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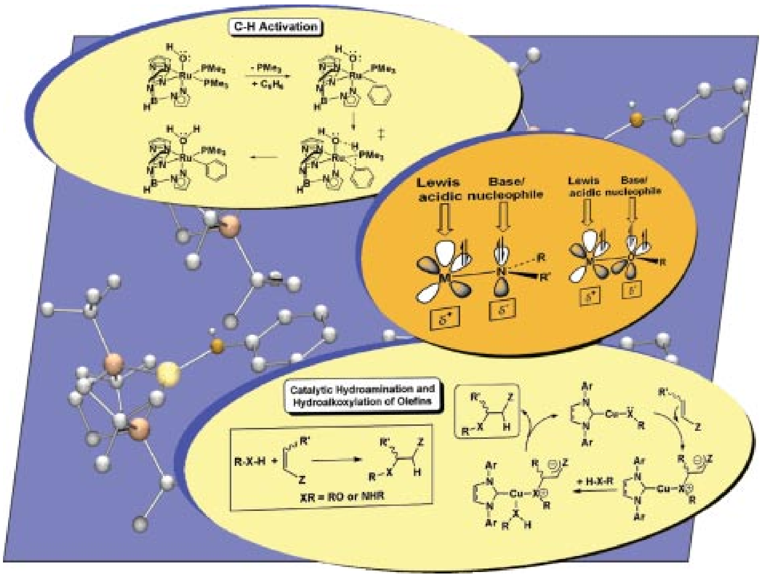
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the disruption of amido- and alkoxo-to-metal π-donation because of a filled dπ manifold, which occurs for metal centers in low oxidation states and which renders the anionic amido, alkoxo and related ligands highly reactive. The low oxidation states decrease the predilection toward metal-center reduction and, as a result, tend to promote "even-electron" chemistry over odd-electron radical chemistry that is based on net single-electron reduction of the metal. For Ru^{II} and Cu^{I} complexes, evidence for the enhanced reactivity of the heteroatomic ligands is derived from acid/base reactions as well as from nucleophilic additions. The combination of a Lewis acid metal center and a basic/nucleophilic heteroatomic ligand (amido, hydroxo, alkoxo, etc.) can be exploited for the activation of substrates that possess polar and nonpolar bonds, for example for metal-mediated C−H activation and for catalytic hydroamination and hydroalkoxylation of activated olefins. Details are presented in the Microreview by T. B. Gunnoe on p. 1185 ff.



CONTENTS

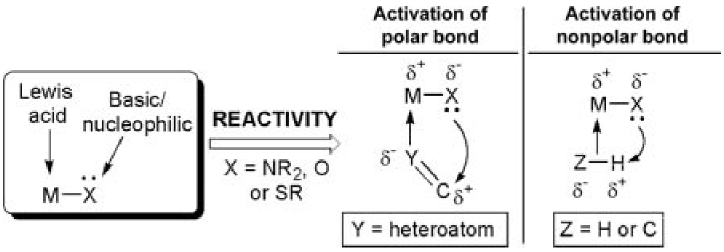
MICROREVIEW

Organometallic Chemistry

T. B. Gunnoe* 1185–1203

Reactivity of Ruthenium(II) and Copper(I) Complexes that Possess Anionic Heteroatomic Ligands: Synthetic Exploitation of Nucleophilicity and Basicity of Amido, Hydroxo, Alkoxo, and Aryloxo Ligands for the Activation of Substrates that Possess Polar Bonds as well as Nonpolar C–H and H–H Bonds

Keywords: Nondative heteroatomic ligands / Ruthenium / Copper / C–H Activation



The coordination of amido, sulfido alkoxo, aryloxo, and hydroxo ligands to late transition-metal complexes in low oxidation states can disrupt ligand-to-metal π bonding. As a result, anionic and heteroatomic ligands coordinated to metals with high d-electron counts often exhibit highly basic and nucleophilic reactivity. The microreview summarizes the preparation, characterization, and reactivity of a series of Ru and Cu complexes with these and related ligands.

