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## COVER PICTURE

The cover picture shows the electrostatic interaction between a cationic antiproliferative platinum compound  $\text{cis}[\text{PtCl}(\text{NH}_3)_2(\text{py})]^+$  and novel poly(methyl methacrylate) core-shell nanoparticles bearing anionic ( $-\text{SO}_3^-$ ) arms. This interaction was studied by electrochemical techniques to determine whether such particles might serve as drug carriers for Pt drugs. Details on these Pt-nanosphere conjugates can be found in the article by D. Osella et al. on p. 3289ff.



# CONTENTS

## SHORT COMMUNICATIONS

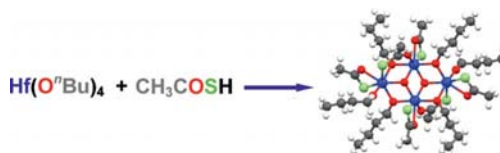
### Oxothioclusters

F. Maratini, L. Pandolfo,\* S. Rizzato,  
A. Albinati,\* A. Venzo, E. Tondello,  
S. Gross\* ..... 3281–3283



A Tetranuclear Planar Hafnium Complex  
Containing O–Hf–S Moieties

**Keywords:** Hafnium / Cluster compounds /  
S ligands / Polynuclear complexes



By reacting  $\text{Hf}(\text{OnBu})_4$  with an excess of thioacetic acid, the first crystallographically authenticated hafnium oxothiocluster, containing O–Hf–S moieties was ob-

tained. In the planar  $\text{Hf}_4$  core, the Hf ions are connected through  $\mu_3\text{-O}$  and  $\mu_2\text{-OBU}$  bridges, while the thioacetate ions behave both as chelating and bridging ligands.

### Magnesium Complexes

P. Haiss, A. Kuhn, N. Kuhn,\*  
C. Maichle-Mößmer, S. Laufer,\*  
M. Steimann, K.-P. Zeller\* ..... 3284–3287

Alkoxy magnesium Iodide Complexes

**Keywords:** Magnesium / Metallacycles /  
Grignard reaction / X-ray diffraction /  
Mass spectrometry



The complexes  $\text{R}^1(\text{Ph})\text{MeCOMg}(\text{Et}_2\text{O})\text{I}$  [**1**,  $\text{R}^1 = \text{Me}$  (**a**),  $\text{Ph}$  (**b**)] are obtained by the reaction of  $\text{R}^1(\text{Ph})\text{C}=\text{O}$  with  $\text{MeMgI}$  in diethyl ether in good yields. Crystallisation of **1** from acetonitrile results in single crystals of di- and trinuclear complexes (**2**, **3** and **4**) in which the metal centres are linked by alkoxy substituents. The thermal decomposition of the complexes **1** is monitored by mass spectral detection of the decomposition products.

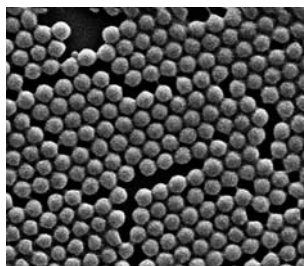
## FULL PAPERS

### Nanoparticle–Drug Conjugates

M. Gál, J. Híveš, M. Laus,  
K. Sparnacci, M. Ravera, E. Gabano,  
D. Osella\* ..... 3289–3294

Electrostatic Interaction of Negatively  
Charged Core–Shell Nanoparticles with  
Antitumoral Cationic Platinum-Based  
Complexes

**Keywords:** Platinum / Antitumor agents /  
Nanoparticles / Electrochemistry / Electro-  
static interactions



The interaction between two cationic antiproliferative Pt compounds and novel poly(methyl methacrylate) core–shell nanoparticles bearing sulfonic arms has been studied by electrochemical techniques to determine whether such particles might serve as drug carriers.

