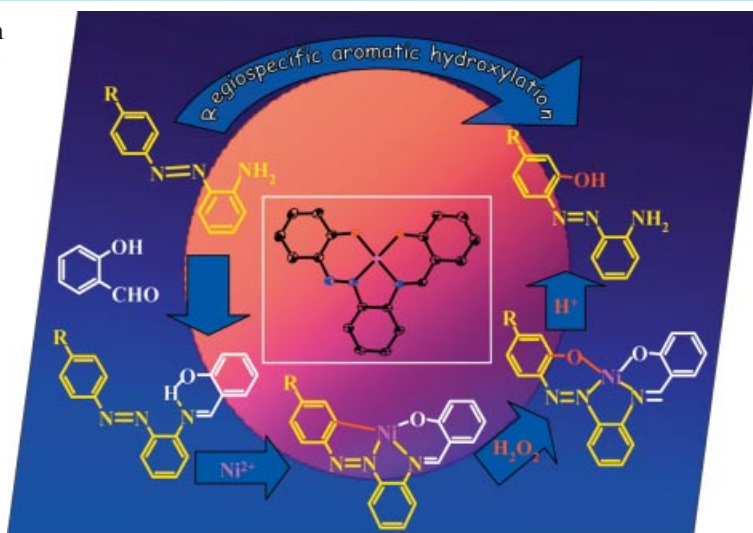


The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows the reaction sequence of an  $\text{Ni}^{\text{II}}$ -assisted regiospecific *ortho*-aromatic hydroxylation. Sequential events of orthonickelation, oxygen insertion into the Ni–C bond induced by  $\text{H}_2\text{O}_2$  and demetallation have been demonstrated to be involved in the aromatic hydroxylation in 2-(aryl-azo)aniline. The  $\text{H}_2\text{O}_2$ -induced O insertion into the Ni–C bond led to the formation of *metalloazo-salophen* analogues of *metallo-salophens* for the first time. Details are discussed in the article by S. Chattopadhyay et al. on p. 4263f.



## FULL PAPERS

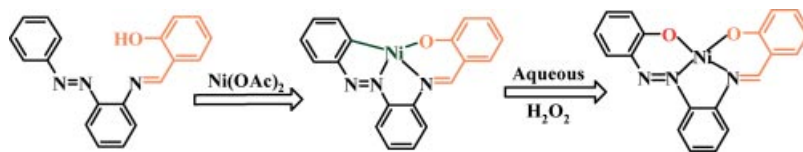
### Metal-Assisted Synthesis

P. Pattanayak, J. Lal Pratihari, D. Patra,  
A. Burrows, M. Mohan,  
S. Chattopadhyay\* ..... 4263–4271



Regiospecific *ortho*-Aromatic Hydroxylation via Cyclonickelation Using Hydrogen Peroxide and Other Oxygen Donors: Synthesis of Metalloazosalophens

**Keywords:** Nickel / N,O ligands / Metallacycles / Oxygenation / Peroxo reagents / C–H activation



The first metalloazosalophen complexes, (OL<sub>sal</sub>)Ni, were prepared by a Ni<sup>II</sup>-assisted route. Ni–C bond formation and sub-

sequent facile oxygen insertion induced by peroxo reagents *m*CPBA, TBHP, or aqueous H<sub>2</sub>O<sub>2</sub> were exploited for this purpose.

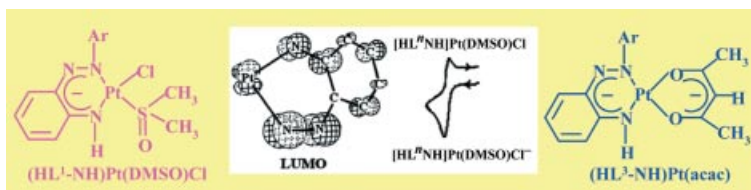
### Pt<sup>II</sup> and Pd<sup>II</sup> Chelates

J. Lal Pratihari, B. Shee, P. Pattanayak,  
D. Patra, A. Bhattacharyya, V. G. Puranik,  
C. H. Hung,  
S. Chattopadhyay\* ..... 4272–4281



