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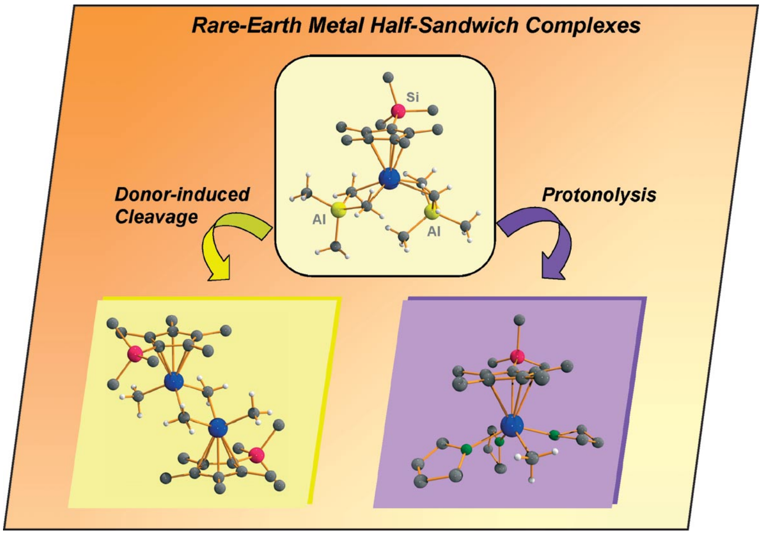
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the reactivity of half-sandwich bis(aluminate) complexes of the rare-earth metals that can be converted either into cationic methyl species by protonolysis or into dimeric dimethyl species by donor-induced cleavage of the aluminate moieties. Details are discussed in the article by J. Okuda et al. on p. 2801ff.



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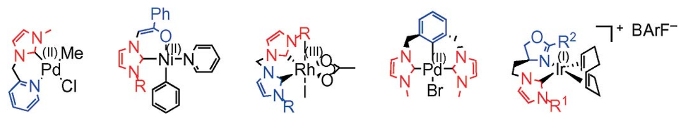
MICROREVIEW

N-Heterocyclic Carbenes

A. T. Normand, K. J. Cavell* ... 2781–2800

Donor-Functionalised N-Heterocyclic Carbene Complexes of Group 9 and 10 Metals in Catalysis: Trends and Directions

Keywords: N-Heterocyclic carbenes / Functionalised ligands / Homogeneous catalysis



Donor-functionalised NHCs can create a wide variety of coordination environments for metals (e.g. hemilabile, chelating, bis(carbene), pincer or chiral). These features generate impressive catalytic activities for the resulting complexes, especially in the case of group 9 and 10 metals. This Microreview focuses on the latest achievements obtained in homogeneous catalysis with these complexes.

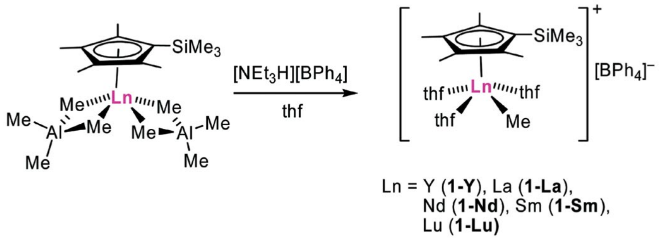
FULL PAPERS

Alkyl Rare-Earth Metal Cations

D. Robert, T. P. Spaniol,
J. Okuda* 2801–2809

Neutral and Monocationic Half-Sandwich Methyl Rare-Earth Metal Complexes: Synthesis, Structure, and 1,3-Butadiene Polymerization Catalysis

Keywords: Rare-earth metals / Half-sandwich complexes / Alkyl complexes / Cationic complexes / Butadiene polymerization



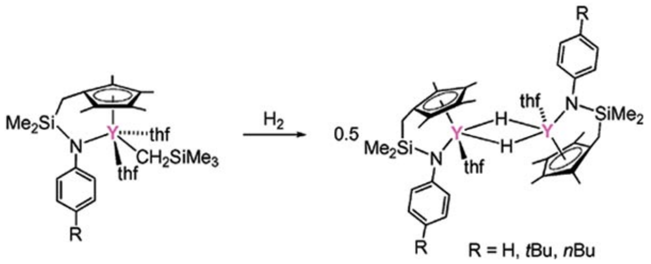
Half-sandwich rare-earth metal tetramethylaluminate complexes $[Ln(\eta^5\text{-}C_5Me_4SiMe_3)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$ (Ln = Y, La, Nd, Sm, Lu) were protonolyzed to give monocationic methyl complexes $[Ln(\eta^5\text{-}C_5Me_4SiMe_3)Me(thf)_3]^+[BPh_4]^-$. Upon activation with $[Ph_3C]^+[B(C_6F_5)_4]^-$, the neutral half-sandwich tetramethylaluminate complex catalyzed the polymerization of butadiene in the presence of $[Al\mathit{i}Bu_3]$ to give *trans*-1,4-polybutadiene with narrow polydispersities (M_n/M_w = 1.05–1.09).

