





















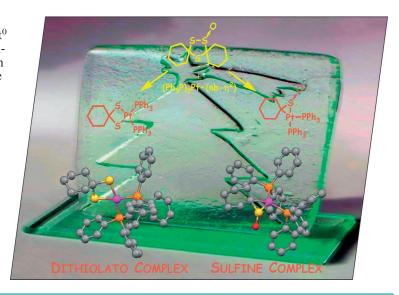


EUChemSoc

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 insertion of a Pt⁰ complex fragment into the S-S bond of a 1,2,4-trithiolane 1-S-oxide. Reactions of Pt⁰ complexes with small sulfur-containing heterocycles have become more and more popular in order to generate and stabilize reactive sulfur-containing species. The reaction presented leads to three- and four-membered platinacycles by ring contraction with expulsion of the reactive thiocarbonyl derivatives. The postulated mechanism for the fragmentation of 1,2,4-trithiolane 1-S-oxide, as well as the molecular structures, give a reasonable explanation for the observed selectivity. Details are discussed in the article by W. Weigand, G. Mloston et al. on p. 5627 ff. We thank Dr. Jaroslaw Romanski for decorating our Christmas tree (background) for this year and designing the cover picture.



SHORT COMMUNICATION

Silver Coordination Oligomer

Y. Wang, U. Englert* 5623-5625

The First Linear Coordination Oligomer Linked by 4,4'-Bipyridine

Keywords: Coordination polymers / Chain structures / Polycations / Oligomers / X-ray diffraction



Quite long, but no polymers yet! Coordination oligomers [Ag₄(bipy)₅]⁴⁺ and [Ag₂- $(bipy)_3$ ²⁺ were trapped in the same salt. A change in the counteranion was sufficient to induce polymerization.

FULL PAPERS

Pt Chemistry

H. Petzold, S. Bräutigam, H. Görls,

W. Weigand,* J. Romanski,

G. Mloston* 5627-5632



Oxidation of Spirocyclohexyl-1,2,4-trithiolane and Complexation Reaction with $[Pt(\eta^2-nb)(PPh_3)_2]$

Keywords: Insertion reactions / 1,2,4-Trithiolanes / Platinum / S ligands / Thioketone complexes

$$+ 2 \left[Pt(\eta^2-nb)(PPh_3)_2\right] \longrightarrow S Pt(PPh_3)_2 + Pt(PPh_3)_2$$

Insertion of a Pt⁰ complex fragment into the S-S bond of a 1,2,4-trithiolane as well as into that of its 1-S and 4-S-oxide is presented. Subsequent ring contraction with expulsion of reactive thiocarbonyl derivatives leads to three- and four-membered platinacycles that include thiolato and sulfenato structures. The postulated mechanism and the molecular structures give a reasonable explanation for the observed selectivity.

Heteroleptic Ruthenium(II) Complexes

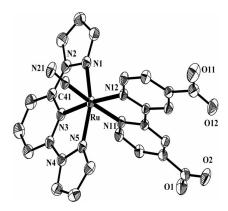
A. I. Philippopoulos,* A. Terzis,

C. P. Raptopoulou, V. J. Catalano,

P. Falaras 5633-5644

Synthesis, Characterization, and Sensitizing Properties of Heteroleptic RuII Complexes Based on 2,6-Bis(1-pyrazolyl)pyridine and 2,2'-Bipyridine-4,4'-dicarboxylic Acid Ligands

Keywords: 2,6-Bis(1-pyrazolyl)pyridine Heteroleptic RuII complexes / Dye-sensitized solar cells / Ruthenium / Protonation



The synthesis and characterization of a series of novel heteroleptic ruthenium(II) complexes bearing the 2,6-bis(1-pyrazolyl)pyridine (bpp) and 2,2'-bipyridine-4,4'-dicarboxylic acid (dcbpyH2) ligands, as well as their performance as dye sensitizers in nanocrystalline solar cells for the conversion of visible light into electricity, is presented. These complexes efficiently sensitize nanostructured TiO2 films and the resulting photoelectrodes incorporated in solid-state DSSCs show enhanced overall power conversion efficiency, which strongly depends on their molecular structure and their degree of protonation.

