HUNGARY ITALY GERMANY GREECE

BELGIUM FRANCE

EUChemSoc

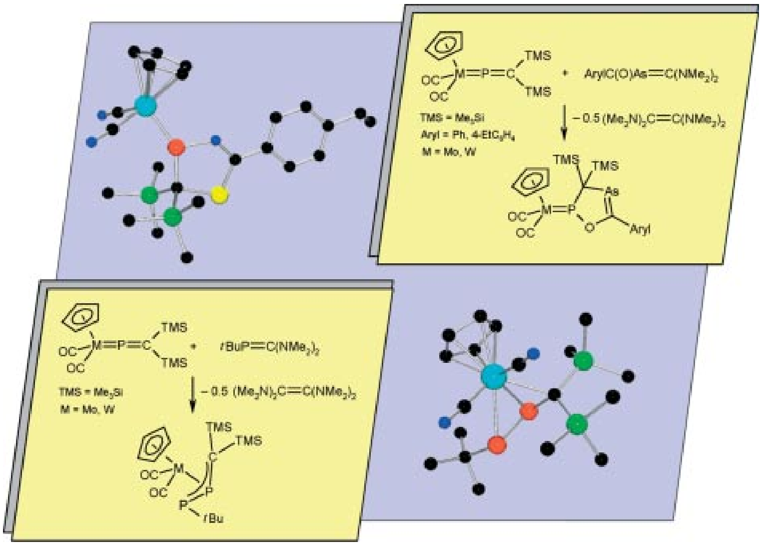
SWEDEN CZECH REPUBLIC

AUSTRIA PORTUGAL SPAIN NETHERLANDS

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 between the phosphavinylidene complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M{=}P{=}C(SiMe_3)_2]$ and the inversely polarized phosphaalkene $t\mathrm{Bu}P{=}C(NMe_2)_2$, which affords η^3-1,2-diphosphaallyl complexes by smooth transfer of the phosphinidene unit onto the electrophilic ligand of the precursors. The molecular structure underlines the unsymmetrical η^3-ligation of the heteroallyl ligand to the metal with the *tert*-butyl substituent *syn* to the central phosphorus atom. Treatment of the phosphavinylidene complexes with *P*-aroylphosphaalkenes leads to decomposition. In contrast, phosphavinylidene complexes and *As*-aroylarsaalkenes yield complexes featuring cyclic phosphenium ligands with an As=C bond. It is believed that the first step of this process is a formal [2+1] cycloaddition between the P=C bond and the aroylarsinidine to give a three-membered ring, which subsequently incorporates the CO unit to afford the final product. In all cases, tetrakis(dimethylamino)ethene is formed as a byproduct. Details are presented in the Microreview by L. Weber on p. 4095ff.



CONTENTS

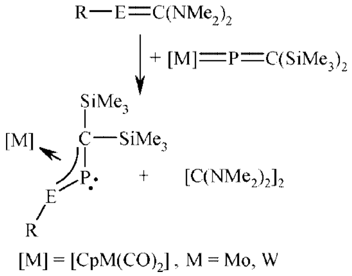
MICROREVIEW

Inversely Polarized Phosphaalkenes

L. Weber* **4095–4117**

Phospha- and Arsaalkenes RE=C(NMe$_2$)$_2$ (E = P, As) as Novel Phosphinidene- and Arsinidene-Transfer Reagents

Keywords: Phosphaalkenes / Arsaalkenes / Phosphinidene / Arsinidene



Inversely polarized phosphaalkenes RP=C(NMe$_2$)$_2$ serve as convenient sources of the phosphinidene unit PR, which can be transferred onto a broad variety of electrophilic ligands in transition-metal complexes such as complexes with carbene, vinylidene, phosphenium, and phosphavinylidene ligands. Similarly, inversely polarized arsaalkenes behave as arsinidene transfer reagents under mild conditions.