Rare-Earth Metal Hydride Complexes

D. Robert, P. Voth, T. P. Spaniol,
J. Okuda* 2810–2819

Rare-Earth Metal Alkyl and Hydride Complexes Supported by a Linked Anilido–cyclopentadienyl Ligand: Synthesis, Structure, and Reactivity

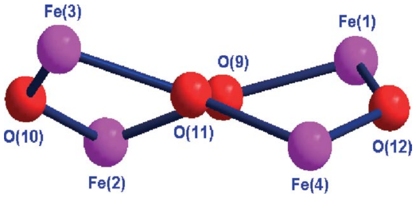
Keywords: Rare-earth metals / Half-sandwich complexes / Alkyl complexes / Hydride complexes / Pyridine / Alkyne



"Constrained geometry" alkyl complexes containing a ligand with an anilido group and a CH_2SiMe_2 link were converted into dimeric hydride complexes $[Y(\eta^5\text{-}C_5Me_4CH_2SiMe_2NC_6H_4R\text{-}4\text{-}\kappa N)(\mu\text{-}H)(thf)]_2$. Pyridine inserts into the Y–H bond in a 1,2-fashion to afford an isolable 2-hydropyridyl complex, which reacts with $\mathit{t}BuC{\equiv}CH$, to form the dimeric alkynyl complex $[Y(\eta^5\text{-}C_5Me_4CH_2SiMe_2NPh\text{-}\kappa N)(\mu\text{-}C{\equiv}C\mathit{t}Bu)]_2$.

An $\{Fe^{III}_4(\mu\text{-}OH)_2(\mu\text{-}OHO)\}^{7+}$ Core

The metric parameters of $[Fe_4(H_2bpp)_4(\mu\text{-}OH)_2(\mu\text{-}OHO)][ClO_4]_7\cdot 2H_2O\cdot 3MeCN$ (**1**·3MeCN) [H_2bpp = 1,3-bis(2-pyridinecarboxamido)propane] reveals that the four iron atoms are located at the vertices of a $\{Fe^{III}_4(\mu-OH)_2(\mu-OHO)\}^{7+}$ flattened tetragon, which is unique amongst Fe–(OHO)–Fe bridged tetrairon(III) complexes reported so far.



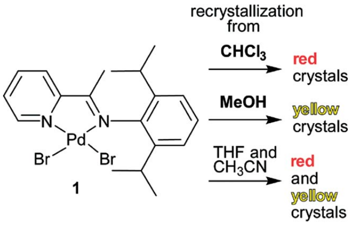
A. K. Singh, W. Jacob, A. K. Boudalis, J.-P. Tuchagues, R. Mukherjee* 2820–2829

A Tetragonal Core with Asymmetric Iron Environments Supported Solely by Bis(μ-OH){μ-(O–H···O)} Bridging and Terminal Pyridine Amide (N, O) Coordination: A New Member of the Tetrairon(III) Family

Keywords: Iron / Hydroxido bridges / Pyridine amide ligands / Magnetism / Mössbauer spectroscopy

Polymorphism

The polymorphism in the dimorphs of the palladium title compound **1** is traced to packing differences due to Br···π contacts between the $Br\cdots PdN_2C_2$ heterocycle together with different C–H···Br bonds.



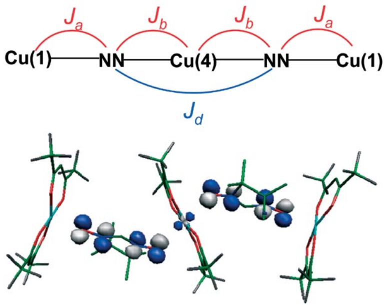
W. Zhang, X. Tang, H. Ma, W.-H. Sun,* C. Janiak* 2830–2836

{2-[1-(2,6-Diisopropylphenylimino)ethyl]-pyridyl}palladium Dibromide Polymorphs Originating from Different Br···π and C–H···Br Contacts

Keywords: Palladium complexes / Polymorphism / Supramolecular interactions / C–H···Br / Br···π

Molecular Magnetism

Quantum chemical analyses allowed us to reconstruct the complicated picture of exchange pathways inherent in the nature of heterospin chains based on the $Cu(hfac)_2$ complex with a nitronyl nitroxide biradical, and unexpectedly revealed a family of "hidden" interactions in the system of exchange parameters. This opened the way to a meaningful fit of the magnetic data.

