



SWEDEN



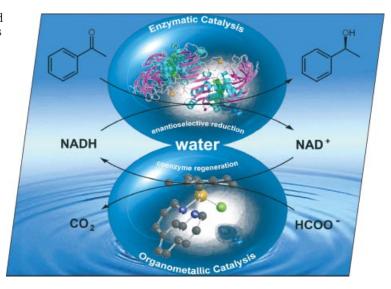


EUChemSoc



COVER PICTURE

The cover picture shows an example of combined organometallic and enzymatic catalysis in aqueous solution. The rhodium complex [(C₅Me₅)Rh-(phenanthroline)Cl]⁺ continuously regenerates NADH from NAD+ by using formate as hydrogen source, and the enzyme alcohol dehydrogenase from Rhodococcus erythropolis enantioselectively reduces the ketone to the corresponding alcohol by means of the NADH formed. This work illustrates the increasing interest in enantioselective catalysis with the environmentally friendly water as solvent. Details are discussed in the article by G. Süss-Fink et al. on p. 4736ff.



MICROREVIEW

Pt Intermolecular Hydroamination

J.-J. Brunet,* N.-C. Chu, M. Rodriguez-Zubiri* 4711–4722

Platinum-Catalyzed Intermolecular Hydroamination of Alkenes: Halide-Anion-Promoted Catalysis

Keywords: Alkenes / Homogeneous catalysis / Intermolecular hydroamination / Ionic liquids / Platinum

Tetraalkylphosphonium halides play the role of "promoters" for the Pt^{II}-catalyzed hydroamination of alkenes. The promoting effect of these "cocatalysts" depends only upon their anionic moiety. The Pt^{II}/

 $n\mathrm{Bu_4PBr}$ system exhibits an unprecedented catalytic activity (aerobic conditions) for the hydroamination of ethylene and 1-hexene (regioselectivity > 95%, Markovnikov).

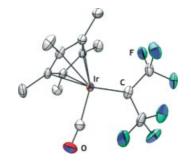
SHORT COMMUNICATION

A Bis(trifluoromethyl)carbene Complex

J. Yuan, R. P. Hughes,*
A. L. Rheingold 4723-4725

The First Example of a Bis(trifluoromethyl)carbene Transition-Metal Complex and Its Reduction to a Perfluoroallene Complex

Keywords: Carbene / Iridium / Fluorine / Ligands / Structure



Na/Pb alloy reduction of the (perfluoroiso-propyl)iridium complex $Cp^*(CO)IrI[CF-(CF_3)_2]$ afforded the first example of a bis-(trifluoromethyl)carbene complex, $Cp^*-(CO)Ir=C(CF_3)_2$, which has been crystal-lographically characterized. Further reduction of this carbene complex with KC_8 yielded the (perfluoroallene)iridium complex $Cp^*Ir(CO)(\eta^2-CF_2CCF_2)$.

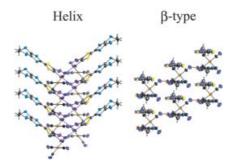
FULL PAPERS

Supramolecular Conductors

T. Imakubo,* T. Shirahata, M. Kibune, H. Yoshino 4727–4735

Hybrid Organic/Inorganic Supramolecular Conductors $D_2[Au(CN)_4]$ [D = Diiodo-(ethylenedichalcogeno)tetrachalcogenofulvalene], Including a New Ambient Pressure Superconductor

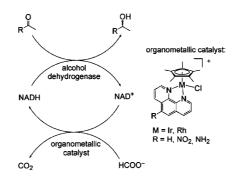
Keywords: Supramolecular chemistry / Conducting materials / Iodine / Superconductors / Selenium heterocycles



Depending on the number and positions of the selenium atoms on the iodinated donor molecule, a helical or $\beta\text{-type}$ structure has been tailored by the characteristic I···N iodine bonds in the crystals of $D_2[Au(CN)_4],$ and one of the $\beta\text{-type}$ salts shows superconducting transition at around 2 K (onset, ambient pressure).



Water-soluble (chlorido)(cyclopentadien-yl)rhodium and -iridium complex cations, accessible from dinuclear precursors and phenanthroline derivatives, catalyse the transfer hydrogenation of NAD+ to NADH in aqueous solution by using HCOONa as hydrogen source. The combination of an alcohol dehydrogenase with this NADH-regenerating system for the chemoenzymatic reduction of prochiral ketones results in *ee* values up to 98 % under biological conditions.



Organometallic-Enzymatic Catalysis

Water-Soluble Phenanthroline Complexes of Rhodium, Iridium and Ruthenium for the Regeneration of NADH in the Enzymatic Reduction of Ketones

Keywords: Cationic complexes / Cofactor regeneration / Chemoenzymatic catalysis / Enantioselective catalysis / Transfer hydrogenation

Energetic Materials

Copper bis(1-methyl-5-nitrimino-tetrazole)
(1) was synthesized by a facile route and investigated as a new primary explosive. It shows the unusual combination of high impact and moderate friction sensitivity, which are five times higher and ten times lower than that of lead azide, respectively. In addition, 1 is stable up to 250°C and shows long term stability up to 200°C.

