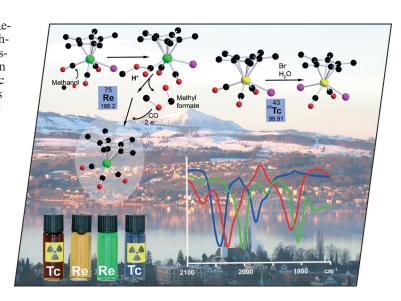




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## **COVER PICTURE**

The cover picture shows new aspects of [Cp\*Re-(CO)<sub>3</sub>Br]<sup>+</sup> and [Cp\*Tc(CO)<sub>3</sub>Br]<sup>+</sup> chemistry. High-yield preparation of these basic complexes (especially for <sup>99</sup>Tc) enabled a comparative exploration of the respective chemistries in water and organic solvents. The Lewis acidic Re<sup>III</sup> and Tc<sup>III</sup> centres activate the CO ligands for directed substitutions and nucleophilic attack. The reaction with CH<sub>3</sub>OH gave a methyl formate complex which reduced to [Cp\*M(CO)<sub>3</sub>] under acidic conditions. IR spectroscopy and kinetic studies with <sup>13</sup>C-labelled formate revealed the source for CO in [Cp\*-Re(CO)<sub>3</sub>]. Shown are the different colours of homologous Re and Tc complexes against a background of the Zurich lake area. The reactivity of the title compounds with alcohols implies potential for targeted inorganic medicinal chemistry if the OH group is pendent to a (radio)pharmaceutical. Details are discussed in the article by R. Alberto et al. on p. 4205ff. We thank Dr. F. Wild for designing this picture.



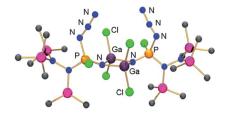
# SHORT COMMUNICATION

## **Phosphorus Azides**

A. Schulz,\* A. Villinger ....... 4199-4203

Staudinger Reaction as a Way Out To Avoid Cyclization in the Reaction of Silylated Dichloro(hydrazino)phosphane with Trimethylsilyl Azide

**Keywords:** Gallium / Azides / NBO analysis / Phosphorus heterocycles / Nitrogen heterocycles / Structure elucidation



A new phosphorus azide attached to a  $Ga_2N_2$  ring was synthesized from dichloro-(hydrazino)phosphane with trimethylsilyl azide. After an initial chlorine/azide exchange at the phosphorus atom, a series of reactions including a Staudinger reaction and a cyclization occurs finally resulting in a cyclic diazadigallane bearing two  $P-N_3$  groups.

# **FULL PAPERS**

### **Radiopharmaceutical Prodrugs**

F. Zobi, B. Spingler, R. Alberto\* ...... 4205-4214

Syntheses, Structures and Reactivities of [CpTc(CO)<sub>3</sub>X]<sup>+</sup> and [CpRe(CO)<sub>3</sub>X]<sup>+</sup>

**Keywords:** Rhenium / Technetium / Cyclopentadienyl ligand / Prodrug



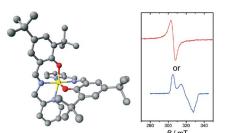
The chemistry of the [Cp\*MIII(CO)<sub>3</sub>Br]<sup>+</sup> complexes (M = Re, <sup>99</sup>Tc) was studied in water and in organic solvents in order to understand if these species could be synthons for the preparation of new Re and <sup>99</sup>Tc-based cyclopentadienyl cores for (radio)pharmaceutical applications. Although the [Cp\*MIII(CO)<sub>3</sub>Br]<sup>+</sup> ion cannot be used as formulated, it could provide a prodrug in stabilized form.

#### **Oxidation State of Ni Complexes**

O. Rotthaus, V. Labet, C. Philouze, O. Jarjayes,\* F. Thomas\* ...... 4215-4224

Pseudo-Octahedral Schiff Base Nickel(II) Complexes: Does Single Oxidation Always Lead to the Nickel(III) Valence Tautomer?

**Keywords:** Phenoxyl / Radicals / Nickel / Valence tautomerism / Schiff bases

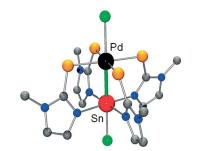


The exception that proves the rule: the oxidative chemistry of apparently simple Schiff base nickel complexes is full of surprises and depends on the denticity of the ligands. Among the ligands, which one favours an Ni<sup>2+</sup>-radical species and which one favours an Ni<sup>3+</sup> complex?