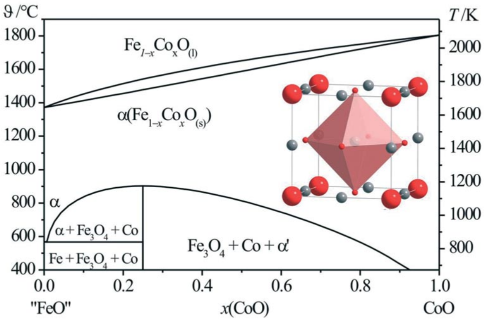


E. V. Gorelik,* V. I. Ovcharenko, M. Baumgarten 2837–2846

"Hidden" Spin–Spin Interactions in Complex Multispin Solids

Keywords: Density functional calculations / Magnetic properties / Heterospin exchange clusters / Nitronyl nitroxide radicals / Copper(II) complexes

Thermodynamics



In spite of the almost perfect crystallographic conditions for the formation of mixed phases $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ no homogeneous solid solutions series exist. Due to the different redox potentials [$p(O_2)$ = f(T)] of the binary phases "FeO" and CoO the solid solution shows a miscibility gap, by reason of the broader difference of redox potentials of "FeO" and NiO a complete series of mixed crystals cannot exist.

P. Schmidt* 2847–2855

How to Get Ternary Solid Solutions $Fe_{1-x}M'_xO$ (M = Co, Ni)? A Thermodynamic Concept

Keywords: Iron cobalt oxide / Iron nickel oxide / Thermodynamic modelling

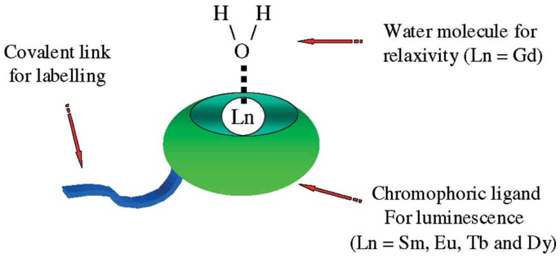
CONTENTS

Lanthanide Labels

S. Claudel-Gillet, J. Steibel,
N. Weibel, T. Chauvin, M. Port, I. Raynal,
E. Toth,* R. F. Ziessel,*
L. J. Charbonnière* 2856–2862

Lanthanide-Based Conjugates as Polyvalent Probes for Biological Labeling

Keywords: Lanthanides / Bio-conjugation / Luminescence / Relaxivity / Time-resolved luminescence microscopy



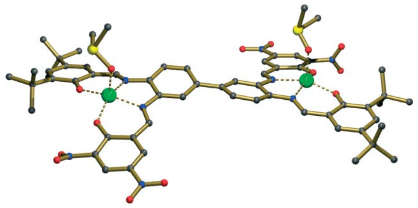
A single family of lanthanide-based labels is shown to be efficient both for time-resolved luminescence microscopy (Ln = Sm, Eu, Tb, and Dy) and for MRI contrast agent applications (Ln = Gd).

Bis(metallosalen) Building Blocks

S. Curreli, E. C. Escudero-Adán,
J. Benet-Buchholz,
A. W. Kleij* 2863–2873

A Modular Approach Towards Nonsymmetrical Bis(metallosalen) Building Blocks

Keywords: N,O ligands / Salen ligands/ Zinc / Supramolecular chemistry



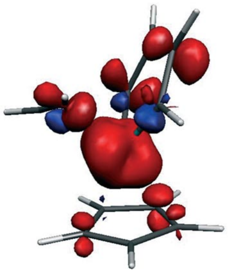
A modular approach towards the formation of nonsymmetrical bis(metallosalen)s was developed starting from readily accessible bis(imine) precursors, which allowed the subsequent introduction of various other peripheral groups. The bis(metallosalen) complexes can be used as supramolecular building blocks.

Acetylene Cyclooligomerisation

R. Xu, P. Winget, T. Clark* 2874–2883

The Cyclooligomerisation of Acetylene at Metal Centres

Keywords: Ab initio calculations / DFT calculations / Transition states / Electron transfer / Electron-transfer catalysis



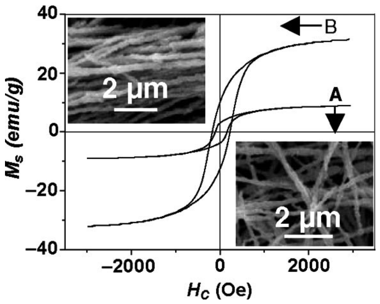
Density-functional theory and ab initio calculations on the trimerisation of acetylene at CoCp centres reveal an additional, previously unknown reaction path. An analysis of the mechanisms of the individual steps in the reaction reveals the role of electron-transfer catalysis and the connection to two-state reactivity.