(Guanidine)zinc Catalysts

[Bis(guanidine)]zinc Complexes and Their Application in Lactide Polymerisation

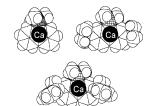
Keywords: Guanidine / D,L-Lactide / N ligands / Ring-opening polymerization / Zinc

$$\begin{array}{c|c}
\hline
\frac{1}{2}n & \xrightarrow{\text{cat.}} & \text{H} & \xrightarrow{\text{o}} & \text{H} \\
\hline
D,L-lactide & polylactide}$$

The first examples of aliphatic [bis(guanidine)]zinc complexes [Zn(DMEG₂e)Cl₂], $[Zn(DMEG_2e)(CH_3COO)_2]$ and $(DMEG_2e)_2](CF_3SO_3)_2$ containing N^1,N^2 bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine have been synthesised and fully characterised. These compounds are able to catalyse the polymerisation of D,Llactide. PLAs with molecular weights (M_w) up to 59000 g/mol could be obtained.



Increase of the steric bulk in the 2- and 7-positions of the fluorenyl ligands in several new organocalcium initiators led to a considerable improvement in the stereoselectivity for styrene polymerization. Syntheses, structures and polymerization results are discussed.



Ca-Mediated Styrene Polymerization

D. F.-J. Piesik, K. Häbe, S. Harder* 5652-5661

Ca-Mediated Styrene Polymerization: Tacticity Control by Ligand Design

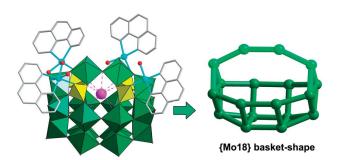
Keywords: Alkaline-earth metals / Calcium / Polymerization catalysis / Fluorene ligands / Polystyrene

Modified Polyoxoanions

K. Yu, Y.-G. Li,* B.-B. Zhou,* Z.-H. Su, Z.-F. Zhao, Y.-N. Zhang 5662-5669

A Basket-Like $[Sr \subset P_6Mo^V_4Mo^{VI}_{14}O_{73}]^{10-}$ Polyoxoanion Modified with $\{Cu(phen)-(H_2O)_x\}$ (x=1-3) Fragments: Synthesis, Structure, Magnetic, and Electrochemical Properties

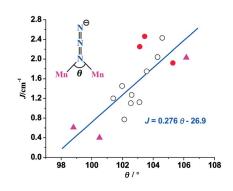
Keywords: Polyoxometalate / Organic—inorganic hybrid / Basket-like / Electrocatalysis



A basket-like mixed-valent polyoxoanion $[Sr \subset P_6Mo_4^VMo_{14}^{VI}O_{73}]^{10-}$ modified with $\{Cu(phen)(H_2O)_x\}$ (x=1-3) fragments was hydrothermally synthesized and struc-

turally characterized. The compound shows good electrocatalytic activity to reduce hydrogen peroxide.

Three end-on azido dinuclear $Mn^{\rm II}$ complexes based on tripyridyl ligands show intramolecular ferromagnetic superexchange. Clearer magnetostructural correlation for end-on azido-bridged $Mn^{\rm II}$ complexes was obtained.

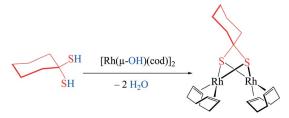


Magnetostructural Correlation

M.-M. Yu, Z.-H. Ni, C.-C. Zhao, A.-L. Cui, H.-Z. Kou* 5670-5676

Synthesis and Magnetic Study of $\mu_{1,1}$ -Azido-Bridged Dinuclear Manganese(II) Complexes Based on Tripyridyl Ligands

Keywords: Manganese / Dinuclear complexes / Crystal structures / Magnetic properties / Azido bridge



