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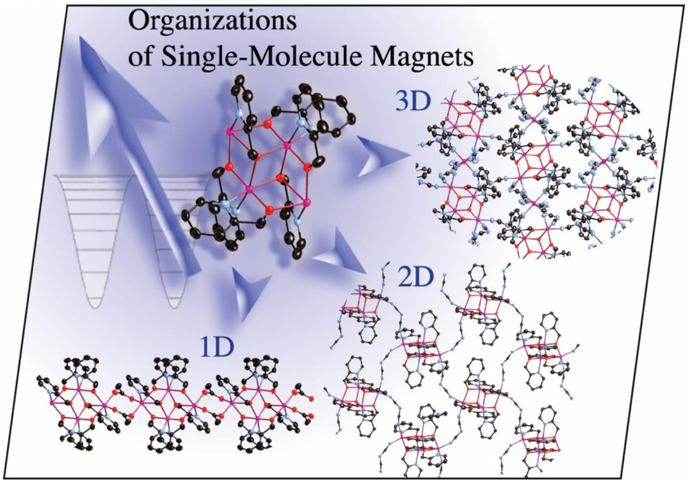
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further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

COVER PICTURE

The cover picture shows the assembly of a [Mn_4] single-molecule magnet building block into various extended coordination networks of different dimensionalities. The rational assembly of such high-spin complexes, as well as their original magnetic properties are reviewed and discussed in the Microreview by O. Roubeau and R. Clérac on p. 4325ff.



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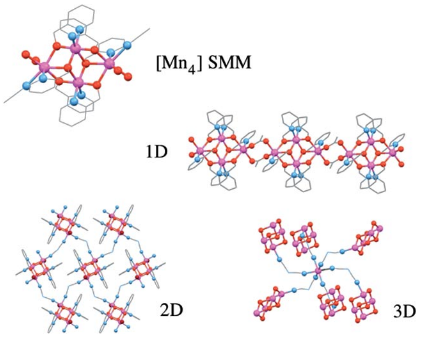
MICROREVIEW

Assemblies of High-Spin Complexes

O. Roubeau,* R. Clérac 4325–4342

Rational Assembly of High-Spin Polynuclear Magnetic Complexes into Coordination Networks: the Case of a $[Mn_4]$ Single-Molecule Magnet Building Block

Keywords: Coordination polymers / Magnetic properties / Single-molecule magnets / Manganese / Hydrogen bonds



The different forms of a rhombic $[Mn_4]$ single-molecule magnet and their assembly into infinite coordination networks are reviewed as a case study of how the rational design of extended arrays of high-spin complexes may afford unprecedented, interesting magnetic properties. Potential synthetic strategies and outcomes are discussed.

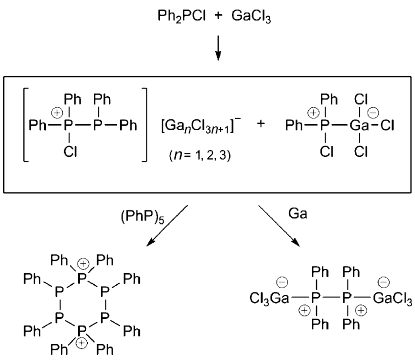
SHORT COMMUNICATIONS

Room-Temperature Molten Medium

J. J. Weigand,* N. Burford,
A. Decken 4343–4347

The Binary $Ph_2PCl/GaCl_3$ System: A Room-Temperature Molten Medium for P–P Bond Formation

Keywords: Melt reaction / Phosphorus cations / Structure elucidation / Coordination complexes



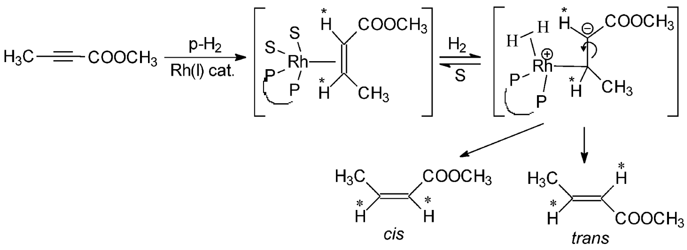
An equimolar reaction mixture of Ph_2PCl and $GaCl_3$ at room temperature results in the formation of a melt. The melt provides a facile and reactive source of the Ph_2P^+ cation, as demonstrated by P–P bond insertion into $(PhP)_5$ to give the $[Ph_4P_6]^{2+}$ dication and reductive coupling with gallium metal to give the diadduct $Cl_3GaPPh_2PPh_2GaCl_3$.

