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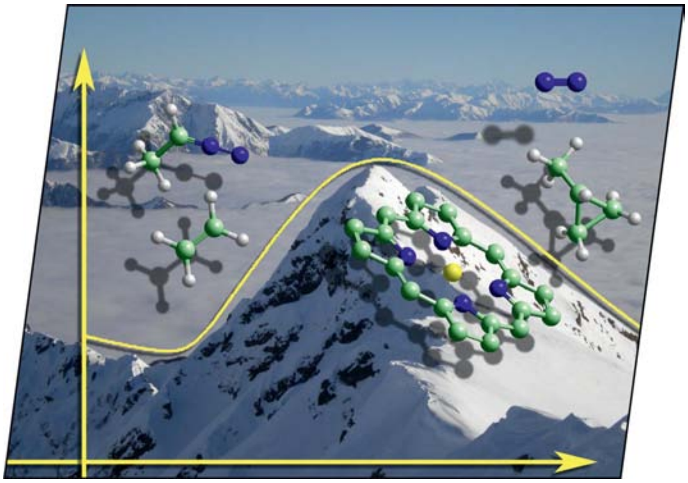
COVER PICTURE

The cover picture shows the Monte Eyehorn (2131 m), Italy. The cyclopropanation of olefins mediated by porphyrin complexes of group IX metals has been reviewed, and several methodologies affording cyclopropanes with good diastereo- and enantioselectivity have been described. The efficiency of porphyrin complexes to reduce the activation barrier (as symbolically represented in the photo) allows the synthesis of a wide class of compounds bearing a large number of different substituents on the cyclopropane ring. An overview of the mechanistic aspects of these reactions, explored over the years to improve the performance of porphyrin-catalysed cyclopropanations, has also been provided. Details are presented in the Microreview by E. Gallo et al. on p. 5071ff.



MICROREVIEW

Metal Porphyrin Catalysts

D. Intrieri, A. Caselli,
E. Gallo* 5071–5081

Cyclopropanation Reactions Mediated by Group 9 Metal Porphyrin Complexes

Keywords: Cyclopropanation / Diazo compounds / Porphyrins / Cobalt / Rhodium / Iridium

The reaction of diazo derivatives with olefins represents a valid tool to synthesise cyclopropanes. Rhodium and cobalt porphyrin complexes have been extensively employed as catalysts, and in several cases outstanding stereocontrol has been achieved. Recent advances in understanding the reaction mechanism will be crucial to plan new and more efficient catalytic systems.

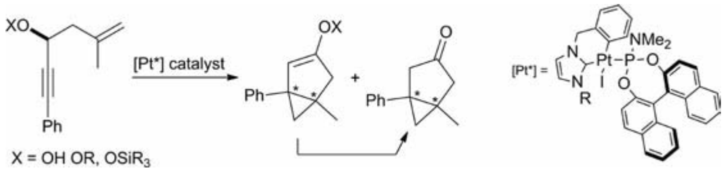
SHORT COMMUNICATION

Enantioselective Cycloisomerizations

H. Jullien, D. Brissy, P. Retailleau,
A. Marinetti* 5083–5086

Enantioselective Cycloisomerization of 1,5-Enynes Promoted by Cyclometalated NHC–Pt^{II}–Monophos Catalysts

Keywords: Platinum / Isomerization / Enantioselectivity



A Monophos–Pt complex has been used to catalyze the enantioselective cycloisomerization of 1,5-enynes displaying a non-migrating oxygen function at the propargylic carbon. Significant matching–mismatching effects have been highlighted between the chiral catalyst and chiral substrates with opposite configurations at the stereogenic carbon.