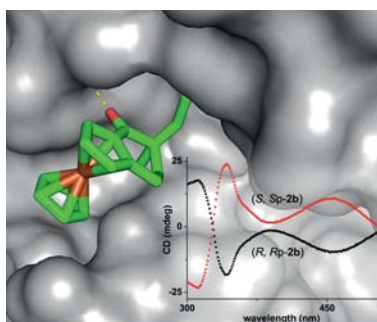
### Platensimycin Derivatives

M. Patra, G. Gasser,  
M. Wenzel, K. Merz, J. E. Bandow,  
N. Metzler-Nolte\* ..... 3295–3302



Synthesis of Optically Active Ferrocene-  
Containing Platensimycin Derivatives with  
a C6–C7 Substitution Pattern

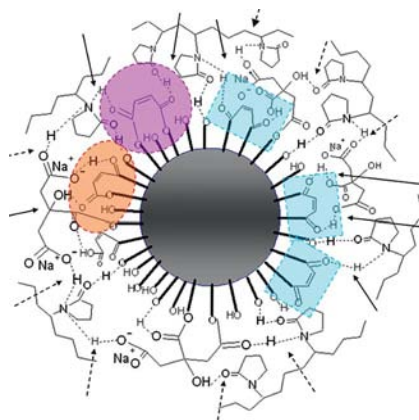
**Keywords:** Bioinorganic chemistry / Sand-  
wich complexes / Michael addition / Anti-  
bacterial agents / Planar chiral ferrocene /  
Platensimycin



An efficient synthetic route to optically active planar chiral ferrocene-containing bioorganometallics (**2b**) inspired by the antibiotic platensimycin lead structure has been developed. The absolute configurations were confirmed by X-ray crystallography. Docking experiments with (*S,S*)-**2b** showed the existence of a pocket for the ferrocene fused at C6–C7 position of the cyclohexenone moiety. Compounds **2b** represent a new family of compounds with an as yet unexplored substitution pattern compared to the reported purely organic analogues of platensimycin.

## Magnetite Nanoparticles as MRI Agents

Ultrasmall aqueous-phase magnetite nanoparticles, stabilized by poly(vinylpyrrolidone), trisodium citrate, and maleic anhydride, exhibit long-term aqueous dispersion stability, excellent biocompatibility, and superparamagnetic properties. A stabilizing synergistic effect is proposed from the strong chelating effect (shaded) of maleic anhydride, and the hydrogen bond interaction between the three stabilizers (arrowed).



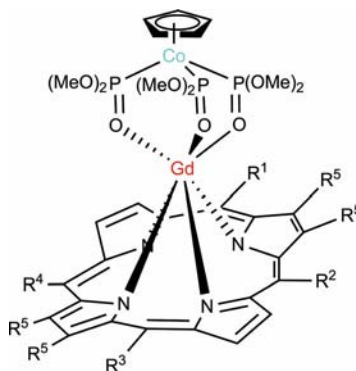
Y. Song,\* R. Wang, R. Rong, J. Ding,  
J. Liu, R. Li, Z. Liu, H. Li, X. Wang,\*  
J. Zhang,\* J. Fang ..... 3303–3313

Synthesis of Well-Dispersed Aqueous-Phase Magnetite Nanoparticles and Their Metabolism as an MRI Contrast Agent for the Reticuloendothelial System

**Keywords:** Nanoparticles / Magnetite / Aqueous phase / Metabolism / Magnetic resonance imaging / Magnetic properties / Reticuloendothelial system

## Gadolinium Porphyrinates

A series of gadolinium(III) porphyrinate complexes was synthesized and fully characterized by spectroscopic and X-ray crystallographic methods. The electronic spectra show near-infrared phosphorescence from the triplet state of the porphyrin rings and exhibit a very characteristic vibronic-structured emission.



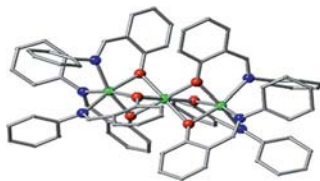
X.-J. Zhu,\* T. Zhang, S. Zhao,  
W.-K. Wong,\* W.-Y. Wong\* ... 3314–3320

Synthesis, Structure, and Photophysical Properties of Some Gadolinium(III) Porphyrinate Complexes

**Keywords:** Photophysics / Lanthanides / Gadolinium / Porphyrin / Near-infrared phosphorescence / IR spectroscopy

## Aggregation States of Mg Complexes

A series of bis(salicylaldiminato)magnesium complexes have been synthesized and characterized in the solid state. Substitution of the ligand backbone was found to influence both the aggregation and the magnesium coordination state in these complexes.