Olefin Isomerisation Mechanism

A. Viale, D. Santelia, R. Napolitano,
R. Gobetto, W. Dastrù,
S. Aime* 4348–4351

The Detection of PHIP Effects Allows New Insights into the Mechanism of Olefin Isomerisation during Catalytic Hydrogenation

Keywords: Isomerization / Parahydrogen / Olefins / Hydrogenation / Catalysis

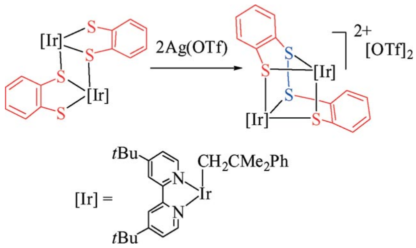


The use of parahydrogen to observe PHIP (parahydrogen-induced polarisation) effects in the ^1H NMR spectra of the products provides more insight into the mechanism of isomerisation of olefins formed by hydrogenation of alkynes in the presence of Rh^I catalysts.

FULL PAPERS

Iridium Dithiolate Complexes

Treatment of $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4\text{-}(Ir-C^c)\}(C_6H_4tBu\text{-}2)]$ with R_2Q_2 in refluxing toluene afforded $[Ir(dtbpy)\{CH_2CMe_2C^c{}_6H_4(Ir-C^c)\}]_2(\mu\text{-}QR)_2$ (RQ = pTolS, PhSe). Reaction of $[Ir(dtbpy)(CH_2CMe_2Ph)Cl]_2(\mu\text{-}Cl)_2$ with $Na_2(bdt)$ gave $[Ir(dtbpy)(CH_2CMe_2Ph)(bdt)]_2$. Oxidation of $[Ir(dtbpy)(CH_2CMe_2Ph)(bdt)]_2$ with silver triflate led to dimerization of the bdt^{2-} ligand by formation of an S−S bond.

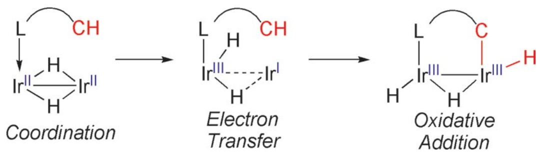


K.-W. Chan, Y.-K. Sau, Q.-F. Zhang, W.-Y. Wong, I. D. Williams, W.-H. Leung* .... 4353−4359

Synthesis, Structures, and Oxidation of Iridium(III) Alkyl Compounds Containing Thiolate and Dithiolate Ligands

Keywords: Iridium / S ligands / Oxidation

C−H Bond Activation



Mild oxidative addition of C−H bonds took place by the reaction of a hydrido-bridged dinuclear iridium(II) complex, $[Cp^*Ir(\mu\text{-}H)]_2$, with donor ligands such as phosphorus compounds and sulfoxides. The proximity of the two iridium centers combined with the characteristic electron configuration ($Ir^{II}-Ir^{II}$) of $[Cp^*Ir(\mu\text{-}H)]_2$ provides unique reactivities for these systems based on cooperative effects.

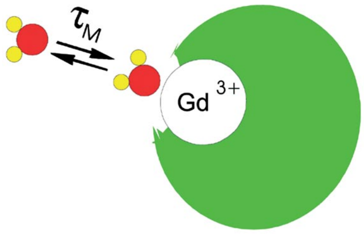
Y. Takahashi, K.-i. Fujita,* R. Yamaguchi* .... 4360−4368

Mild Oxidative Addition of C−H Bonds to a Hydrido-Bridged Dinuclear Complex of Iridium(II) Induced by the Coordination of Heteroatomic Ligands

Keywords: Cooperative effects / Iridium / C−H activation / P ligands / S ligands

Gd−DTPA Derivatives

The residence time of coordinated water (τ_M), a parameter of paramount importance for relaxivity, is compared in a series of Gd−DTPA derivatives carrying different global charges. The importance of the charge in the first coordination sphere of the metal and in its vicinity is reported.



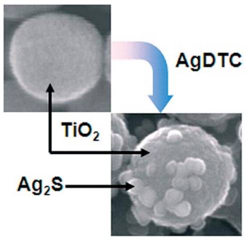
S. Laurent,* L. Vander Elst, F. Botteman, R. N. Muller .... 4369−4379

An Assessment of the Potential Relationship between the Charge of Gd−DTPA Complexes and the Exchange Rate of the Water Coordinated to the Metal

Keywords: Oxygen / Isotopes / Relaxivity / Contrast agents

Nanocomposites

A single-source approach using mild temperatures leads to morphological well-defined and coupled TiO_2/metal−sulfide nanocomposites. Ag_2S nanostructures are observed as nano-islands at the surface of TiO_2 (anatase) particles, which were used as substrates. The growth of the metal sulfide at the surface can be controlled.