Copper Bis(1-methyl-5-nitriminotetrazolate): A Promising New Primary Explosive

Keywords: Primary explosives / Copper / Nitrogen heterocycles / Pyrotechnics / X-ray

Radical Anion Salts

The title heterocycles are prepared and electrochemically and chemically reduced to their long-lived radical anions, which can be isolated in the form of the thermally stable salts of the $[K(18\text{-crown-6})]^+$ cation. These salts reveal low-temperature antiferromagnetic ordering of the spin system $(J = -1.65 \text{ cm}^{-1})$. Color code: gray = C, blue = N, yellow = S, magenta = Se.

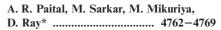


I. Yu. Bagryanskaya, Yu. V. Gatilov, N. P. Gritsan,* V. N. Ikorskii, I. G. Irtegova, A. V. Lonchakov, E. Lork, R. Mews,* V. I. Ovcharenko,* N. A. Semenov, N.V. Vasilieva, A.V. Zibarev* ... 4751–4761

 $\label{eq:continuous} \begin{tabular}{ll} [1,2,5]Selenadiazolo[3,4-c][1,2,5]thiadiazole and [1,2,5]Selenadiazolo[3,4-c][1,2,5]thiadiazolidyl - A Synthetic, Structural, and Theoretical Study \end{tabular}$

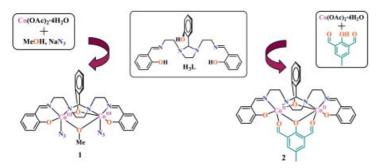
Keywords: Density functional calculations / Magnetic properties / Nitrogen heterocycles / Radical anions / Sulfur / Selenium

Exogenous Bridging Coligands



[(Tmp)Co₂L] Complexes through Preassembly on 2,6-Diformyl- and 2,6-Bis(benzylimino)-4-methylphenolate Templates

Keywords: Cobalt complexes / Bridging ligands / Template synthesis / Imidazolidine / Magnetic properties



Using what are normally dinucleating ligands themselves (Hdfp and Hbip), the desired [Co₂L] species were crystallized by

phenolate templation; dfp⁻ and bip⁻ acted as exogenous bridging coligands.

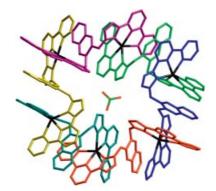
CONTENTS

Metallosupramolecular Chemistry

N. K. Al-Rasbi, H. Adams, L. P. Harding, M. D. Ward* 4770-4780

Coordination Behaviour of Bis-Terdentate N-Donor Ligands: Double- and Single-Stranded Helicates, Mesocates, and Cyclic Oligomers

Keywords: Chelating ligands / Coordination chemistry / Helical structures / Self-assembly



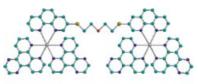
A series of potentially hexadentate ligands comprising two terdentate pyrazolyl-bi-pyridine units connected to a central aromatic spacer forms a range of structures including single- and double-stranded and cyclic polynuclear helicates; the Figure shows a cyclic hexanuclear helicate encapsulating a perchlorate anion.

Bis-Intercalating Metal Complexes

C. R. Brodie, J. R. Aldrich-Wright* 4781-4793

Synthesis of Flexible Bis-Intercalating Ruthenium(II) Complexes

Keywords: Ruthenium(II) / Synthesis / Chiral resolution / TRISPHAT / Dinuclear complexes / Bis-intercalators



 $[\{Ru(dpq)_2\}_2(\mu-phen-5-SOS-5-phen)]^{4+}$

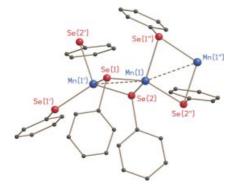
Three dinuclear ruthenium(II) complexes with the flexible linker bis(2-mercaptoethyl) ether have been synthesised in their enantiomerically pure forms and characterised by ¹H NMR, ESI-MS, CD and UV/ Vis spectrometery.

Manganese(II) Selenolate Complexes

A. Eichhöfer,* P. T. Wood, R. Viswanath, R. A. Mole 4794–4799

Synthesis, Structure and Magnetic Behaviour of Manganese(II) Selenolate Complexes $\frac{1}{\infty}[Mn(SePh)_2]$, $[Mn(SePh)_2(bipy)_2]$ and $[Mn(SePh)_2(phen)_2]$ (bipy = bipyridyl, phen = phenanthroline)

Keywords: Transition-metal complexes / Manganese / X-ray structure analysis / Magnetism



The manganese selenolate complexes ${}^1_\infty[Mn(SePh)_2]$ and $[Mn(SePh)_2(L)_2]$ (L=2,2'-bipy, 1,10-phen) have been prepared and their structures characterised by X-ray analysis. The magnetic and optical properties have been investigated.