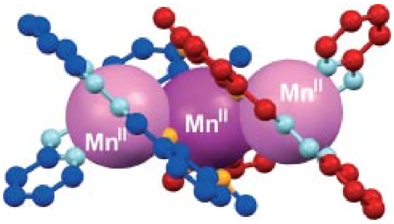
SHORT COMMUNICATIONS

Click Assemblies

J. Tang, J. S. Costa, G. Aromí,
I. Mutikainen, U. Turpeinen, P. Gamez,
J. Reedijk* **4119–4122**

Supramolecular Click Assembly of a Fused Double-Stranded [Mn$^{II}_3$] Dihelicate

Keywords: Self-assembly / Helicates / Click chemistry / Manganese / Ferromagnetic interactions



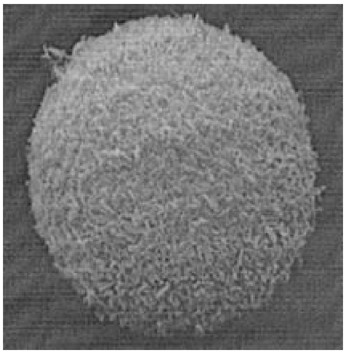
The self-assembly between 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol and Mn^{II} ions leads to a remarkable supramolecular arrangement, where two helicates are “clicked” together to produce a bent linear metal array with ferromagnetic interactions.

Carbonate Apatites

L.-F. Olsson, K. Sandin, R. Odselius,
L. Kloo* **4123–4127**

In Vitro Formation of Nanocrystalline Carbonate Apatite – A Structural and Morphological Analogue of Atherosclerotic Plaques

Keywords: Carbonate apatite / Crystallization / Calcification / Nanocrystalline / Calcium

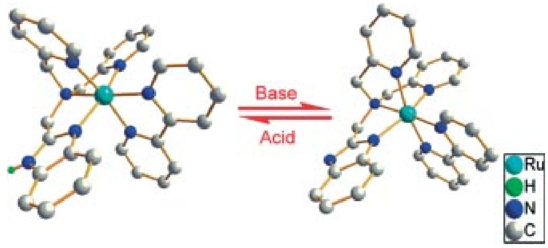


Carbonate apatites, analogous to the so-called bioapatites presumed only to precipitate in vivo, were also shown to form spontaneously in vitro in solutions mimicking the ion concentrations in human blood serum. The formed precipitates display a hierarchical morphology made from nanocrystalline building blocks into a spherical precipitate.

A Redox Switch

H. Sun, M. Wang,* K. Jin, C. Ma, R. Zhang, L. Sun* 4128–4131

Effect of Deprotonation of a Benzimidazolyl Ligand on the Redox Potential and the Structures of Mononuclear Ruthenium(II) Complexes



A monoruthenium(II) complex of the benzimidazolyl ligand and its deprotonated counterpart were prepared and structurally characterized. The reversible protonation/deprotonation process of the ancillary ligand switches the redox potential of the ruthenium(II) core from 0.69 to 0.26 V vs. Ag/AgNO$_3$.

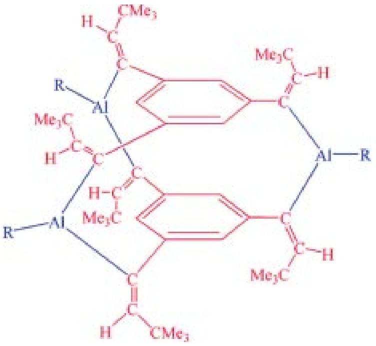
Keywords: Benzimidazolyl ligand / Redox switch / Reversible protonation and deprotonation / Ru^{II} complex

FULL PAPERS

Al-Bridged [3,3,3]Cyclophanes

W. Uhl,* A. Hepp, M. Matar, A. Vinogradov 4133–4137

Facile Synthesis of Aluminum-Bridged [3,3,3]Cyclophanes by Hydroalumination



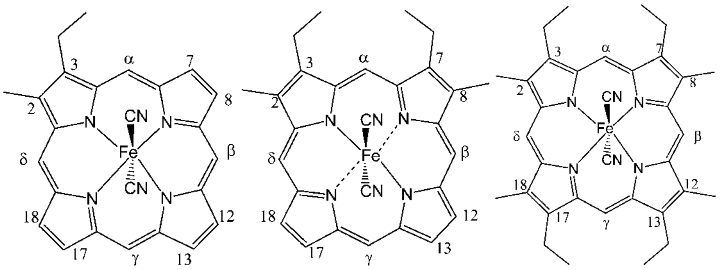
The addition of Al–H bonds of dialkylaluminum hydrides to the C≡C bonds of 1,3,5-tris(*tert*-butylethynyl)benzene (hydroalumination) did not result in the formation of the expected simple addition products, but yielded cyclophane-type molecules by condensation and release of the corresponding trialkylaluminum compounds.