M. C. Neves, O. C. Monteiro, R. Hempelmann, A. M. S. Silva, T. Trindade* .... 4380−4386

From Single-Molecule Precursors to Coupled Ag_2S/TiO_2 Nanocomposites

Keywords: Nanostructures / Molecular precursors / Metal sulfides / Semiconductors

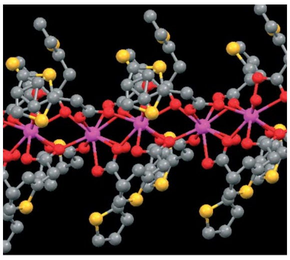
CONTENTS

Luminescent Materials

S. Raphael, M. L. P. Reddy,*
A. H. Cowley, M. Findlater 4387–4394

2-Thiopheneacetato-Based One-Dimensional Coordination Polymer of Tb^{3+}: Enhancement of Terbium-Centered Luminescence in the Presence of Bidentate Nitrogen Donor Ligands

Keywords: Enhanced terbium luminescence / 2-Thiopheneacetic acid / Bidentate nitrogen donors / 1D Coordination polymer



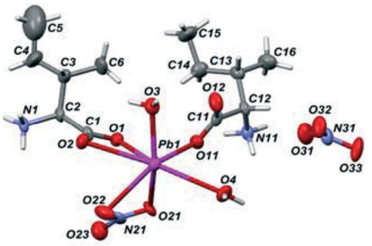
Three new complexes of Tb^{3+} with 2-thiopheneacetic acid have been synthesized and their photophysical properties investigated. The quantum yields of the ternary complexes were found to be significantly enhanced by the presence of the bidentate nitrogen donor ligands due to the effective energy transfer from the co-ligands (1,10-phenanthroline or bathophenanthroline).

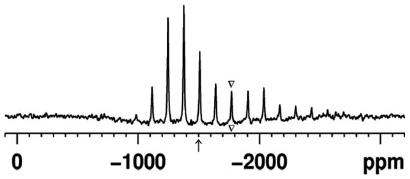
Pb Amino Acid Complexes

L. Gasque,* M. A. Verhoeven, S. Bernès,
F. Barrios, J. G. Haasnoot,
J. Reedijk 4395–4403

The Added Value of Solid-State Pb NMR Spectroscopy to Understand the 3D Structures of Pb Amino Acid Complexes

Keywords: Lead / Amino acids / NMR spectroscopy / X-ray diffraction





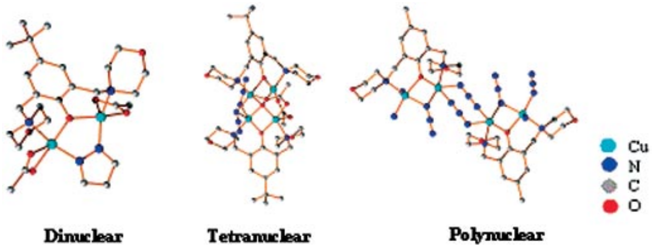
Single-crystal X-ray diffraction and solid-state ^{207}Pb NMR spectroscopy experiments have been conducted on four lead amino acid complexes. The NMR spectroscopic experiments show one, two, one, and four lead sites for the Hile, leu^-, $Hasp^-$, and Hval complexes, respectively, in agreement with the crystal structures.

Cu^{II} Catalysts for Oxidation

P. Roy, K. Dhara, M. Manassero,
P. Banerjee* 4404–4412

Di-, Tetra-, and Polynuclear Copper(II) Complexes: Active Catalysts for Oxidation of Toluene and Benzene

Keywords: Copper / N,O ligands / Oxidation



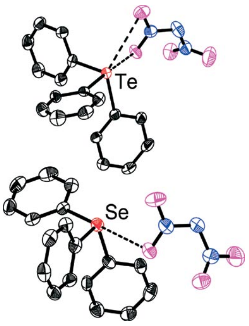
A series of di-, tetra-, and polynuclear copper(II) complexes with N_2O donor ligand has been synthesized, and it was found that they are active catalysts for the oxidation of toluene and benzene by using hydrogen peroxide as a catalyst.

