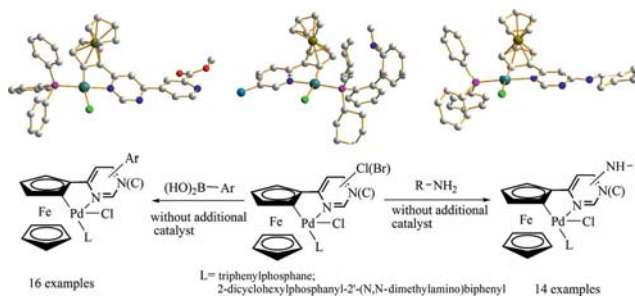
## Halide-Containing Palladacycles

C. Xu,\* Z.-Q. Wang, Y.-P. Zhang,  
X.-M. Dong, X.-Q. Hao, W.-J. Fu,  
B.-M. Ji, M.-P. Song ..... 4878–4888



Synthesis and Structural Characterization of Palladacycles with Polydentate Ligands by a Stepwise Coupling Route – Palladacycles Containing Halides as Efficient Catalysts and Substrates

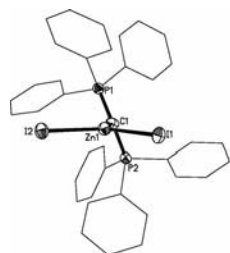
**Keywords:** Palladium / Sandwich complexes / Homogeneous catalysis / Amination / Halides / Palladacycles



An efficient method for the synthesis of palladacycles with polydentate ligands by a stepwise coupling route without additional catalysis is presented. The halide-contain-

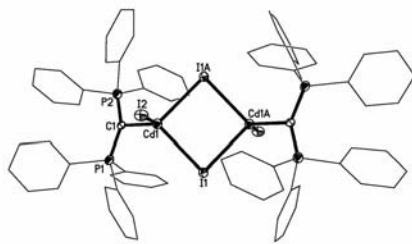
ing palladacycles act as efficient catalysts and substrates in coupling reactions. 37 examples and the crystal structures of eight samples are reported.





$\text{I}_2\text{Zn}-\text{C}(\text{PPh}_3)_2$

The reaction of the  $\text{C}(\text{PPh}_3)_2$  with  $\text{ZnI}_2$  in 2-bromofluorobenzene yields the monomeric adduct  $[\text{I}_2\text{Zn}\{\text{C}(\text{PPh}_3)_2\}]$ , whereas with  $\text{CdI}_2$  the dimeric complex  $[\text{I}_2\text{Cd}\{\text{C}(\text{PPh}_3)_2\}]_2$  is formed. For steric reasons, the change in ionic radius from  $\text{Zn}^{2+}$



$(\text{PPh}_3)_2\text{C} \rightarrow \text{CdI}(\mu\text{-I})_2\text{ICd}-\text{C}(\text{PPh}_3)_2$

to  $\text{Cd}^{2+}$  allows dimerization only for the Cd complex. In THF or DME proton abstraction from the solvent gives rise to the salt-like compounds  $(\text{HC}\{\text{PPh}_3\}_2)[\text{MI}_3(\text{THF})]$  ( $\text{M} = \text{Zn}, \text{Cd}$ ).

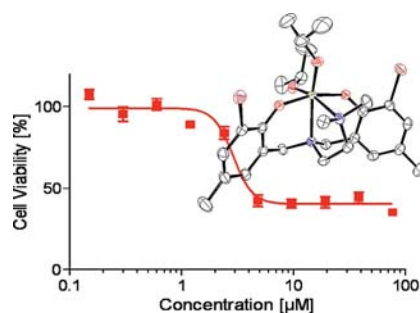
W. Petz,\* B. Neumüller\* ..... 4889–4895

Reaction of  $\text{C}(\text{PPh}_3)_2$  with  $\text{MI}_2$  Compounds ( $\text{M} = \text{Zn}, \text{Cd}$ ) – Formation and Crystal Structures of  $[\text{I}_2\text{Zn}\{\text{C}(\text{PPh}_3)_2\}]$ ,  $[\text{I}_2\text{Cd}\{\text{C}(\text{PPh}_3)_2\}]_2$  and the Salt-Like Compounds  $(\text{HC}\{\text{PPh}_3\}_2)[\text{MI}_3(\text{THF})]$  and  $(\text{HC}\{\text{PPh}_3\}_2)_2[\text{ZnI}_4]$

**Keywords:** Ylides / Zinc / Cadmium / Addition compounds / Carbodiphosphorane

## Cytotoxic Metal Complexes

The cytotoxicity and hydrolysis of  $\text{Ti}^{\text{IV}}$  complexes of branched diamine bis(phenolato) ligands are reported. Alkylated complexes exhibit poor stability presumably due to weaker binding of the side arm, with negligible cytotoxicity. In contrast, *ortho*-halogenated complexes, although hydrolytically unstable, demonstrate marked cytotoxicity.

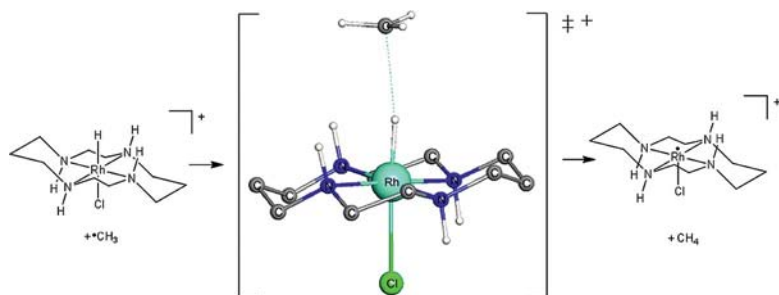


D. Peri, C. M. Manna, M. Shavit, E. Y. Tshuva\* ..... 4896–4900

$\text{Ti}^{\text{IV}}$  Complexes of Branched Diamine Bis(phenolato) Ligands: Hydrolysis and Cytotoxicity

**Keywords:** Titanium / Antitumor agents / Cytotoxicity / Phenolato ligands / Hydrolysis

## H-Abstraction Mechanism



The controversy in the reported kinetics for the hydrogen-atom abstraction reaction by methyl radicals for *cis*- and *trans*-[(Cyclam)- $\text{Rh}^{\text{III}}\text{HCl}]^+$  and *trans*-[(Cyclam)( $\text{H}_2\text{O}$ )-

$\text{Rh}^{\text{III}}\text{H}]^{2+}$  has been resolved by studying several feasible mechanistic pathways with density functional theory.

J. M. Keith\*, D. Meyerstein, M. B. Hall\* ..... 4901–4905

Computational Investigations into Hydrogen-Atom Abstraction from Rhodium Hydride Complexes by Methyl Radicals in Aqueous Solution

**Keywords:** Kinetics / Rhodium / Radical reactions / Density functional calculations

## Porphyrin-Stabilized Au Nanoparticles

A porphyrin-bridged Pd complex was prepared and used for the stabilization of gold nanoparticles (AuNPs). AuNPs with a mean diameter of 5 nm and plasmon resonance at 500 nm were obtained. XPS, NMR spectroscopic and elemental analyses indicate the presence of about 120 tilted porphyrin-based complexes physisorbed onto the Au core, with no evidence of covalent bonds.



I. Fratoddi,\* C. Battocchio, G. Polzonetti, F. Sciubba, M. Delfini, M. V. Russo ..... 4906–4913

A Porphyrin-Bridged Pd Dimer Complex Stabilizes Gold Nanoparticles

**Keywords:** Gold / Nanoparticles / Porphyrinoids / Palladium / NMR spectroscopy

\* Author to whom correspondence should be addressed.

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