Keywords: Aluminum / Hydroalumination / Cage compounds / Cyclophanes

Iron(III) Porphyrins

S. Juillard, A. Bondon, G. Simonneaux* 4138–4144

Proton NMR Study of Low-Spin *meso*-Unsubstituted β-Substituted Alkyl Iron Porphyrins: Remarkable Influence of Peripheral Substitution on Spin Density



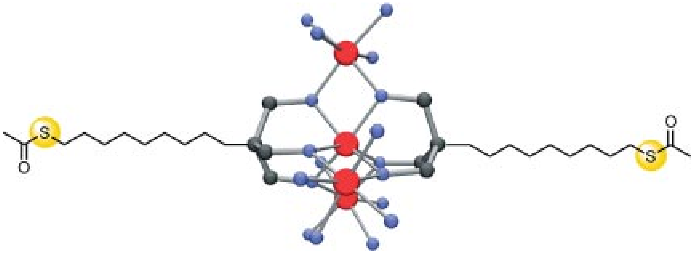
Paramagnetic ^{1}H and ^{13}C NMR spectroscopy were used to characterize the influence of small alkyl groups on the spin density of a series of high-spin and low-spin iron(III) porphyrins. Analysis of the chemical shifts of the pyrrole proton and *meso*-carbon of porphyrins reveals that all complexes show a low-spin $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic ground state.

Keywords: NMR spectroscopy / Porphyrinoids / Iron / HMBC / Saturation transfer

Single-Molecule Magnets

A.-L. Barra, F. Bianchi, A. Caneschi, A. Cornia,* D. Gatteschi, L. Gorini, L. Gregoli, M. Maffini, F. Parenti, R. Sessoli,* L. Sorace, A. M. Talarico 4145–4152

New Single-Molecule Magnets by Site-Specific Substitution: Incorporation of “Alligator Clips” into Fe$_4$ Complexes



Single-molecule magnets of the Fe$_4$ family have been functionalized with terminal “alligator clips” by exploiting the site-specific coordinating ability of 2-(hydroxymethyl)propane-1,3-diol derivatives. The complexes have an $S = 5$ ground state and energy barriers exceeding 15 K.

Keywords: Iron / Ligand design / Magnetic properties / EPR spectroscopy / Single molecule magnets

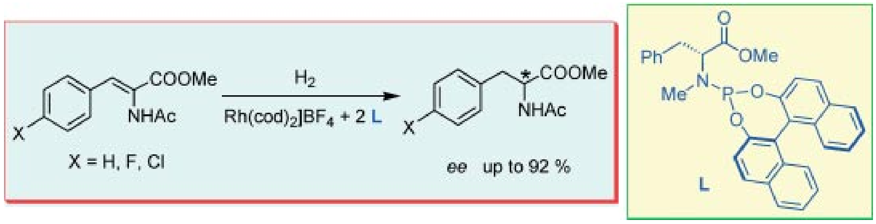
CONTENTS

Asymmetric Catalysis

L. Eberhardt, D. Armspach,* D. Matt,*
L. Toupet, B. Oswald .... 4153−4161

Synthesis of Chiral, Monodentate Aminophosphane and Phosphoramidite Ligands Derived from Amino Acid Esters: Application in Rh-Catalysed Asymmetric Olefin Hydrogenation Reactions

Keywords: Phosphoramidites / Binol / Asymmetric catalysis / Rhodium / Olefin hydrogenation / Amino acid esters



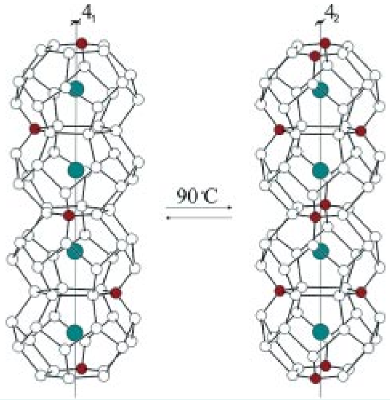
A series of chiral monodentate ligands combining a 3,5-dioxa-4-phosphacycloheptadinaphthyl unit either with a phenylalanine- or with an alanine-derived fragment were synthesised and tested in the hydrogenation of 2-(acetylamino)-3-(aryl)propenoic methyl esters.