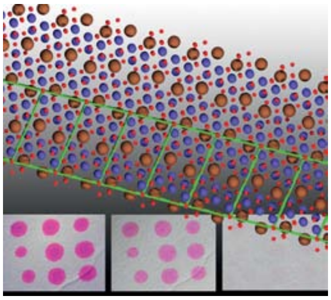
FULL PAPERS

Titanate Calcination

M. B. Cortie,* L. Xiao, L. Erdei,
C. S. Kealley, A. R. Dowd, J. A. Kimpton,
A. M. McDonagh 5087–5095

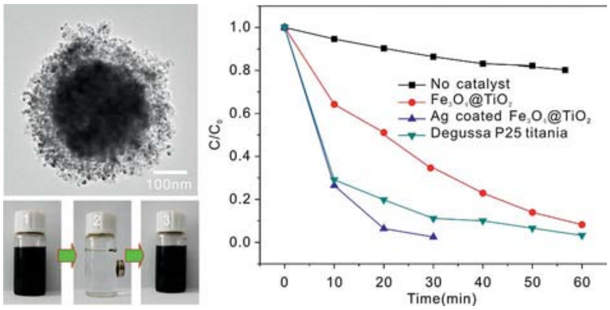
Thermal Stability of $(K_xNa_yH_{1-x-y})_2Ti_6O_{13}$ Nanofibers

Keywords: Nanostructures / Nanofibres / Layered compounds / High-temperature chemistry / Titanates / Solid-state reactions



The thermal stability of hexatitanate nanowires produced by hydrothermal digestion of TiO$_2$ in concentrated KOH solution followed by ion exchange depends acutely on their composition. Depending on the mix of cations present, behavior can range from rapid conversion to anatase, retarded conversion to anatase or recrystallization of a mixed-cation titanate.

Recyclable Photocatalyst



Ag-coated Fe_3O_4@TiO_2 microspheres with a very good core/shell structure, show excellent magnetic properties at room temperature. The formation of a $Ag-TiO_2$ heterojunction results in good photodegradation properties of the products. The results show that the as-prepared composites can be used as convenient and recyclable photocatalysts.

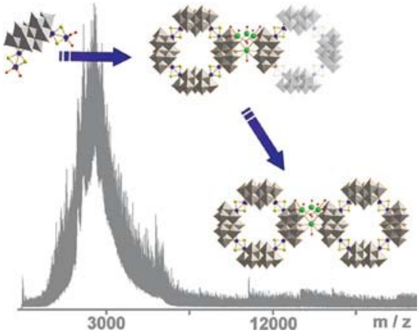
Y. Zhang, X. Yu, Y. Jia, Z. Jin, J. Liu,* X. Huang* 5096–5104

A Facile Approach for the Synthesis of Ag-Coated Fe_3O_4@TiO_2 Core/Shell Microspheres as Highly Efficient and Recyclable Photocatalysts

Keywords: Nanoparticles / Silver / Iron / Titanium / Magnetic properties / Photocatalyst / Organic pollutants

Oxothiometalates

A direct synthesis giving improved yields as well as detailed solution and solid-state characterisation of the oxothiometalate $\{Mo_{40}\}$ wheel is reported. High resolution ESI-MS studies allowed the direct observation of the discrete wheel and its assembly stages towards the 1D chain formation.

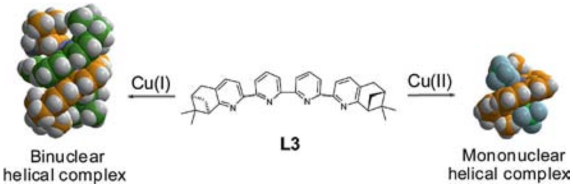


H. N. Miras,* H. Y. Zang, D.-L. Long, L. Cronin* 5105–5111

Direct Synthesis and Mass Spectroscopic Observation of the $\{M_{40}\}$ Polyoxothiometalate Wheel

Keywords: Molybdenum / Sulfur / Self-assembly / Oxothiometalates

Helical Metal Complexes



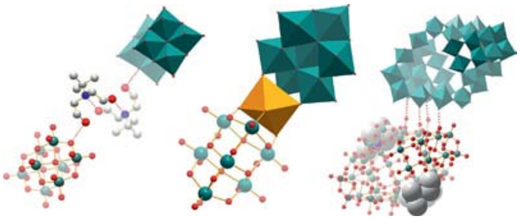
Bi- and mononuclear chiral helical copper–quaterpyridine complexes were prepared by treating chiral ligands like **L3** with Cu^{I} and Cu^{II} precursors. They were studied by ESI-MS, elemental analysis, and CD spectroscopy. Solution-NMR studies of the dinuclear Cu^{I} complexes show that each sample consists of two diastereomers with moderate to high diastereoselectivity (52–99%).