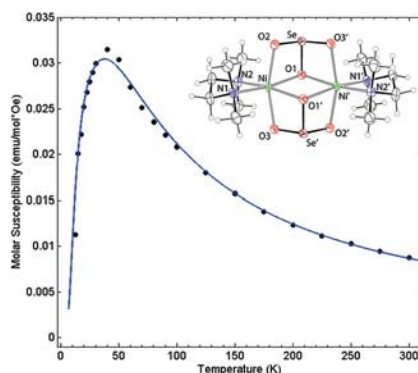
G. T. Quinque, A. G. Oliver,  
J. A. Rood\* ..... 3321–3326

Synthesis and Structural Characterization of Bis(salicylaldiminato)magnesium Complexes of Varying Aggregation and Coordination State

**Keywords:** Magnesium / Salicylaldiminato ligands / Coordination number / Aggregation / X-ray diffraction

## Heteroleptic Dinickel Selenite Complexes

The reaction of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{Na}_2\text{SeO}_3$  in the presence of tetramethylethylenediamine (TMEDA) yielded the heteroleptic complex  $[\{\text{Ni}(\text{TMEDA})\text{SeO}_3\}_2]$ . The two nickel ions exhibit antiferromagnetic coupling with  $J = -25.7 \pm 0.1 \text{ cm}^{-1}$ , in good agreement with DFT calculations.



M. Delferro,\* C. Graiff, L. Marchi,  
L. Elviri, M. Mazzani, M. Ricci,  
G. Predieri\* ..... 3327–3333

Synthesis, Structural Characterization, and Magnetic Properties of the Heteroleptic Dinuclear Nickel Selenite Complex  $[\{\text{Ni}(\text{TMEDA})\text{SeO}_3\}_2]$

**Keywords:** Nickel / Selenium / Density functional calculations / Magnetic properties

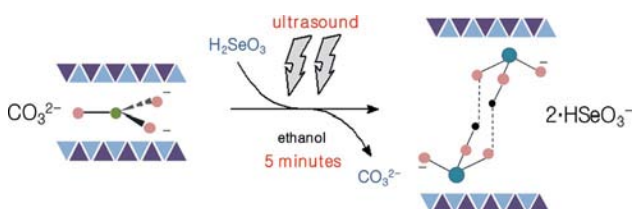
# CONTENTS

## Selenium Scavenger

J. H. Lee, Y. S. Lee, H. Kim,  
D.-Y. Jung\* ..... 3334–3339

Ultrasound-Induced Rapid Intercalation of  
Biselenite in Layered Double Hydroxides

**Keywords:** Clays / Layered compounds /  
Layered double hydroxides / Ion exchange /  
Selenium / Intercalations / Decarbonation



By using facile ultrasonic treatment in ethanol, carbonate ions in the interlayer spaces of layered double hydroxides can be

successfully exchanged with biselenite ions within a few minute.

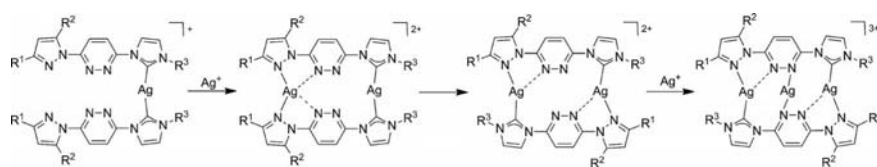
## Silver Complexes

J. Wimberg, U. J. Scheele, S. Dechert,  
F. Meyer\* ..... 3340–3348



New Pyridazine-Bridged NHC/Pyrazole  
Ligands and Their Sequential Silver(I) Co-  
ordination

**Keywords:** Carbene ligands / Nitrogen  
heterocycles / Ligand design / Silver /  
Oligometallic complexes



A family of new pyridazine-bridged ditopic ligands has been prepared, which provide both an organometallic NHC and a classic N-donor compartment. Two opposing strands of these ligands sequentially bind up to three silver(I) ions. Complexation

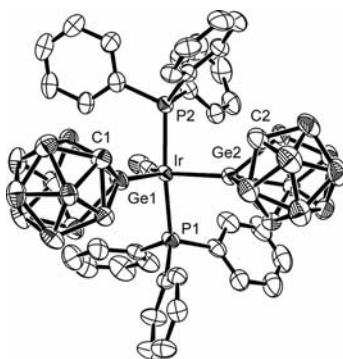
starts at the NHC subunit and involves some ligand reshuffling to form a trisilver arrangement, which has been elucidated by NMR spectroscopy and X-ray crystallography.