Understanding Clathrate-I Structures

A. Kaltzoglou, S. D. Hoffmann,
T. F. Fässler* .... 4162−4167

Order-Disorder Phase Transition in Type-I Clathrate $Cs_8Sn_{44}\square_2$

Keywords: Clathrates / Order-disorder transitions / Single-crystal structure analysis / Thermoelectricity / Tin



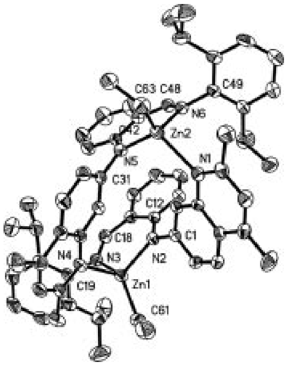
$Cs_8Sn_{44}\square_2$ adopts a 2 × 2 × 2 superstructure of the type-I clathrate ($Ia\bar{3}d$) at room temperature and exhibits a high ordering of the vacancies (□) in the Sn framework (left). Its single crystals transform at 90 °C to a high-temperature modification ($Pm\bar{3}n$) with a lower ordering of the defects (right). DTA corroborates the totally reversible character of the phase transition.

Zinc(II) Complexes

Q. Su, W. Gao, Q.-L. Wu, L. Ye,
G.-H. Li, Y. Mu* .... 4168−4175

Syntheses, Characterization, and Luminescent Properties of Monoethylzinc Complexes with Anilido−Imine Ligands

Keywords: Luminescence / N ligands / Quinoline / Zinc



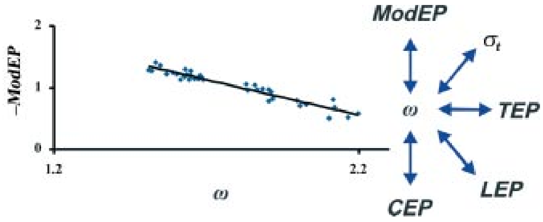
Dinuclear four-coordinate zinc complexes were synthesized from the alkane elimination reaction of $ZnEt_2$ with the corresponding anilido−imine ligands. The molecular structures of **3b** and **3c** were characterized by spectroscopy and X-ray crystallography. Luminescent properties of four zinc complexes in both solution and the solid state were explored.

Ligand Properties

C. Makedonas,
C. A. Mitsopoulou* .... 4176−4189

Introduction of Modified Electronic Parameters − Searching for a Unified Ligand Properties Scale through the Electrophilicity Index Concept

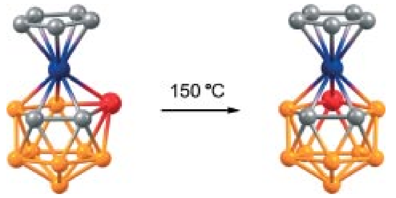
Keywords: Modified electronic parameters / Electrophilicity index / Diimine complexes / Reduction potential / Charge-transfer bands



The contribution of the diimine ligands to the electronic properties of the corresponding metal complexes is quantified by two novel indices, namely Modified Electronic Parameters, *ModEP*, and the electrophilicity, *ω*. The latter correlates well with all known electronic parameters, such as *CEP*, *LEP*, *TEP*, *ModEP* and the Hammett constant. The method in which it is calculated avoids any experimental limitation; thus, it can be employed even for ligands that have not yet been synthesized, and its correlation with the known scales could provide the properties of the corresponding complexes.