Chalcogenium Dinitramides

T. M. Klapötke,* B. Krumm,
M. Scherr 4413–4419

Synthesis and Structures of Triorganochalcogenium (Te, Se, S) Dinitramides

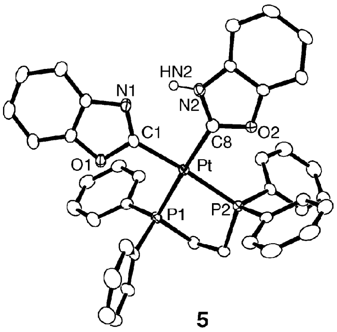
Keywords: Tellurium / Selenium / Sulfur / Dinitramide / NMR spectroscopy / Crystal structure



The reactions of triorganochalcogenium halides with a dinitramide transfer reagent result in the first triorganochalcogenium dinitramides, which were characterized by NMR spectroscopy and vibrational data. The crystal structures for the phenyl salts $[Ph_3Te][N(NO_2)_2]$ and $[Ph_3Se][N(NO_2)_2]$ are reported.

Carbene Complexes

Dicarbene complex **5** was obtained from the corresponding 2-(trimethylsiloxy)phenyl isocyanide complex by cleavage of the O–$SiMe_3$ bonds and subsequent cyclization of the isocyanide ligands to N-heterocyclic carbene (NHC) ligands. The carbene ligands in **5** were found in an unusual coplanar arrangement enforced by the formation of an N2–HN2···N1 hydrogen bond.



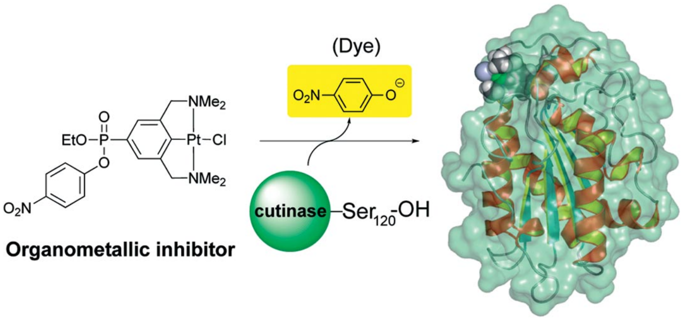
5

F. E. Hahn,* D. Klusmann, T. Pape **4420–4424**

Template Synthesis of Platinum Complexes with Benzoxazolin-2-ylidene Ligands

Keywords: Isocyanide ligands / Carbene ligands / Platinum / Template synthesis / Cyclization

Metallic Phosphonate Inhibitors



A straightforward protocol is described to place non-natural organometallic fragments into the active site of lipases, giving easy access to enzyme-organometallic hybrids. Thereby, the possibility for fine-tuning of the chemical environment (second coordination sphere) around a synthetic metal center inside a protein pocket for diagnostic and catalytic purposes is opened up.

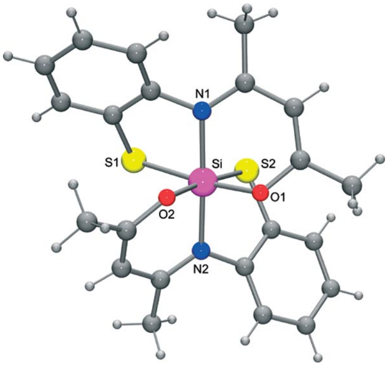
C. A. Kruithof, H. P. Dijkstra, M. Lutz, A. L. Spek, M. R. Egmond, R. J. M. Klein Gebbink,* G. van Koten* **4425–4432**

Non-Tethered Organometallic Phosphonate Inhibitors for Lipase Inhibition: Positioning of the Metal Center in the Active Site of Cutinase

Keywords: Protein modifications / Inhibitors / Phosphonates / ECE-Pincer complexes / Hydrolases

Hexacoordinate Si–S Complexes

Neutral hexacoordinate silicon(IV) complexes with Si–S bonds were synthesized, starting from $Si(NCO)_4$, and were structurally characterized by single-crystal X-ray diffraction and solid-state and solution NMR spectroscopy.



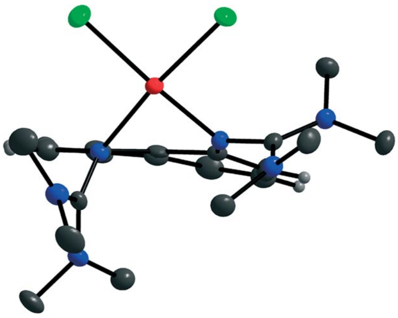
S. Metz, C. Burschka, R. Tacke* **4433–4439**

Synthesis and Structural Characterization of Novel Neutral Hexacoordinate Silicon(IV) Complexes with $SiS_2O_2N_2$ Skeletons

Keywords: Coordination chemistry / Hexacoordination / Silicon / Sulfur / Tridentate ligands

Proton Sponges

Pd and Pt complexes of the proton sponge 1,8-bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)naphthalene were synthesized which exhibit unusual structural details pointing to interesting chemical properties.



