

















SWEDEN

Austria



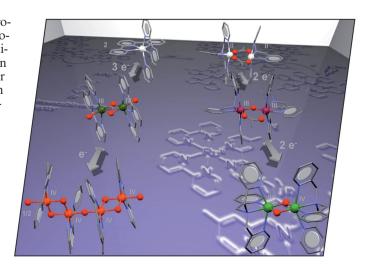






COVER PICTURE

The cover picture shows two examples of electroinduced formation and transformation of oxidobridged manganese complexes with polypyridyl ligands. The first example displays interconversion between mononuclear, dinuclear and tetranuclear cores accompanied by the concomitant formation (by oxidation) or breaking (by reduction) of μ-oxido bridges. In the second example, core interconversion between μ-oxido and μ-acetato bridges in dinuclear manganese complexes is depicted. The background picture shows a schematic representation of the photoinduced formation of a dinuclear di-μ-oxido-bridged manganese core from a mononuclear one in a superstructured complex of ruthenium and manganese. Details are presented in the Microreview by M.-N. Collomb and A. Deronzier on p. 2025 ff. The authors thank Dr. Damien Jouvenot for his help in designing the cover picture.

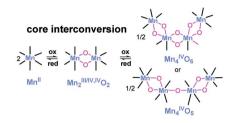


MICROREVIEWS

Oxido-Bridged Manganese Complexes

Electro- and Photoinduced Formation and Transformation of Oxido-Bridged Multinuclear Mn Complexes

Keywords: Manganese / Oxido ligands / Carboxylato ligand / Electrochemistry / Photochemistry



μ-oxo/acetato exchange

Mn ox red ox red ox red ox red ox mn2 lll (OAc)3 Mn2 lll (OAc)2 Mn2 lll (OAc)4 Mn2 lll (OAc)5 Mn2 lll (OAc)6 Mn2 lll

This microreview focuses on literature studies dedicated to the formation and transformation of μ -oxido-bridged manganese complexes that are induced by electrochemical or photochemical means. This manganese chemistry is relevant to redoxactive manganese metalloenzymes such as manganese catalases and the oxygen-evolving complex of photosystem II.

SHORT COMMUNICATIONS

Semiconducting Thin Films

T. Chen,* W. Hunks, P. S. Chen,

G. T. Stauf, T. M. Cameron, C. Xu,

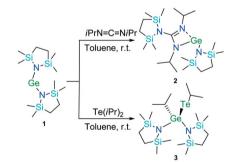
A. G. DiPasquale,

A. L. Rheingold 2047-2049



Insertion Reactions of an Aminogermylene and Formation of a Single-Source Precursor for GeTe Thin Films

Keywords: Main group elements / Germanium / Tellurium / Metal-organic chemical vapor deposition / Semiconductors / Thin films



Insertion reactions between a liquid germylene 1, and either a carbodiimide or dialkyl telluride lead to the novel guanidinate complex 2 or the terminal alkyl tellurolate compound 3, respectively. The use of 3 as a SSP for the MOCVD of stoichiometric GeTe films was demonstrated.

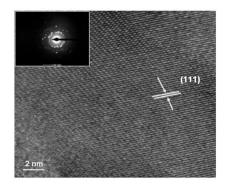
Aluminum Nanoparticles

C. Mahendiran, R. Ganesan,

A. Gedanken* 2050-2053

Sonoelectrochemical Synthesis of Metallic Aluminum Nanoparticles

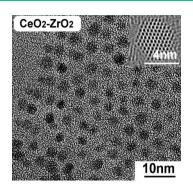
Keywords: Electrochemistry / Aluminum / Nanoparticles



This paper describes a simple and singlestep pulsed sonoelectrochemical process for the synthesis of metallic aluminum nanoparticles, at room temperature by using anhydrous AlCl₃ (99.99%) and LiAlH₄ in tetrahydrofuran.



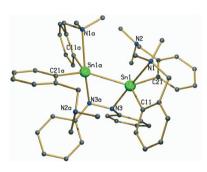
Monodisperse $Ce_{0.5}Zr_{0.5}O_2$ nanocrystals were synthesized by the hydrothermal method using a metal oleate precursor. The results showed that the 3.0-nm-sized nanocrystals possess a metastable CeO_2 - ZrO_2 tetragonal phase with a well-designed chemical composition and are nearly monodisperse.

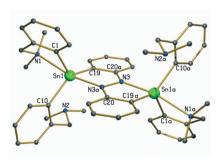


Oleate-Stabilized Nanocrystals

Keywords: Nanostructures / Hydrothermal synthesis / Solid solutions / Heterogeneous catalysis

Stannylene





Z. Padělková, M. S. Nechaev, A. Lyčka, J. Holubová, T. A. Zevaco, A. Růžička* 2058–2061

2002

Reactivity of C,N-Chelated Stannylene with Azobenzene

Keywords: Stannylene / Azobenzene / C-H activation / N ligands

The reactivity of a C,N-chelated stannylene $L_2Sn\ [L=2\text{-}(Me_2NCH_2)C_6H_4]$ with azobenzene has been studied.