H.-L. Yeung, K.-C. Sham, W.-Y. Wong, C.-Y. Wong,* H.-L. Kwong* 5112–5124

Helical Complexes of Chiral Quaterpyridines – Mononuclear Cu^{II} and Dinuclear Cu^{I} Complexes

Keywords: Copper / Helical structures / Quaterpyridine ligands / Circular dichroism

Hybrid Metal Oxides



The ability of amphiphilic cations to control the assembly of hybrid organic-inorganic frameworks through hydrophobic interactions was evaluated using a polyoxometalate-based model system. It is shown that the formation of hydrophobic regions seems to be dependent on the size of the inorganic building block used. The structural analysis is further substantiated by theoretical Hirshfeld analysis.

K. Heussner, M. Grabau, J. Forster, C. Streb* 5125–5131

Can Hydrophobic Interactions Influence Supramolecular Aggregation in Self-Assembled Organic–Inorganic Hybrid Structures?

Keywords: Supramolecular chemistry / Aggregation / Crystal engineering / Polyoxometalates / Organic-inorganic hybrid composites / Amphiphiles / Hirshfeld analysis

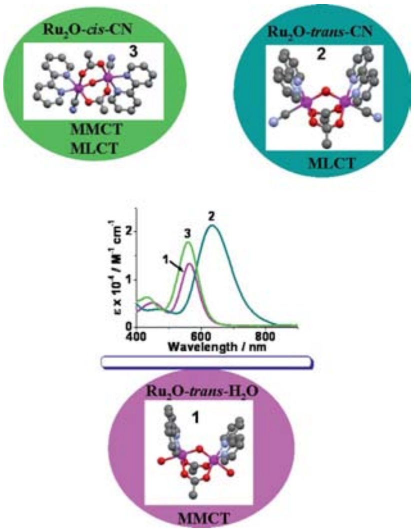
CONTENTS

Diruthenium Complexes

H.-X. Zhang,* K. Tsuge, Y. Sasaki,*
M. Osawa, M. Abe 5132–5143

Cyano- and Aqua-Coordinated Diruthenium(III) Complexes with Oxo-Bis-(acetato) Bridge: Preparation and Steric and Electronic Structures

Keywords: Ruthenium / Bridging ligands / Cyano complexes / Electronic structure / Charge transfer



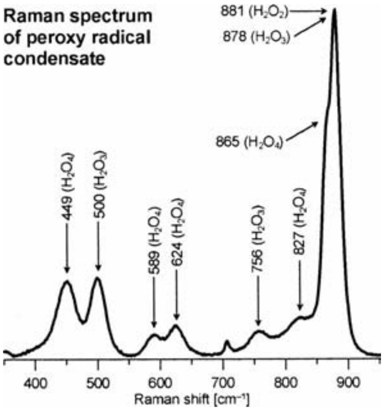
Two cyano- and one aqua-coordinated diruthenium(III) complexes with an oxo-bis-(acetato) bridge have been isolated. The cyano ligand has a strong effect on the properties of complexes. MO calculations revealed that visible absorption bands of complexes without a cyano ligand are ascribed to the transitions within Ru(dπ)–μ-O(pπ) molecular orbitals, whereas those of cyano complexes are different.