## Germylene Ligands

A. Wagenpfeil, C. Nickl, H. Schubert,  
K. Eichele, M. A. Fox,  
L. Wesemann\* ..... 3349–3356

1,2-Carbagerma-*closo*-dodecaborate as a  
Germanium Ligand in Coordination  
Chemistry – Synthesis, Structure and  
Reactivity

**Keywords:** Boranes / Cluster compounds /  
Germanium / Iridium / Ruthenium / Quan-  
tum chemical calculations

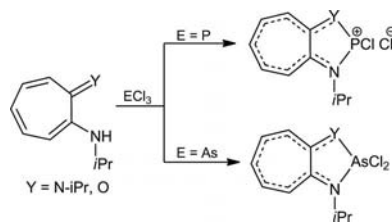


An improved synthesis of carbagerma-*closo*-dodecaborate is presented. Coordination compounds with this type of germylene ligands are structurally characterized, and the ligand properties are discussed by using the results of quantum chemical calculations.

## Cationic Group 15 Species

L.-C. Pop, A. Castel,\*  
L. Silaghi-Dumitrescu,\*  
N. Saffon ..... 3357–3364

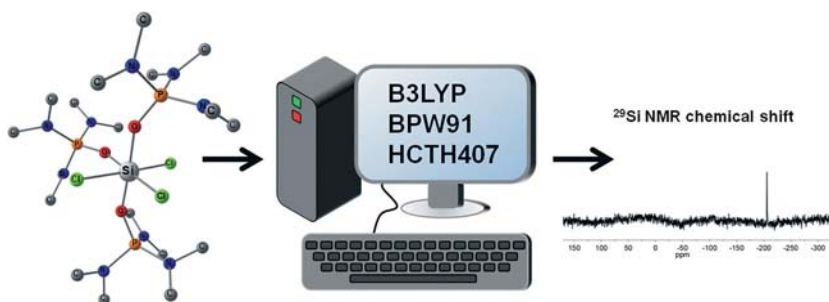
Aminotroponiminato and Aminotroponate  
Complexes of Group 15 (P, As) Elements:  
Synthesis, X-ray Diffraction Analysis and  
Reactivity



**Keywords:** Phosphorus / Arsenic / N,N  
ligands / N,O ligands / Cycloaddition /  
Tungsten

Aminotroponiminato and aminotroponate ligands have proved to be particularly effective in the stabilization of phosphonium and arsenium cations. NMR and X-ray diffraction studies highlight perfect chelation with the formation of three-coordinate Group 15 elements. The reactivities of these species towards *o*-quinone and transition-metal complexes were investigated.





$^{29}\text{Si}$  NMR chemical shifts of 41 silicon-containing compounds were calculated by employing DFT. The choice of a suitable basis set had a much larger influence on the accuracy of the results than the choice

of functional. For a subset of compounds, GIAO-HF and MP2 ab initio calculations were performed and compared with the DFT results.

V. A. Du, G. N. Stipicic,  
U. Schubert\* ..... 3365–3373

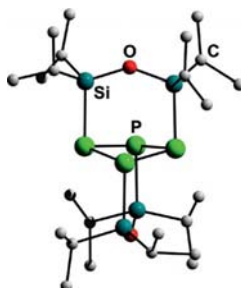
$^{29}\text{Si}$  NMR Shielding Calculations Employing Density Functional Theory, Focusing on Hypervalent Silicon Compounds



**Keywords:** Silicon /  $^{29}\text{Si}$  NMR spectroscopy / Density functional calculations / Hypervalent compounds

## Oligophosphane Synthesis

Siloxane-bridged  $\text{P}_2$  and  $\text{P}_4$  compounds can be synthesized from metalated primary or cyclic diphosphanylsiloxane compounds via oxidative coupling using  $\text{C}_2\text{H}_4\text{Br}_2$  as reagent. These metalated compounds are obtained from the reaction of earth alkaline amides and the protonated species of the corresponding diphosphanylsiloxane compounds.



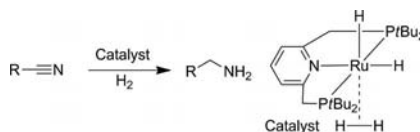
A. Kracke, C. von Hänisch\* ... 3374–3380

Stepwise Synthesis of Siloxane-Substituted Oligophosphanes  $\text{P}_n[\text{O}(\text{iPr}_2\text{Si})_2]_2$  ( $n = 2, 4$ )

**Keywords:** Phosphorus / Siloxanes / Metalation / Oxidative coupling

## Hydrogenation

Selective synthesis of primary amines by the catalytic hydrogenation of nitriles with nonclassical ruthenium hydride pincer complexes is reported. Use of water as additive increases the selectivity and rate of the reactions. Possible catalytic cycles were identified for this important reaction of industrial significance by means of DFT calculations.