### **Intermetallic Dative Bonding**

Palladastannatrane – a  $Pd^{II} \rightarrow Sn^{IV}$  Dative Bond

**Keywords:** Coordination modes / Heterometallic complexes / Metallastannatrane / Palladium / Tin



Beyond the limits of classic stannylene  $Sn\rightarrow Pd$  and stannyl Sn-Pd bonds the novel tetrabicyclo[3.3.3.3.0] lantern compound  $[PdSn(\mu-mt)_4Cl_2]$  provides support for a reverse  $Pd\rightarrow Sn$  coordination pattern with palladium as a Lewis base to tin.



## Catalytic Hydrogenation

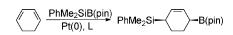
Upon photochemically induced oxidation of Rh<sup>I</sup> and Ir<sup>I</sup> complexes, the hemilabile quinoline moiety coordinates to the metal centers. The resulting Rh<sup>III</sup> complexes show activity for the hydrogenation of olefins.

Rhodium(III) and Iridium(III) Complexes with Quinolyl-Functionalized Cp Ligands: Synthesis and Catalytic Hydrogenation Activity

Keywords: Rhodium / Iridium / Hemilabile ligands / Hydrogenation

## **Pt-Catalyzed Silaboration**

The mechanism of the Pt-catalyzed silaboration of 1,3-cyclohexadiene was investigated by NMR spectroscopy and electrochemistry.



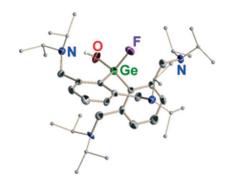
G. Durieux, M. Gerdin, C. Moberg,\* A. Jutand\* ...... 4236-4241

Rate and Mechanism of the Oxidative Addition of a Silylborane to Pt<sup>0</sup> Complexes -Mechanism for the Pt-Catalyzed Silaboration of 1,3-Cyclohexadiene

Keywords: Platinum / Silaboration / Reaction mechanisms / Kinetics

# **Synthesis of Germanones**

The synthesis of heavy analogues of ketones and especially germanones is presented starting from fluorohydroxygermane and its lithio derivative. This lithiogermanolate has reactivity similar to that of germanone and can serve as its synthetic equivalent. This is a promising way to isolate a monomeric germanium-oxygen double-bond compound.



E. Bonnefille, S. Mazières,\* C. Bibal, N. Saffon, H. Gornitzka, C. Couret\* ...... 4242-4247

A Synthetic Equivalent of a Germanone Derivative

**Keywords:** Germanium / Alcohols Fluorine / Germanone / Germanolate

## **Alkyne Ligands**

The reaction of terminal acetylenes with cis-RuMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> proceeds via a σ-bond metathesis to yield the bis(acetylido) complexes cis/trans-Ru(C≡CR)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> in good yield. Ultraviolet irradiation of the complexes results in isomerisation from cis to trans geometry, while heating results in the conversion of trans isomers to cis isomers. Several of the complexes were crystallographically characterised.

L. D. Field,\* A. M. Magill, S. J. Dalgarno, P. Jensen ...... 4248-4254

Bis(acetylido) Complexes of Ruthenium(II) Bearing Monodentate Phosphane Ligands

Keywords: Alkyne ligands / Phosphane ligands / Ruthenium

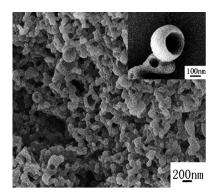
# **CONTENTS**

## **Hollow-Sphere Phthalocyanines**

W. Lv, X. Zhang,\* J. Lu, Y. Zhang, X. Li, J. Jiang\* ...... 4255-4261

Synthesis and Hollow-Sphere Nanostructures of Optically Active Metal-Free Phthalocyanine

Keywords: Phthalocyanines / Chirality / Hollow spheres / Nanostructures / Selfassembly



Optically active metal-free phthalocyanine with low molecular symmetry decorated with four octyl chains linked by binaphthyl units to the phthalocyanine ring was designed and synthesized. With the help of surfactant, this compound was fabricated into nanostructures with a hollow sphere morphology.