Hydrogen Polyoxides

A. V. Levanov,* D. V. Sakharov,
A. V. Dashkova, E. E. Antipenko,
V. V. Lunin 5144–5150

Synthesis of Hydrogen Polyoxides H_2O_4 and H_2O_3 and Their Characterization by Raman Spectroscopy

Keywords: Hydrogen tetroxide / Hydrogen trioxide / Raman spectroscopy / Oxygen / Radical reactions



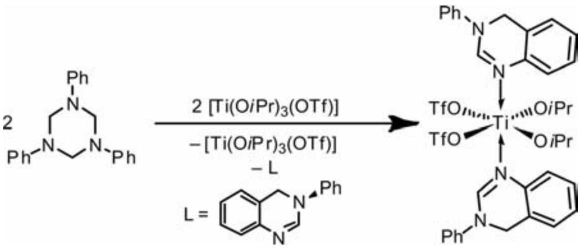
Peroxy radical condensates have been synthesized from O_2/H_2 gas mixtures dissociated by a microwave discharge (pressure ca. 1 Torr). They consist of hydrogen tetroxide (H_2O_4, up to 20 mol-%) and hydrogen trioxide (H_2O_3, up to 30 mol-%), hydrogen peroxide, and water. The polyoxides have been characterized by vibrational Raman spectroscopy of their oxygen frameworks.

Titanium Alkoxides

M. G. Davidson,
A. L. Johnson* 5151–5159

Synthesis, Isolation and Structural Characterisation of Alkoxytitanium Triflate Complexes

Keywords: Titanium / Alkoxides / Triflates / Lewis acids



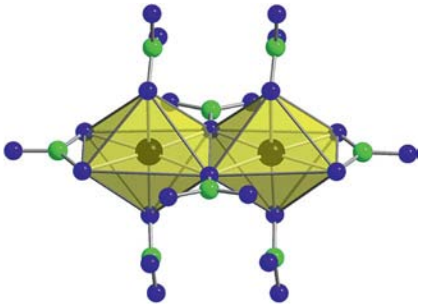
New alkoxytitanium triflate complexes containing a range of facially coordinating N_3 ligands were prepared and structurally characterised. Reaction of [Ti(O*i*Pr$_3$)OTf] with 1,3,5-triphenyl-1,3,5-triazacyclohexane results in the catalytic activation of the triazacyclohexane ligands and isolation of a new titanium complex [{L′}$_2$Ti(O*i*Pr)$_2$-(OTf)$_2$] (L′ = 3-phenyl-3,4-dihydroquinazoline).

Metal Oxidation

S. Gagelmann, K. Rieß,
M. S. Wickleder* 5160–5166

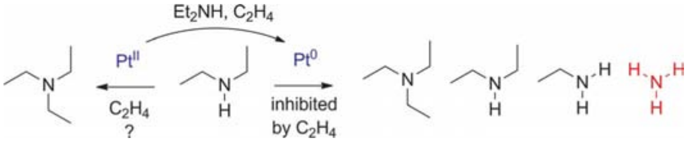
Metal Oxidation with N_2O_5: The Nitrosylium Nitrates (NO)Cu(NO$_3$)$_3$, (NO)$_2$[Zn-(NO$_3$)$_4$] and (NO)$_6$[Ni$_4$(NO$_3$)$_{12}$](NO$_3$)$_2$·(HNO$_3$)

Keywords: Nitrogen oxides / Structure elucidation / X-ray diffraction / Thermal behavior



The oxidation of copper, zinc and nickel with N_2O_5 leads to complex nitrates containing NO^+ cations and nitrate groups in different coordination modes. The thermal decomposition of the copper nitrate yields a mixture of Cu and Cu_2O, whereas (NO)$_2$[Zn(NO$_3$)$_4$] forms ZnO upon heating.

Hydroamination vs. Transalkylation



Pt^{II} salts and Pt^0 promote different reactions in amine/ethylene combinations. Pt^{II} is a catalyst for hydroamination, whereas Pt^0 promotes transalkylation, which is inhibited by the olefin.