Synthesis, Structure, and Reactivity of Diazoketimino Complexes of Platinum(II) and Palladium(II): Cytotoxic Properties of a Platinum Complex

**Keywords:** Chelating ligands / Platinum / Palladium / Redox chemistry / Bioinorganic chemistry



New Pt<sup>II</sup> complexes incorporating delocalized diazoketimino ligands have been prepared and their chemical, electrochemical, and cytotoxic properties studied. A

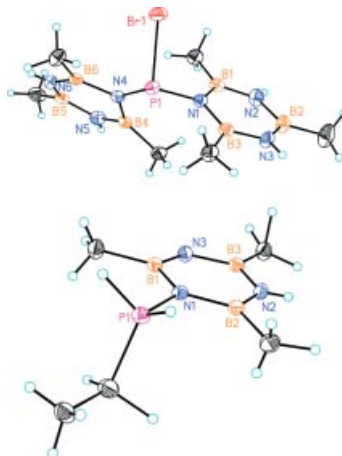
strategy to prepare an electroactive model Pt<sup>II</sup>-based antitumor drug has emerged as a consequence.

### Phosphanes, Arsanes and Stibanes

H. Nöth,\* B. Gemünd,  
R. T. Paine ..... 4282–4297

*N*-(2,4,6-Trimethylborazynyl)-Substituted Phosphanes, Arsanes, and Stibanes

**Keywords:** Boron / Phosphanes / Arsenic / Antimony



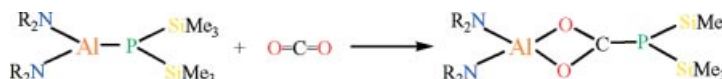
*N*-Monolithio-*B*, *B'*, *B''*-trimethylborazine reacts with PX<sub>3</sub>, AsX<sub>3</sub>, or SbX<sub>3</sub> (X = Cl, Br) to give the *N*-trimethylborazynyl-substituted phosphanes, arsanes, and stibanes (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>n</sub>EX<sub>3–n</sub> (E = P, As, Sb; *n* = 1, 2, 3). Treatment of (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>PBr with LiAlH<sub>4</sub> in diethyl ether gives the phosphane (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>PH, while (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>PBr<sub>2</sub> yields the zwitterionic compound [Me<sub>3</sub>B<sub>3</sub>(NH)N(N<sup>–</sup>–P<sup>+</sup>H<sub>2</sub>Et)]. Dehalogenation of (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>PBr with Na yields the corresponding diphosphane, and dehalogenation of (Me<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>PBr<sub>2</sub> the corresponding cyclotetraphosphane.

### (Amino)(phosphanyl)aluminum Chemistry

T. Haberer, H. Nöth,\*  
R. T. Paine\* ..... 4298–4305

Synthesis and Reactivity of New Bis(tetramethylpiperidino)(phosphanyl)aluminas

**Keywords:** Aminoaluminas / Phosphanylaluminas / Carbon dioxide insertion / Phosphanylcarbonate ligand / Structure elucidation

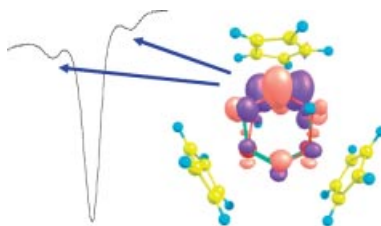


The bis(amino)(phosphanyl)aluminum, tmp<sub>2</sub>AlP(SiMe<sub>3</sub>)<sub>2</sub>, undergoes selective in-

sertion in the Al–P bond, not the Al–N bonds, with CO<sub>2</sub>, COS and CS<sub>2</sub>.

## Aqueous Reduction of [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>]

Two related triangular tungsten clusters, 3-electron [Cp\*<sub>3</sub>W<sub>3</sub>O<sub>4</sub>(OH)<sub>2</sub>]<sup>2+</sup> and 2-electron [Cp\*<sub>3</sub>W<sub>3</sub>O<sub>6</sub>]<sup>+</sup> obtained by aqueous reduction of [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>], are described.