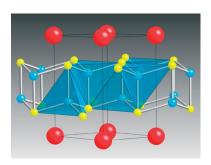
# **Ternary Intermetallic Structures**

S.-Q. Xia, C. Myers, S. Bobev\* ...... 4262-4269



Combined Experimental and Density Functional Theory Studies on the Crystal Structures and Magnetic Properties of  $Mg(Mg_{1-x}Mn_x)_2Sb_2$  (x  $\approx$  0.25) and  $BaMn_2Sb_2$ 

Keywords: Alloys / Density functional calculations / Manganese / Pnictides / Solidstate structures



Two transition-metal intermetallics.  $Mg_{2.50(3)}Mn_{0.50(3)}Sb_2$  and  $BaMn_2Sb_2$ , have been synthesized from Sn flux and their crystal structures determined. Spin-polarized DFT calculations account for magnetic structures, where Mn atoms form two parallel magnetic layers with ferromagnetic coupling within them and antiferromagnetic coupling between them.

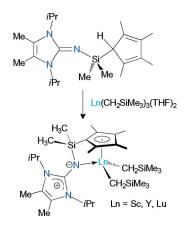
### **Constrained-Geometry Catalysts**

T. K. Panda, C. G. Hrib, P. G. Jones, J. Jenter, P. W. Roesky,

M. Tamm\* ...... 4270-4279

Rare Earth and Alkaline Earth Metal Complexes with Me<sub>2</sub>Si-Bridged Cyclopentadienyl-Imidazolin-2-Imine Ligands and Their Use as Constrained-Geometry Hydroamination Catalysts

**Keywords:** Rare earth metals / Calcium / Cyclopentadienyl ligands / Constrainedgeometry complexes / Hydroamination



Sc, Y, Lu and Ca constrained-geometry catalysts for the hydroamination/cyclization of aminoalkenes and aminoalkynes have been obtained by using a Me<sub>2</sub>Sicyclopentadienyl-imidazolin-2bridged imine ligand, in which the ability of the imidazole ring to effectively stabilize a positive charge leads to a strong electrondonating capacity of the tethered nitrogen atom.

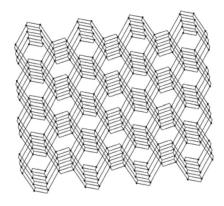
### **Terbium Polymers**

Y.-X. Zhou, X.-O. Shen, C.-X. Du, B.-L. Wu,\* H.-Y. Zhang\* ..... 4280-4289



1D, 2D and 3D Coordination Polymers of Aromatic Carboxylate Tb<sup>III</sup>: Structure, Thermolysis Kinetics and Fluorescence

Keywords: Coordination modes / Polymers / Structure elucidation / Kinetics / Fluorescence



Reactions of TbCl<sub>3</sub>·6H<sub>2</sub>O with aromatic pyridine-2,3-dicarboxylic isophthalic acid and isonicotinic acid gave rise to new 1D, 2D and 3D polymers, depending on the features of the ligands. Their fluorescence spectra are alike, but the intensity and lifetime are affected by their architectures. The fluorescence intensity can be enhanced by coordination of KI in the Tb<sup>III</sup>-carboxylate network.



#### **Linear Metal Chains**



The new pyrimidyl- and naphthyridylmodulated pentapyridyltetramine ligand (H<sub>3</sub>N<sub>9</sub>-2pm) and its linear nona- and octanickel chain complexes were successfully synthesized and structurally characterized. magnetic and electrochemical properties were investigated. (Color code: blue = N, green = Ni, red = Cl)

R. H. Ismayilov, W.-Z. Wang, R.-R. Wang, Y-L. Huang, C.-Y. Yeh, G.-H. Lee, S.-M. Peng\* ...... 4290-4295

Stabilization of Long Cationic EMACs by Reduction or Loss of One Metal Ion



Keywords: Metal-metal interactions / N ligands / Nickel / Magnetic properties

### Ni<sup>II</sup> and Pd<sup>II</sup> N,N,S Complexes

In the presence of methylaluminoxane (MAO), N,N,S tridentate nickel(II) complexes showed moderate activity for ethylene oligomerization, but the corresponding palladium complexes were inactive. All the nickel and palladium complexes exhibited very high activity for norbornene polymerization with MAO as a cocatalyst.

J.-M. Long, H.-Y. Gao,\* K.-M. Song, F.-S. Liu, H. Hu, L. Zhang, F.-M. Zhu, Q. Wu\* ...... 4296-4305

Synthesis and Characterization of Ni<sup>II</sup> and Pd<sup>II</sup> Complexes Bearing N,N,S Tridentate Ligands and Their Catalytic Properties for Norbornene Polymerization

Keywords: Tridentate ligands / Nickel / Palladium / Norbornene polymerization

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

If not otherwise indicated in the article, papers in issue 26 were published online on September 1, 2008

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