C. Gunanathan, M. Hölscher,  
W. Leitner\* ..... 3381–3386

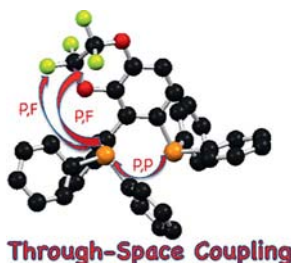
Reduction of Nitriles to Amines with  $\text{H}_2$  Catalyzed by Nonclassical Ruthenium Hydrides – Water-Promoted Selectivity for Primary Amines and Mechanistic Investigations



**Keywords:** Ruthenium / Reduction / Amines / Hydrogenation / Pincer complexes

## Through-Space NMR Coupling

The first simultaneous  $^{31}\text{P}$ ,  $^{31}\text{P}$  and  $^{31}\text{P}$ ,  $^{19}\text{F}$  solution-phase through-space nuclear spin–spin coupling in biphenyl derivatives is reported. Their observation became possible through access to a recently developed class of  $C_1$ -symmetric biphenyl diphosphanes.



L. Bonnafoux, L. Ernst,\* F. R. Leroux,\*  
F. Colobert ..... 3387–3397

Through-Space  $J(\text{P},\text{P})$  and  $J(\text{P},\text{F})$  Spin–Spin Coupling in  $C_1$ -Symmetric Biaryl Diphosphanes



**Keywords:** Biphenyl / Coupling / Phosphanes / Fluorine / NMR spectroscopy

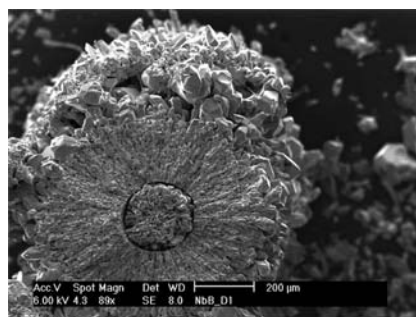
# CONTENTS

## Metal Diboride Layers

W. Friedhoff, E. Milke,  
M. Binnewies\* ..... 3398–3402

The Unexpected Formation of  $\text{MB}_2$  Layers  
(M = Refractory Metal) on Metal Surfaces

**Keywords:** Refractory metals / Boron /  
Synthesis design / Transition metals / High-  
temperature chemistry



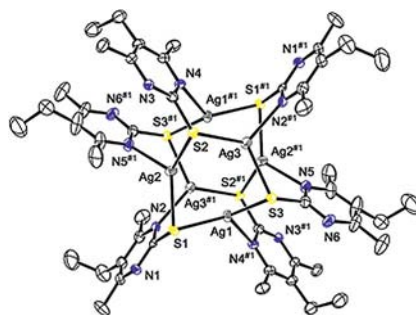
In the course of reactions between refractory metals (Ti, Zr, V, Nb, Ta) with boron(III) chloride at temperatures of about 1500 K, layers of the diborides of these metals are formed. The coexistence of the refractory metal with its diboride is impossible from a thermodynamic viewpoint. The formation of metal diborides in the presence of the metal is discussed.

## Metal(I)–N,S-Ligand Complexes

A. Rodríguez,\* A. Sousa-Pedrares,  
J. A. García-Vázquez,\* J. Romero,  
A. Sousa ..... 3403–3413

Synthesis and Structural Characterization  
of Copper(I), Silver(I) and Gold(I) Com-  
plexes with Pyrimidine-2-thionato Ligands  
and their Adducts with Phosphanes

**Keywords:** Copper / Silver / Gold / N,S li-  
gands / Phosphanes / Electrochemistry



Electrochemical oxidation of anodic metal (copper or silver) in a cell containing a substituted pyrimidine-2-thione and acetonitrile affords homoleptic complexes  $[\text{M}(\text{RpymS})]$ . The reactions of these homoleptic complexes with phosphanes yield heteroleptic complexes. Mixed gold(I) complexes were also easily prepared by reaction between the corresponding thione and the precursor  $[\text{AuCl}(\text{PPh}_3)]$ .

\* Author to whom correspondence should be addressed.

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If not otherwise indicated in the article, papers in issue 21 were published online on July 12, 2011