The gem-dithiolato-bridged dinuclear compound $[Rh_2(\mu-S_2Chxn)(cod)_2]$ was obtained in a straightforward manner from 1,1-dimercaptocyclohexane and $[Rh(\mu-OH)(cod)]_2$. This compound is an efficient catalyst precursor in the presence of P-do-

nor ligands for the hydroformylation of oct-1-ene under mild conditions. The trans-dinuclear species [Rh₂(μ -S₂Chxn)(CO)₂-(PPh₃)₂] was isolated from the catalytic solutions

Dimetallic Hydroformylation Catalysts

Novel *gem*-Dithiolato-Bridged Rhodium Hydroformylation Catalysts: Bridging the Gap in Dinuclear Rhodium Thiolate Chemistry

Keywords: Homogeneous catalysis / Hydroformylation / Dinuclear complexes / *gem*-Dithiolato ligands / Rhodium

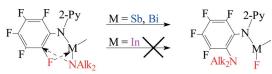
CONTENTS

Fluoride/Amide Exchange

P. L. Shutov, S. S. Karlov,* K. Harms, M. V. Zabalov, J. Sundermeyer,* J. Lorberth, G. S. Zaitseva 5684-5692

ortho-Directed Metathetical Fluoride/ Amide Exchange in (Pentafluorophenyl)amides

Keywords: Fluorinated ligands / Amides / Nucleophilic substitution / Density functional calculations



Metathetical fluoride/amide exchange has been examined in pentafluoro(2-pyridyl)-anilides of Sb, Bi, and In by synthetic and X-ray studies and density functional calculations. The tendency for this rearrange-

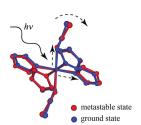
ment increases with an increase of the covalent radius and decreases with an increase of the coordination number of the central atom.

The Spin-Crossover Metastable State

V. Legrand, S. Pillet, C. Carbonera, M. Souhassou, J.-F. Létard, P. Guionneau, C. Lecomte* 5693-5706

Optical, Magnetic and Structural Properties of the Spin-Crossover Complex [Fe(btr)(NCS)]·HO in the Light-Induced and Thermally Quenched Metastable States

Keywords: Iron(II) / Photoswitching / Structural analysis / Photomagnetism / Spin crossover



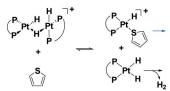
The light-induced and thermally induced structural reorganization of the spin-cross-over complex [Fe(btr)₂(NCS)₂]·H₂O are discussed together with photomagnetic and optical reflectivity results.

Hydrodesulfurization (HDS)



C-S Bond Activation and Partial Hydrogenation of Thiophene by a Dinuclear Trihydride Platinum Complex

Keywords: C-S activation / Desulfurization / Thiophene / Hydride ligands / Platinum / Reaction mechanisms



Hydrodesulfurization reactions with transition metals: the reaction of [(dppp)₂Pt₂H₃]-ClO₄ with thiophene achieves activation of the C-S bond. The corresponding mechanism has been interpreted on the basis of



DFT calculations. The reactivity of the complexes obtained in this reaction has led to the characterization of new platinum species.

Zeolite-Y-Encapsulated Complexes

M. R. Maurya,* B. Singh, P. Adão, F. Avecilla, J. Costa Pessoa ... 5720-5734

Zeolite-Encapsulated Copper(II) Complexes of Pyridoxal-Based Tetradentate Ligands for the Oxidation of Styrene, Cyclohexene and Methyl Phenyl Sulfide

Keywords: Zeolites / Copper(II) complexes / Heterogeneous catalysis / Oxidation reactions

$$HO \xrightarrow{N=CH_3} H_3C = N$$

$$= N \quad N = O$$

$$= N \quad N = O$$

$$= O$$

[Cu(pydx-en)] (1) and [Cu(pydx-1,3-pn)-(MeOH)] (2) have been encapsulated in the supercages of zeolite-Y and used as

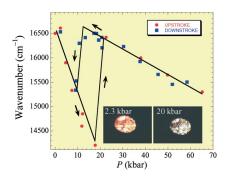
$$HO \xrightarrow{N=CH_3} H_3C \\ N=O_{Cu} O \xrightarrow{N} OH \\ CH_3 \\ [Cu(pydx-1,3-pn)(MeOH)] (2)$$

catalysts for the oxidation of styrene, cyclohexene and methyl phenyl sulfide.