Ferraphosphacarboranes

Room-temperature reactions of the phosphadicarbollide anion $[7,8,9\text{-}PC_2B_8H_{10}]^-$ with $[(C_5R_5)Fe]^+$ cations afford the expected 12-vertex ferraphosphadicarbollides $[1\text{-}C_5R_5\text{-}1,2,3,4\text{-}FePC_2B_8H_{10}]$, which undergo polyhedral rearrangement at 150 °C. The calculated value of the root-mean-square-amplitude-of-vibration of the iron atom, based on the Mössbauer effect data, is in good agreement with crystallographic data.



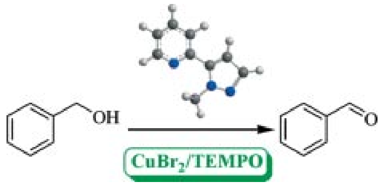
A. R. Kudinov,* R. H. Herber,* P. Zanello,* D. S. Perekalin, I. V. Glukhov, I. Nowik, M. Corsini, S. Fedi, F. Laschi 4190–4196

Synthesis, Structure, Electrochemistry, and Mössbauer Effect Studies of the Ferraphosphadicarbollides $[(C_5R_5)Fe(PC_2B_8H_{10})]$ (R = H, Me)

Keywords: Iron / Carboranes / Electrochemistry / X-ray diffraction / Mössbauer spectroscopy

Copper Complexes for Catalysis

Pyrazole-pyridine and pyrazole-naphthol ligands have been used in the [copper/TEMPO]-catalysed oxidation of benzyl alcohol to benzaldehyde. The results so far obtained suggest that the combination of pyrazole/pyridine coordinating groups is crucial to generate active copper catalysts.



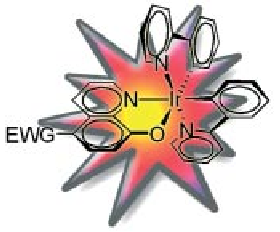
J. Salinas Uber, Y. Vogels, D. van den Helder, I. Mutikainen, U. Turpeinen, W. T. Fu, O. Roubeau, P. Gamez, J. Reedijk* 4197–4206

Pyrazole-Based Ligands for the [Copper–TEMPO]-Mediated Oxidation of Benzyl Alcohol to Benzaldehyde and Structures of the Cu Coordination Compounds

Keywords: Copper(I) and copper(II) complexes / Catalysis / Oxidation / Luminescence / Bioinorganic chemistry

Iridium Complexes

The synthesis, structures, thermal stabilities and photophysical properties of a series of heteroleptic iridium(III) complexes of the type bis[$\kappa^2(C^2,N)$-2-phenylpyridine]-[$\kappa^2(N,O)$-8-quinolinolato]iridium(III) are discussed. Substitution of the quinolinolato ligand with electron-withdrawing functional groups results in absorption features in the visible and quinolinolato-governed emission of the complexes.



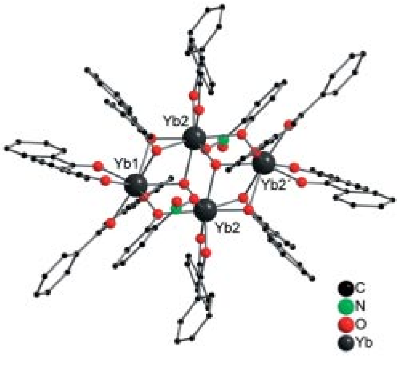
S. Kappaun, S. Eder, S. Sax, K. Mereiter, E. J. W. List, C. Slugovc* 4207–4215

Organoiridium Quinolinolate Complexes: Synthesis, Structures, Thermal Stabilities and Photophysical Properties

Keywords: Iridium / N,O ligands / Luminescence / Nitrogen heterocycles

Coordination Oligomers

Tetra- and pentanuclear lanthanide clusters $HNEt_3{}^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7\text{-}(o\text{-}O_2NC_6H_4O)_3Cl]^-$ (Ln = Er, Tm) and $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ (Ln = Yb, Lu) having dibenzoylmethanido and *o*-nitrophenolato as ligands in the coordination sphere were prepared.