Heteroleptic Tris(phthalocyaninates)

Diphthalocyaninatolanthanum as a New Phthalocyaninato-Dianion Donor for the Synthesis of Heteroleptic Triple-Decker Rare Earth Element Crown-Phthalocyaninato Complexes

Keywords: Rare earths / Macrocyclic ligands / Phthalocyanines / Sandwich complexes / Heteroleptic complexes

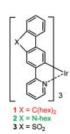


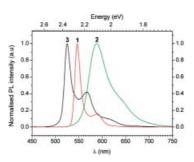
A new source of phthalocyaninato-dianion – diphthalocyaninatolanthanum – has been discovered. Its reaction with tetra-15-crown-5-phthalocyanine and rare-earth element (REE) acetylacetonato complexes

leads to heteroleptic triple-decker phthalocyaninato complexes (Pc)M[(15C5)₄-Pc]M(Pc) and [(15C5)₄Pc]M[(15C5)₄Pc]-M(Pc) both of which are potential components of new supramolecular materials.



Electrophosphorescent Ir Complexes





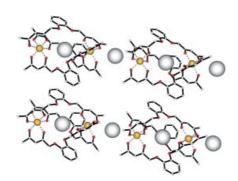
The substituent para to the Ir atom, i.e. CR2 in 1, NR in 2 and SO2 in 3, has a major influence on the redox and emission

properties in this series of tris-cyclometalated complexes.

A Tris-Cyclometalated Iridium(III) Complex of 2-(5,5-Dioxido-dibenzothiophen-3-yl)pyridine: Synthesis, Structural, Redox and Photophysical Properties

Keywords: Dibenzothiophene S,S-dioxide / Iridium / Cyclometalation / Luminescence / Electrochemistry

An appropriate choice of ligand substitution and metal ions enables the syntheses of {2}-metallacryptates or linear/meandering coordination polymers in the solid state. Exemplarily, a detailed analysis of the stereogenic centres in racemic Δ/Λ -(2)_n revealed the formation of homochiral layers in the crystal [see picture; Λ -(2)_n: Mg gold, Cs silver, O red, C white].



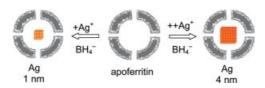
Self-Assembly of Metallacryptates

R. W. Saalfrank,* N. Mooren, A. Scheurer, H. Maid, F. W. Heinemann, F. Hampel, W. Bauer 4815-4822

Synthesis and Structure of Self-Complementary {2}-Metallacryptates and Their Linear or Meandering Infinite Arrangements in the Solid State

Keywords: Metallacryptate / Coordination polymers / O ligands / X-ray diffraction / Chirality

Ag Nanoparticles



Size-controlled Ag nanoparticles were prepared by using an Ag+-loaded apoferritin as a nanoconfined environment for their construction. The protein shell of the

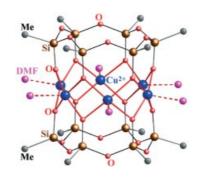
particles prevents bulk aggregation of the metal particles, which renders them water soluble and extremely stable.

J. M. Domínguez-Vera,* N. Gálvez, P. Sánchez, A. J. Mota, S. Trasobares, J. C. Hernández, J. J. Calvino* 4823-4826

Size-Controlled Water-Soluble Ag Nanoparticles

Keywords: Silver / Nanoparticles / Apoferritin / Water-soluble particles

A new hexanuclear copper(II) sandwich complex based on two 12-membered macrocyclic methylsiloxanolate ligands, [Cu₆{(MeSiO₂)₆}₂]·6DMF, was synthesized and characterized by single-crystal X-ray diffraction analysis and magnetic measurements.



L. Zherlitsyna, N. Auner*, M. Bolte, Yu. Pozdniakova, O. Shchegolikhina,

Copper(II) Sandwich Complex

K. Lyssenko, V. Pashchenko*, B. Wolf, M. Lang, F. Schütz, M. Kollar, F. Sauli, P. Kopietz 4827-4838

Synthesis, Structure and Magnetic Properties of a Novel Hexanuclear Copper Methylsiloxane Complex

Keywords: Copper / Cluster compounds / Sandwich complexes / Magnetic properties

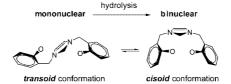
CONTENTS

Carbene Complexes

D. Zhang* 4839-4845

Dinuclear Titanium(IV) Complexes Bearing Phenoxide-Tethered N-Heterocyclic Carbene Ligands with *cisoid* Conformation through Control of Hydrolysis

Keywords: Titanium / Carbene ligands / Phenoxides



Two oxygen-bridged titanium dimers, $\{[(L)TiBr]_2(\mu\text{-O})\}$ (4) and $\{[(L)Ti(\mu\text{-O})]_2\}$ (5) — $[H_3(L)]Br=1,3\text{-bis}(4,6\text{-di-}tert\text{-butyl-}2\text{-hydroxybenzyl})imidazolium bromide) — were obtained by control of hydrolysis of <math display="inline">[(L)TiBr_2(thf)]$ (1) and $[(L)Ti(CH_2Ph)_2]$ (3) in tetrahydrofuran and diethyl ether. The phenoxide-functionalized NHC ligand adopts transoid conformation in mononuclear complex 2 but rare cisoid conformation in dinuclear complexes 4 and 5.

If not otherwise indicated in the article, papers in issue 29 were published online on September 25, 2007