U. Wild, O. Hübner, A. Maronna, M. Enders, E. Kaifer, H. Wadepohl, H.-J. Himmel* **4440–4447**

The First Metal Complexes of the Proton Sponge 1,8-Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)naphthalene: Syntheses and Properties

Keywords: Proton sponge / Coordination compounds / Palladium / Platinum / Guanidine / Chelates

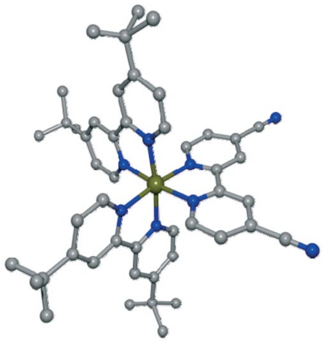
CONTENTS

Red-Emitting Ru Complexes

S. Losse, H. Görls, R. Groarke, J. G. Vos, S. Rau* .... 4448−4452

One-Step Synthesis of 4,4′-Dicyano-2,2′-bipyridine and Its Bis(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) Complex

Keywords: Nitrogen heterocycles / Bipyridine / Ruthenium / Coordination chemistry



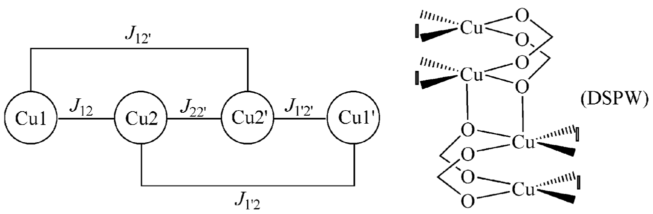
This report describes a new route for the synthesis of 4,4′-dicyano-2,2′-bipyridine. With the developed synthetic route we are able to obtain the ligand in a fast, economical and effective one-step synthesis with a facile workup procedure. The ability of this bipyridine derivative to serve as a chelating ligand in a ruthenium(II) complex is investigated.

Tetranuclear Copper(II) Clusters

Y.-Q. Zheng,* D.-Y. Cheng, J.-L. Lin, Z.-F. Li, X.-W. Wang .... 4453−4461

💻 Adipato-Bridged Copper(II) Complexes

Keywords: Copper / Cluster compounds / Bridging ligands / Carboxylate ligands / Coordination polymers



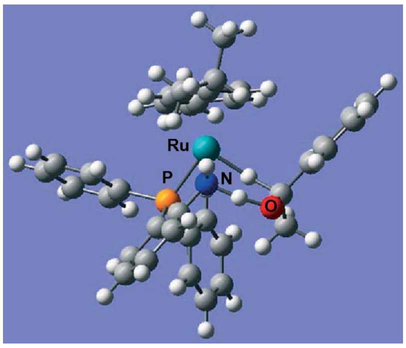
Double-semi-paddle-wheel tetranuclear copper(II) clusters are bridged as secondary building units by adipato ligands into 2D (4,4) networks. Magnetic analyses suggest that the *syn*−*syn* carboxylate bridges within the semi-paddle-wheel unit mediate considerate antiferromagnetic interactions, whereas the monoatomic μ_2-O bridges in the middle Cu_2O_2 rings transmit a small ferromagnetic coupling.

Hydrogen Transfer Reactions

A. Bacchi, M. Balordi, R. Cammi, L. Elviri, C. Pelizzi, F. Picchioni, V. Verdolino, K. Goubitz, R. Peschar, P. Pelagatti* .... 4462−4473

💻 Mechanistic Insights into Acetophenone Transfer Hydrogenation Catalyzed by Half-Sandwich Ruthenium(II) Complexes Containing 2-(Diphenylphosphanyl)aniline − A Combined Experimental and Theoretical Study

Keywords: Density functional calculations / Mass spectrometry / Hydrogen transfer / N,P ligands / Ruthenium



Complexes of the type {Ru[(κ^{2}P,N)-PNH_2](*p*-cymene)Cl}Y [PNH_2 = 2-(diphenylphosphanyl)aniline, Y = Cl, PF_6, BF_4, BPh_4, and TfO] promote the reduction of acetophenone through Noyori's bifunctional mechanism, as evidenced by MS (ESI) and DFT calculations, and the inertness of the complex {Ru[(κ^{2}P,N)-$PNMe_2$](*p*-cymene)Cl}Cl avoid of N−H functionalities.

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* Author to whom correspondence should be addressed.

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