$OC)_5W$ R 1) PhC \equiv CH, TfOH $OC)_5M$ R 1) CyNC, TfOH $OC)_5W$ P NCy $OC)_5W$

Dichotomy of 2*H*-azaphosphirene complexes was observed in acid-induced ring enlargement reactions; whereas a P-N bond-selective reaction was observed in the case of an isocyanide, phenylacetylene was

selectively inserted into the P-C bond. DFT calculations on structures, charges and compliance constants of an *N*-protonated 2*H*-azaphosphirene complex provide first insight into this surprising result.

Acid-Induced Ring Enlargement

H. Helten, G. von Frantzius, G. Schnakenburg, J. Daniels,

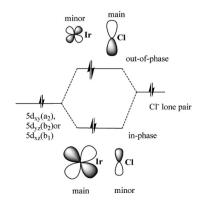
R. Streubel* 2062-2065

How To Tune Acid-Induced Ring Enlargement Reactions – The Strange Case of 2*H*-Azaphosphirene Complexes and Its Surprising Dichotomy

Keywords: 2*H*-Azaphosphirene complexes / Tungsten / Bond activation / Ring expansion / Compliance constant

FULL PAPERS

Iridum(III) terpyridine complexes with three Cl⁻ anions having intrinsic $C_{2\nu}$ symmetry are suitable for analyzing orbital interactions. By introducing three Cl⁻ anions to the Ir³⁺ cation, it can be expected that the absorption and emission properties of the complexes change from $\pi-\pi^*$ to metalto-ligand charge transfer.



Monoterpyridine Iridium Complexes

N. Yoshikawa,* S. Yamabe, N. Kanehisa, T. Inoue, H. Takashima,

K. Tsukahara 2067-2073

Detailed Description of the Metal-to-Ligand Charge-Transfer State in Monoterpyridine Ir^{III} Complexes

Keywords: Iridium / N ligands / Charge transfer / Emission / Density functional calculations

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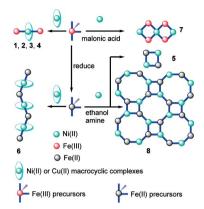
Cyanido-Bridged Complexes

H. Xiang, S.-J. Wang, L. Jiang, X.-L. Feng, T.-B. Lu* 2074–2082



Self-Assembly from Discrete Clusters to 2D Network Based on $[Fe(phen)(CN)_4]^-$ and $[Fe(bipy)(CN)_4]^-$: Synthesis, Structures and Magnetic Properties

Keywords: Iron / Nickel / Macrocyclic ligands / Bridging ligands / Magnetic properties



Eight cyanido-bridged complexes, from clusters to 2D networks, were synthesized with H[Fe(phen)(CN)₄]·2H₂O and H[Fe(bipy)(CN)₄]·2H₂O as precursors. Ferromagnetic couplings are found between the low-spin Fe^{III} ions and Ni^{II} ions through the cyanido groups in the complexes and a metamagnetic behavior and a frequency dependence of the out-of-phase ac susceptibility are observed in one complex.

Rhodium 4,5-Diazafluorene Chemistry

Syntheses, Structures and Reactivities of Rhodium 4.5-Diazafluorene Derivatives

Keywords: Heterocycles / Rhodium / Hydrogenation / Alkenes



We report the syntheses, structures and reactivities of a series of rhodium 4,5-diazafluorene derivatives, including the inter-

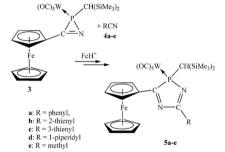
conversion of these complexes and catalytic olefin hydrogenation activities.

Ring Expansion by SET

R. Streubel,* M. Beckmann, C. Neumann, S. Fankel, H. Helten, O. Feier-Iova, P. G. Jones, M. Nieger 2090–2095

Synthesis, Structure, and Ring-Expansion Reactions of a 3-Ferrocenyl-Substituted 2*H*-Azaphosphirene Tungsten Complex

Keywords: Carbenes / Heterocycles / Phosphorus / Ring expansion / Electron transfer

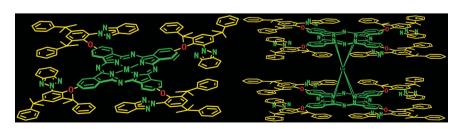


Synthesis and reactions of the first *C*-ferrocenyl-substituted 2*H*-azaphosphirene complex **3** are presented. Under oxidative single-electron transfer conditions, and by using ferrocenium hexafluorophosphate as a mild oxidant, complex **3** reacted with various nitrile derivatives **4** to give regioselectively 2*H*-1,4,2-diazaphosphole complexes **5**.