**C. Dinoi, P. Sözen, G. Taban, D. Demir,**  
**F. Demirhan,\* P. Prikhodchenko,**  
**J. Gun, O. Lev, J.-C. Daran,**  
**R. Poli\* ..... 4306–4316**

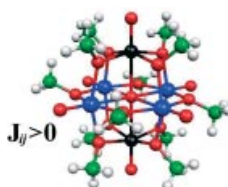
Aqueous Reduction of [Cp\*<sub>2</sub>W<sub>2</sub>O<sub>5</sub>]:  
 Characterization of the Triangular Clusters  
 [Cp\*<sub>3</sub>W<sub>3</sub>O<sub>4</sub>(OH)<sub>2</sub>]<sup>2+</sup> and [Cp\*<sub>3</sub>W<sub>3</sub>O<sub>6</sub>]<sup>+</sup> –  
 Comparison with Molybdenum



**Keywords:** Tungsten / O ligands / Metal  
 clusters / Density functional calculations

## Ferroexchange in Polyoxovanadates

DFT calculations suggest that the V<sup>IV</sup>/V<sup>V</sup> mixed-valence alkoxo-polyoxovanadate [4V<sup>IV</sup> + 2V<sup>V</sup>] is valence-trapped and characterized by ferromagnetic interactions between the vanadium(IV) centers.



**E. M. Zueva,\* S. A. Borshch,\***  
**M. M. Petrova, H. Chermette,**  
**A. M. Kuznetsov ..... 4317–4325**

Ferromagnetic Coupling in a Mixed-  
 Valence Hexavanadate Core: Quantum-  
 Chemical Forecast

**Keywords:** Mixed-valent compounds /  
 Vanadates / Density functional calcula-  
 tions / Exchange interactions / Electron  
 transfer

## Fe<sup>II</sup> Spin-Crossover Complexes

1-*N*-R<sup>2</sup>-Imidazole-2-carboxaldehyde (R<sup>2</sup> = H, Me) was used as a carbonyl synthon for the synthesis of symmetrical and dissymmetrical tetradentate Schiff bases. In the symmetrical series the NCS<sup>−</sup> moieties are *trans* for R<sup>2</sup> = H and *cis* for R<sup>2</sup> = Me. In the dissymmetrical series the electronic behaviour evidences that the combination of pyridyl and imidazolyl rings allows the generation of an intermediate ligand field suitable for spin crossover.



**N. Bréfuel,\* S. Shova,**  
**J.-P. Tuchagues\* ..... 4326–4334**

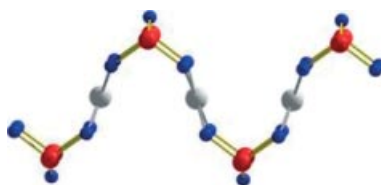
Fe<sup>II</sup> Bistable Materials with Dissymmetrical  
 Ligands: Synthesis, Crystal Structure,  
 Magnetic and Mössbauer Properties of Fe<sup>II</sup>  
 Complexes Based on N<sub>4</sub> Schiff Bases Pos-  
 sessing 2-Pyridyl and 1-*R*-Imidazol-2-yl  
 Rings



**Keywords:** Schiff bases / N ligands / Iron /  
 Spin crossover / Magnetic properties /  
 Mössbauer spectroscopy

## Oxoanionic Palladium Compounds

Elemental palladium can be oxidized by selenic acid at elevated temperatures to form Pd(SeO<sub>3</sub>), Pd(SeO<sub>4</sub>), or Pd(Se<sub>2</sub>O<sub>5</sub>), depending on the reaction conditions. These compounds are the first oxoselenates of a platinum-group metal.