Phase Transition in Pt(bpy)Cl₂

Luminescence of the red form of Pt(bpy)-Cl₂ has been measured as a function of hydrostatic pressure. The band maximum is shifted by -147 cm⁻¹ kbar⁻¹. Strong discontinuities in the optical properties at 17.7 kbar were interpreted in terms of a crystallographic phase transition from the red to a denser yellow form of Pt(bpy)Cl₂. First-principles calculations based on density functional theory were used to study this transformation.

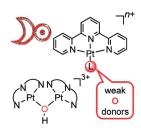


Red-to-Yellow Pressure-Induced Phase Transition in Pt(bpy)Cl: Spectroscopic Study Supported by DFT Calculations

Keywords: Phase transition / High-pressure chemistry / DFT calculations / Platinum(II) / Metal-metal interactions

Acidolysis of the complexes [Pt(CH₃)(terpy)]Y (Y = PF₆, CH₃SO₃, CF₃SO₃, ClO₄, BF₄; terpy = 2,2':6',2''-terpyridine) with CH₃SO₃ affords the corresponding methanesulfonato derivatives [Pt(OSO₂CH₃)-(terpy)]Y. A mixture of the methanesulfonato and nitrato complexes is obtained when Y = NO₃, whereas the reaction of [Pt(CH₃)(terpy)](CF₃SO₃) with triflic acid gives the aqua species [Pt(terpy)(H₂O)]-(SO₃CF₃)₂. The new hydroxido-bridged dimers [Pt₂(μ -OH)(terpy)₂](X) [X = (ClO₄)₃, (PF₆)₂(CF₃SO₃)] are isolated and their X-

ray crystal structures determined.



Platinum(II) Complexes with O-Donors

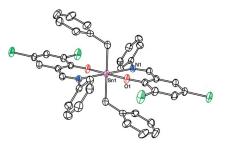
G. Annibale,* P. Bergamini, V. Bertolasi, M. Bortoluzzi, M. Cattabriga, B. Pitteri 5743-5751

The Relative Coordinating Ability of Some Weak O-Donor Anions and Water Towards the $[Pt(terpy)]^{2+}$ (terpy = 2,2':6',2''-terpyridine) Center - X-ray Crystal Structures of $[Pt(terpy)(H_2O)](CF_3SO_3)_2$ and $[Pt_2(\mu-OH)(terpy)_2](PF_6)_2(CF_3SO_3)$

Keywords: Platinum / Bridging ligands / N ligands / O ligands

Octahedral Organotin Compounds

The compounds L_2SnR_2 [L = N-(3,5-dichlorosalicylidene)aniline; R = CH₃ (1), R = CH₂Ph (2)] and L'₂SnR₂ [3: L' = N-(3-tert-butylsalicylidene)aniline, R = CH₂Ph] have been synthesized and characterized. The X-ray crystal structure of compound 2 showed an octahedral geometry with the alkyl groups in a trans relationship. Cationic species generated therefrom promoted ethylene oligomerization under mild conditions.



L. Annunziata, D. Pappalardo,* C. Tedesco, C. Pellecchia 5752-5759

Octahedral Alkylbis(phenoxy-imine)tin(IV) Complexes: Effect of Substituents on the Geometry of the Complexes and Their Reactivity Toward Ionizing Species and Ethylene

Keywords: Tin / N,O ligands / Cations / Ethylene / Oligomerization

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The editorial staff and the publishers thank all readers, authors, referees, and advertisers for their interest and support over the past year and wish them all a happy new year.

If not otherwise indicated in the article, papers in issue 35 were published online on November 28, 2007