Tetrasubstituted Phthalocyanines

Synthesis, Characterization, Electrochemical, and Optic Limiting Properties of Novel Co^{II}, Cu^{II}, and Double-Decker Lu^{III} Phthalocyanines

Keywords: Phthalocyanines / Sandwich complexes / Electrochemistry / Nonlinear optics / Rare earths



The synthesis and characterization of tetrasubstituted Co^{II}, Cu^{II}, and double-decker Lu^{III} phthalocyanines are reported. Their electrochemistry and nonlinear absorption and optical limiting performance were studied.



OLED Materials

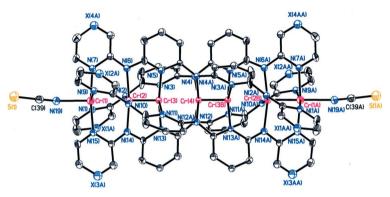
Irradiation of the optically resolved mer- Δ isomer of $Ir(ppz)_3$ with 366-nm light in CH_3CN gave 59:41 ratio of fac- Δ/fac - Λ (18% ee) at the end of geometrical isomerization. This photoisomerization proceeds through axial Ir- N^1 or Ir- N^3 bond dissociation—rehybridization—recoordination; the mechanism is supported by DFT/UB3LYP calculations.

stereochemistry
$$Ir(ppz)_3$$
 $Ir-N_1$ bond $Ir-N_2$ $Ir-N_3$ bond $Ir-N_$

Chirality in the Photochemical $mer \rightarrow fac$ Geometrical Isomerization of Tris(1-phenylpyrazolato, N, $C^{2'}$) iridium(III)

Keywords: Iridium / Isomerization / Chirality / Photochemistry

EMAC Complexes



New linear heptametal(II) EMACs [$M_7(\mu_7-L)_4X_2$] [$L=pzpz^3-$, $M=Ni^{II}$, $X=Cl^-$ (1), NCS $^-$ (2); $M=Cr^{II}$, $X=Cl^-$ (3), NCS $^-$ (4); $L=tpz^3-$, $M=Cr^{II}$, $X=Cl^-$ (5), NCS $^-$ (6)] of pyrazine-modulated tetrapyr-

idyltriamine ligands (H₃pzpz and H₃tpz) were successfully synthesized and their structure, and magnetic and electrochemistry properties studied.

R. H. Ismayilov, W.-Z. Wang, G.-H. Lee, C.-H. Chien, C.-H. Jiang, C.-L. Chiu, C.-Y. Yeh, S.-M. Peng* 2110–2120

Redox Modification of EMACs Through the Tuning of Ligands: Heptametal(II) Complexes of Pyrazine-Modulated Oligoα-pyridylamido Ligands

Keywords: Metal-metal interactions / Nickel / Chromium / Magnetic properties

Metal Nitrates

$$\begin{array}{c} \text{H} \\ \text{H} \\ \text{O} \\ \text{NI} \\ \text{O} \\ \text{O}$$

Gas-phase experiments provide insight into the microsolvation of cobalt and nickel nitrates and their decomposition into metal oxo species. Aqueous solutions of cobalt(II) and nickel(II) nitrate, respectively, were ionized to afford mono- and oligonuclear nitrato complexes. Thermal reactions of the nitrato cations with nitrogen monoxide parallel the NO-assisted pyrolysis of solid metal nitrates.

Gas-Phase Model Studies Relevant to the Decomposition of Transition-Metal Nitrates $M(NO_3)_2$ (M = Co, Ni) into Metal—Oxo Species

Keywords: Cleavage reactions / Cobalt / Gas-phase reactions / Nickel / O ligands

Ring-Opening Polymerization

The aluminum complexes bearing anilidooxazolinate ligands demonstrate efficient activities in catalyzing the ring-opening polymerization of L-lactide or *e*-caprolactone in the presence of benzyl alcohol.

C.-T. Chen,* H.-J. Weng, M.-T. Chen, C.-A. Huang, K.-F. Peng 2129–2135

Synthesis, Characterization, and Catalytic Application of Aluminum Anilido-Oxazolinate Complexes

Keywords: Aluminum / Anilido-oxazolinate ligands / Ring-opening polymerization / Biodegradable polymers

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Spin Crossover

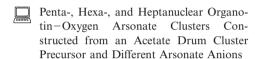
Parallel Crystallization of a "Static" and a Spin-Crossover Polymorph of an Iron(II) Complex from the Same Solution

Keywords: Iron / Spin crossover / Polymorphism / N ligands / Magnetic properties

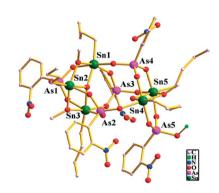


The iron(II) complex $[Fe(L)_2](BF_4)_2$ [L=2,6-bis(1H-pyrazol-1-yl)-4-(thiocyanatometh-yl)pyridine] displays polymorphism in the solid state: it can be obtained in two crystalline forms at room temperature, from the same solution and side-by-side. One (yellow) has the molecules in a high-spin state that is virtually independent of temperature, whereas the other (red-brown) shows spin-crossover behaviour.