**A. Arndt, M. S. Wickleder\* ... 4335–4339**

Pd(SeO<sub>3</sub>), Pd(SeO<sub>4</sub>), and Pd(Se<sub>2</sub>O<sub>5</sub>): The  
 First Palladium Oxoselenates

**Keywords:** Solid-state structures / Palla-  
 dium / Selenium / Lone-pair effect / IR  
 spectroscopy

# CONTENTS

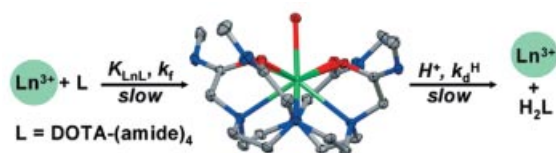
## Ln–DOTA Complexes

A. Pasha, G. Tircsó,\* E. Tircsóné Benyó,  
E. Brücher, A. D. Sherry\* ..... 4340–4349



Synthesis and Characterization of DOTA-(amide)<sub>4</sub> Derivatives: Equilibrium and Kinetic Behavior of Their Lanthanide(III) Complexes

**Keywords:** Magnetic resonance imaging / Contrast agents / Protonation constants / Stability constants / Kinetics



The stabilities of the lanthanide(III) DOTA-(amide)<sub>4</sub> complexes are several orders of magnitude lower than the stabilities of the corresponding [Ln(DOTA)]<sup>−</sup> complexes. The formation rates of the [Ln{DOTA-(MeAm)<sub>4</sub>}]<sup>3+</sup> complexes proved to be slow, following second-order

reaction kinetics. The rates of acid-catalyzed dissociation of [Eu{DOTA-(MeAm)<sub>4</sub>}]<sup>3+</sup> complexes, however, are also quite slow, which suggests that these complexes may ultimately prove suitable for in vivo applications.

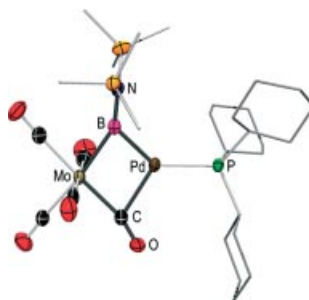
## Molybdenum Borylene Complexes

H. Braunschweig,\* K. Radacki,  
K. Uttinger ..... 4350–4356

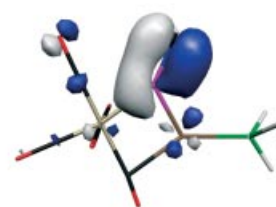


Synthesis and Characterisation of Semi-Bridging Molybdenum Borylene Complexes

**Keywords:** Boron / Borylene complexes / Molybdenum / Palladium / DFT calculations



A variety of heterodinuclear borylene complexes was obtained from the reaction of [(OC)<sub>5</sub>Mo=B=N(SiMe<sub>3</sub>)<sub>2</sub>] with [M(PCy<sub>3</sub>)<sub>2</sub>]



(M = Pd, Pt). Structural studies and DFT computations revealed that the borylene ligand adopts a semi-bridging position.

## Functionalized Polyoxometalates

F. Bannani, R. Thouvenot,\*  
M. Debbabi\* ..... 4357–4363

Synthesis and Characterization of New Organosilyl Derivatives of Polyoxometalates (*n*Bu<sub>4</sub>N)<sub>2</sub>[NbW<sub>5</sub>O<sub>19</sub>SiRR'<sub>2</sub>] (R = R' = Et, *i*Pr, *O*tBu, Ph; R = *t*Bu and R' = Me) – The X-ray Crystal Structure of (*n*Bu<sub>4</sub>N)<sub>2</sub>[NbW<sub>5</sub>O<sub>19</sub>SiPh<sub>3</sub>]

**Keywords:** Polyoxometalates / Organic–inorganic hybrid / Multinuclear NMR spectroscopy



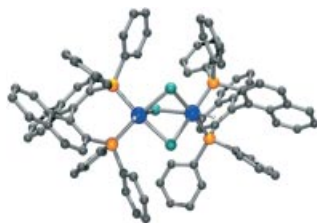
The selective coordination of electrophilic fragments {SiRR'<sub>2</sub>}<sup>+</sup> to the terminal O<sub>t</sub>(Nb) oxygen of the NbW<sub>5</sub>O<sub>19</sub><sup>3−</sup> Lindqvist-type polyoxometalate leads to the formation of organic–inorganic hybrids. These species are characterized by multinuclear NMR, IR, and Raman spectroscopy. A single-crystal X-ray study of (*n*Bu<sub>4</sub>N)<sub>2</sub>[NbW<sub>5</sub>O<sub>19</sub>SiPh<sub>3</sub>] supports the structure postulated on the basis of <sup>183</sup>W NMR study.