Nanocrystallite Nickel Fibers

C. Gong, L. Yu, Y. Duan, J. Tian, Z. Wu,
Z. Zhang* 2884–2891

The Fabrication and Magnetic Properties of Ni Fibers Synthesized Under External Magnetic Fields

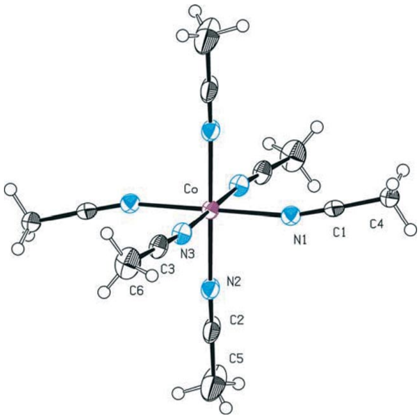
Keywords: Nickel fibers / Nanocrystallites / Chemical reduction / Magnetic fields / Magnetic properties



The ultrafine Ni fibers were easily fabricated, and their mean length increased markedly with increasing Ni^{2+} ion concentration and intensity of the external magnetic field. The present approach has the advantage of having a fast reaction rate and low cost and may be promising for the effective control of the shape and magnetic properties of magnetic materials.

Acetonitrile-Ligated Complexes

Acetonitrile-ligated transition-metal complexes containing tetrakis(pentaflourophenyl)borate as counteranions were prepared in high yields and characterized by IR, NMR, and UV spectroscopy and elemental analysis. The catalytic activity for isobutene polymerization was examined.

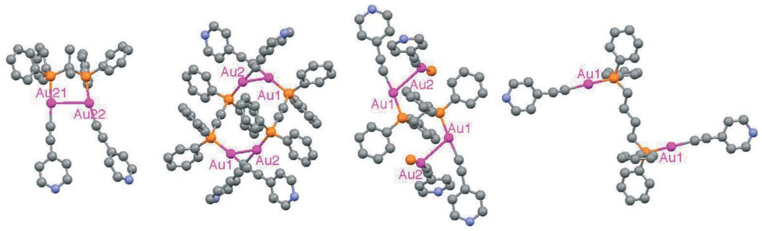


A. K. Hijazi, A. Al Hmaideen, S. Syukri, N. Radhakrishnan, E. Herdtweck, B. Voit, F. E. Kühn* 2892–2898

Synthesis and Characterization of Acetonitrile-Ligated Transition-Metal Complexes with Tetrakis(pentafluorophenyl)borate as Counteranions

Keywords: Acetonitrile ligands / Weakly coordinating anions / Transition metals

Alkynyl Au^{I} Phosphane Complexes



A series of alkynyl phosphane Au^{I} complexes were prepared. The X-ray crystal structures show the influence of the nature of the phosphane spacer on the establishment of aurophilic interactions. The absorption and emission properties of the complexes were studied; although UV/Vis differences were observed for compounds with intramolecular Au–Au contacts, no trend was observed in the emission behaviour.

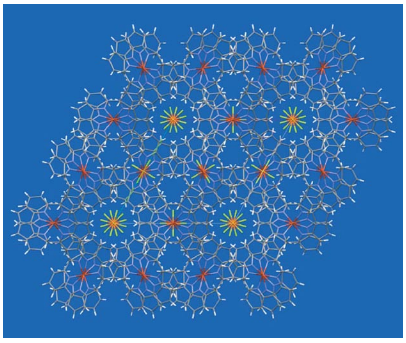
M. Ferrer,* A. Gutiérrez, L. Rodríguez, O. Rossell, J. C. Lima, M. Font-Bardia, X. Solans 2899–2909

Study of the Effect of the Phosphane Bridging Chain Nature on the Structural and Photophysical Properties of a Series of Gold(I) Ethynylpyridine Complexes 💻

Keywords: Gold / Aurophilicity / Phosphanes / Alkynes / Luminescence / UV/Vis spectroscopy

Self-Assembly

The self-assembly of ligands **L1** and **L2** containing N_2- and N_2O-dentate binding units form helicates with copper(I) and silver(I) and mononuclear supramolecular complexes with cobalt(II) and zinc(II). The compounds were characterised by microanalyses and crystallographic and spectroscopic data.



A. R. Stefankiewicz, M. Wałęsa, P. Jankowski, A. Ciesielski, V. Patroniak, M. Kubicki, Z. Hnatejko, J. M. Harrowfield, J.-M. Lehn* 2910–2920

Quaterpyridine Ligands Forming Helical Complexes of Mono- and Dinuclear (Helicate) Forms

Keywords: Helical structures / N ligands / N,O ligands / Self-assembly / Transition metals

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* Author to whom correspondence should be addressed.

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