Organotin-Oxygen Clusters



Keywords: Arsenic / Cluster compounds / Tin / Oxygen



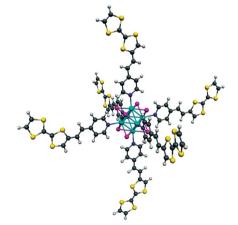
Penta-, hexa-, and heptanuclear organotin—oxygen arsonate clusters were obtained from the acetate drum in displacement reactions with different arsonic acid ligands; the structural interrelationship of these diverse organotin—oxygen clusters is also discussed.

Hybrid Organic/Inorganic Assemblies

G. Prabusankar, Y. Molard,* S. Cordier,* S. Golhen,* Y. Le Gal, C. Perrin,

L. Ouahab,* S. Kahlal,

J.-F. Halet* 2153-2161



Synergetic π -d interactions between the organic ligands and the inorganic cluster core in $[Mo_6X^i{}_8(TTF\text{-}CH=CH\text{-}Py)^a{}_6]^{4+}$ supramolecular assemblies [TTF= tetrathiafulvalene; Py= pyridine; X= Cl (1), Br (2), I (3)] were experimentally evidenced by electrochemistry and absorption measurements, and corroborated by DFT calculations.

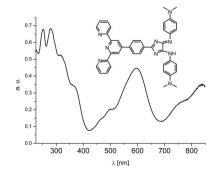
Experimental and Theoretical Evidence of π -d Interactions in Supramolecular Assemblies Based on TTF-CH=CH-Py Ligands Tethered to $Mo_6X^i_8$ Octahedral Molybdenum Halide Cluster Cores

Keywords: Molybdenum / Cluster compounds / Early transition metals / Ligands / Supramolecular chemistry / Charge transfer

Multifunctional Chromophores

Synthesis of Ligands Based on 4*H*-Imidazoles and Pyridine Subunits: Selective Complexation and Bathochromically Absorbing Complexes

Keywords: N ligands / Imidazole / Bipyridine / Palladium / Iridium



New multifunctional ligands based on the combination of 4*H*-imidazoles with pyridine subunits have been synthesised. The long wavelength absorptions can be shifted towards the NIR region by introduction of additional auxochromic groups. Due to different complexation spheres these hybridligands form the requirements for the construction of heterobimetallic complexes.



Molecular Zinc Carbamates

Reaction between [ZnEt(O₂CNR₂)]₄ (R = *i*Pr or *i*Bu) and several nitrogen bases affords new carbamato-Zn complexes of different sizes, which can be used as building blocks for the synthesis of other carbamato complexes.



D. Domide, C. Neuhäuser, E. Kaifer, H. Wadepohl,

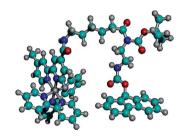
H.-J. Himmel* 2170-2178

Synthesis of Trinuclear, Dinuclear and Mononuclear Carbamato-Zinc Complexes from Tetranuclear Precursors: A Top-Down Synthetic Approach to New Carbamates

Keywords: Zinc / Oligonuclear complexes / Coordination compounds / Carbamates / Amides / Guanidine

Ruthenium PNA Derivatives

Two new monomeric PNA derivatives incorporating a redox and photoactive Ru^{II} polypyridyl complex have been developed which have different length spacers between the complex and the PNA unit. Both derivatives are suitable for biosensor applications as they exhibit a reversible one-electron Ru^{II}-Ru^{III} electron-transfer process and luminescent properties typical of Ru^{II}-polypyridyl complexes.



N. Nickita, G. Gasser, A. M. Bond, L. Spiccia* 2179–2186

Synthesis, Spectroscopic Properties and Electrochemical Oxidation of Ru^{II}-Polypyridyl Complexes Attached to a Peptide Nucleic Acid Monomer Backbone

Keywords: Ruthenium / Peptide nucleic acids / Synthesis / Electrochemistry / Electronic and emission spectroscopy

Keywords: Heterometallic complexes / Cooperative effects / Bridging ligands / Metal-metal interactions

Heterobinuclear *s*-Indacene Rhodium Complexes: Synthesis and Characterization

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

If not otherwise indicated in the article, papers in issue 13 were published online on April 15, 2009

^{*} Author to whom correspondence should be addressed.