## C=O Hydrogenation

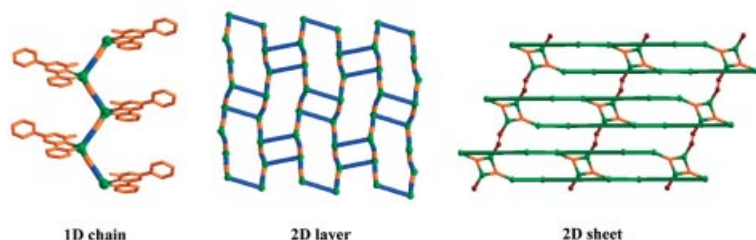
L. Dahlenburg,\* R. Menzel,  
F. W. Heinemann ..... 4364–4374

Synthesis and Catalytic Applications of Chiral Hydrido-iridium(III) Complexes with Diamine/Bis(monophosphane) and Diamine/Diphosphane Coordination

**Keywords:** Iridium / N ligands / P ligands / Asymmetric catalysis



The triply chlorido-bridged cation [(*R*)-binap]<sub>2</sub>Ir<sub>2</sub>H<sub>2</sub>(μ-Cl)<sub>3</sub><sup>+</sup> serves as a source of mixed-ligand compounds [Ir(H)(Cl)-(diamine){(*R*)-binap}]<sup>+</sup> that are otherwise difficult to prepare. The use of such diamine/(*R*)-binap-containing Ir<sup>III</sup> complexes as (pre)catalysts for the enantioselective hydrogenation of acetophenone provides optical yields close to those of established Ru<sup>II</sup> catalysts bearing identical ligands.



Three ligand isomers, namely 2-amino-4,6-bis(2-pyridyl)pyrimidine ( $L^1$ ), 2-amino-4-(2-pyridyl)-6-(4-pyridyl)pyrimidine ( $L^2$ ), and 2-amino-4-(2-pyridyl)-6-(3-pyridyl)pyrimidine ( $L^3$ ), are synthesized and employed in the copper(I) cyanide system. A novel 2D corrugated layer  $[Cu_2(CN)_2L^1]_n$  (**1**), 1D zigzag chains  $[CuCNL^2]_n$  (**2**) and

$[CuCNL^3]_n$  (**4**), and a 2D sheet  $[Cu_3(CN)_3L^3]_n$  (**3**) are successfully synthesized and their structures determined by single-crystal X-ray diffraction. These complexes demonstrate the tuning effect of the ligand isomerism upon the dimensionalities and motifs of the crystal structures.

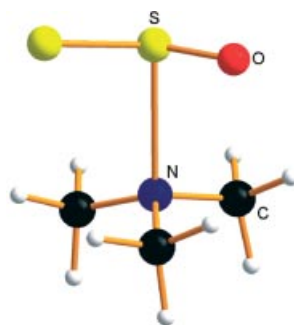
Y.-N. Chi, F.-Y. Cui, Y.-Q. Xu,  
C.-W. Hu\* ..... 4375–4384

The Tuning Effect of 2-Amino-4,6-dipyridylpyrimidine Isomers on the Structural Dimensionalities and Motifs of Copper(I) Cyanide Complexes



**Keywords:** Copper / Chelating ligands / N ligands / Crystal engineering

The acceptor molecules  $SO_2$ ,  $S_2O$ ,  $S_3$ , and  $SOCl_2$  react with  $NH_3$  and  $NMe_3$  to form donor–acceptor complexes that are most stable in a polar environment with a high dielectric constant. The interaction enthalpy and the S–N bond length of the complexes are inversely related to each other.



R. Steudel,\* Y. Steudel ..... 4385–4392

Charge-Transfer Complexes between the Sulfur Molecules  $SO_2$ ,  $S_2O$ ,  $S_3$ ,  $SONH$ , and  $SOCl_2$  and the Amine Donors  $NH_3$  and  $NMe_3$  – A Theoretical Study



**Keywords:** Ab initio calculations / Donor–acceptor systems / Thermodynamics / Sulfur / Solvent effects

If not otherwise indicated in the article, papers in issue 26 were published online on August 23, 2007