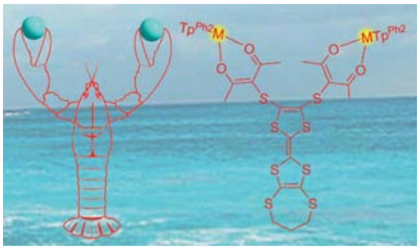
P. A. Dub, A. Béthegnies, R. Poli* .... **5167−5172**

Reactions of Diethylamine and Ethylene Catalyzed by Pt^{II} or Pt^0 − Transalkylation vs. Hydroamination

Keywords: Homogeneous catalysis / Aqueous catalysis / Platinum / Hydroamination / Amines / Transalkylation / Density functional calculations

Multifunctional Materials

A series of tetrathiafulvalenyl-acetylacetonate ligands has been prepared, and their coordination capability has been confirmed by the formation of mono- and dinuclear Co/Ni complexes. Theoretical calculations have determined the nature of the electron absorption phenomena. The results indicate that the acetylacetonate bridge is a useful linkage for the synthesis of new multifunctional materials.

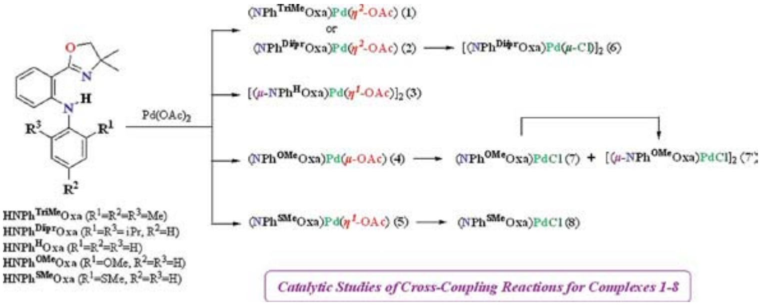


J. Xiong, G.-N. Li, L. Sun, Y.-Z. Li, J.-L. Zuo,* X.-Z. You .... **5173−5181**

Mono- and Dinuclear Co/Ni Complexes Bearing Redox-Active Tetrathiafulvalene-acetylacetonate Ligands − Syntheses, Crystal Structures, and Properties

Keywords: Cobalt / Nickel / Ligand design / Charge transfer / Polynuclear complexes / Density functional calculations

New Palladium Catalysts



The anilido-oxazolinate palladium complexes **1**−**8** have been prepared and their versatile bonding modes demonstrated by X-ray crystallography. The bonding mode of **3** and **7′**, which comprise bridging N$_{anilido}$ atoms in a chelating ligand, is rare. These new palladium complexes have been applied to cross-coupling reactions.

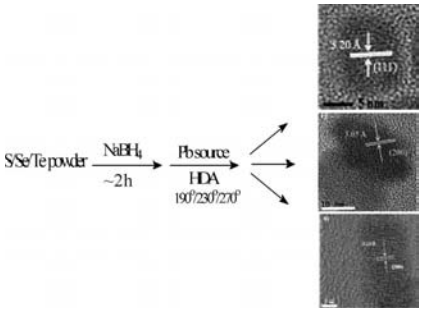
K.-F. Peng, C.-T. Chen* .... **5182−5195**

Synthesis, Structural Studies, and Catalytic Application of Palladium Complexes Containing Anilido-Oxazolinate Ligands

Keywords: Palladium / Bidentate ligands / N ligands / Cross-coupling

Chalcogenide Nanocrystals

Nanoparticles of lead sulfide, selenide and telluride were synthesized by the reduction of sulfur, selenium or tellurium powder with sodium borohydride (NaBH$_4$) to produce sulfide, selenide or telluride ions, followed by their reaction with a lead salt.



K. Ramasamy, A. O. Nejo, N. Ziqubu, P. V. S. R. Rajasekhar, A. A. Nejo, N. Revaprasadu,* P. O'Brien .... **5196−5201**

A New Route to Lead Chalcogenide Nanocrystals

Keywords: Lead / Chalcogens / Nanostructures / Electron microscopy

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* Author to whom correspondence should be addressed.

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