S. Datta, V. Baskar, H. Li, P. W. Roesky* 4216–4220

Synthesis and Structural Characterization of Tetra- and Pentanuclear Lanthanide Hydroxido Clusters

Keywords: Cage compounds / Cluster compounds / Coordination modes / Bridging ligands / Lanthanides

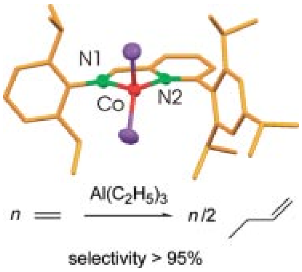
CONTENTS

Selective Ethylene Dimerization

T. Irrgang, S. Keller, H. Maisel, W. Kretschmer, R. Kempe* 4221–4228

Sterically Demanding Iminopyridine Ligands

Keywords: Ethylene polymerization / N ligands / Cobalt / Iron / Nickel / Palladium



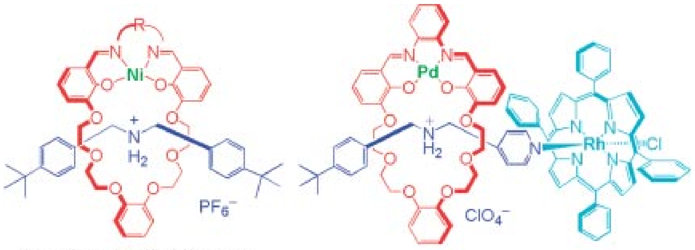
Sterically demanding iminopyridine ligands were prepared by Kumada-type coupling. Ethylene polymerization/oligomerization behavior of the dichlorido complexes (Co, Fe, Ni, and Pd) after activation with methylaluminoxane or triethylaluminum revealed ethylene dimerization selectivity greater than 95% for Co.

Multifunctional Rotaxanes

M. Narita, I. Yoon, M. Aoyagi, M. Goto, T. Shimizu, M. Asakawa* 4229–4237

Transition Metal(II)–Salen and –Salophen Macrocyclic Complexes for Rotaxane Formation: Syntheses and Crystal Structures

Keywords: Rotaxanes / Ring opening / Ring closing / Transition metals / Porphyrinoids



$\mathbf{3a}$-H·PF_6 : R = ethylene, 55%
$\mathbf{3b}$-H·PF_6 : R = *o*-phenylene, 20%

$\mathbf{8}$-H·Rh(TPP)Cl·ClO_4

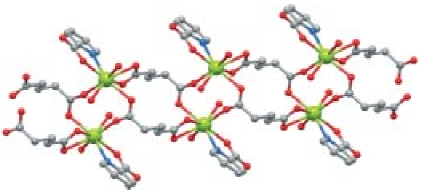
A "threading-followed-by-shrinking" approach afforded [2]rotaxanes **3a/b**-H·PF_6 possessing nickel(II)–salen and –salophen moieties; the salen-containing rotaxane was prepared in remarkably high yields. [2]Rotaxane **8**-H·Rh(TPP)Cl·ClO_4 has potential as a next-generation molecular machine exhibiting catalytic function.

Photoluminescent Lanthanides

P. I. Girginova, F. A. Almeida Paz, P. C. R. Soares-Santos, R. A. Sá Ferreira, L. D. Carlos, V. S. Amaral, J. Klinowski, H. I. S. Nogueira, T. Trindade* 4238–4246

Synthesis, Characterisation and Luminescent Properties of Lanthanide-Organic Polymers with Picolinic and Glutaric Acids

Keywords: Lanthanide complexes / Picolinic acid / Glutaric acid / Luminescence



Lanthanide (Sm^{3+}, Eu^{3+}, Tb^{3+}) coordination polymers containing a flexible bridging ligand and a chelating aromatic ligand have been synthesised and characterised. In these compounds the aromatic ligand acts as an antenna, efficiently transferring energy to the Ln emitting centre and the dicarboxylato ligand controls, to some extent, the dimensionality of the final product.

CORRECTION

E. Pacholska-Dudziak, L. Latos-Grażyński* 4247

NMR Studies of Paramagnetic Metallocarbaporphyrinoids

Keywords: Carbaporphyrinoids / Porphyrinoids / NMR spectroscopy / Organometallic chemistry