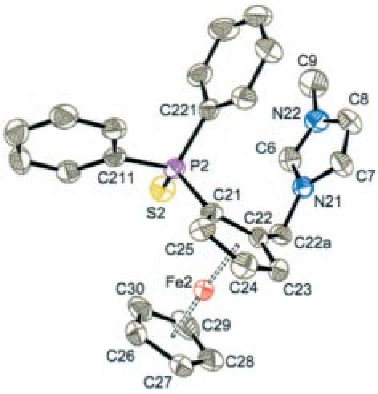
SHORT COMMUNICATIONS

Diaminocarbene Ligands

A. Labande,* J.-C. Daran, E. Manoury, R. Poli* 1205–1209

New (1-Phosphanylferrocen-1′- and -2-yl)-methyl-Linked Diaminocarbene Ligands: Synthesis and Rhodium(I) Complexes

Keywords: Carbene ligands / Phosphane ligands / Ferrocenes / Rhodium



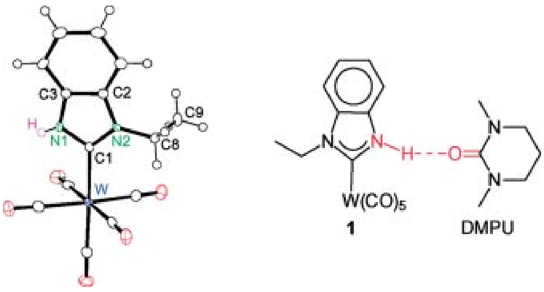
New, bifunctional (1-phosphanylferrocen-1′- and -2-yl)methyl-linked NHC ligands have been accessed by a general and simple method from the corresponding [1-(thiophosphanyl)ferrocen-1′- and -2-yl]methanols and used to prepare rhodium(I) complexes.

NH,NR-Stabilized NHC Ligands

N. Meier, F. E. Hahn,* T. Pape, C. Siering, S. R. Waldvogel* 1210–1214

Molecular Recognition Utilizing Complexes with NH,NR-Stabilized Carbene Ligands

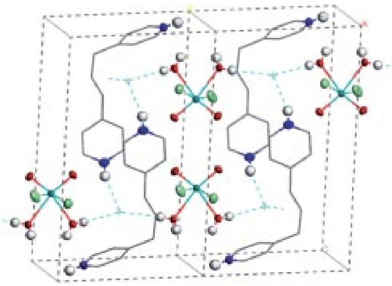
Keywords: Carbene ligands / Supramolecular chemistry / Hydrogen bonds / Homogeneous catalysis / N-Heterocyclic carbenes



The NH group in tungsten complex **1** with an NH,NR-stabilized N-heterocyclic carbene ligand can act as a recognition unit by forming hydrogen bonds to carbonyl compounds.

Hydrogen-Bond Network

A new hybrid inorganic−organic Mo^{VI} polymer with a two-dimensional layer structure has been synthesized and crystallographically characterized. This complex is an efficient catalyst, with H_2O_2 as the oxygen-source oxidant and $NaHCO_3$ as the cocatalyst, in the epoxidation of olefinic compounds under ambient conditions.



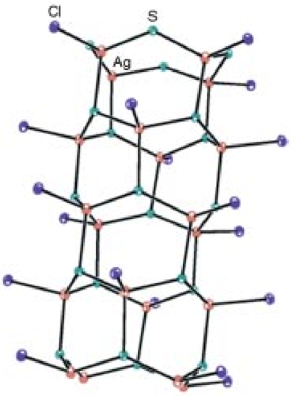
Y. Luan, G. Wang,* R. L. Luck, M. Yang .... 1215−1218

A Two-Dimensional, Hydrogen-Bond-Cross-Linked Molybdenum(VI) Network Polymer with Catalytic Activity

Keywords: Hydrogen bonds / Crystal engineering / Hydrogen peroxide / Epoxidation / Molybdenum

Nanotubes

Silver(I) chloride reacts with 2-mercapto-3,4,5,6-tetrahydropyrimidine ($StpmH_2$, $C_4H_8N_2S$) in DMSO with excess triethylamine to give a complex of formula $\{[Ag_4Cl_4(\mu_3\text{-}StpmH_2)_4]_n\}$ (**1**). The structure consists of octagonal Ag_4S_4 cores where μ_3-S bonding interactions lead to an infinite nanotube assembly which exhibits quasi-aromaticity.

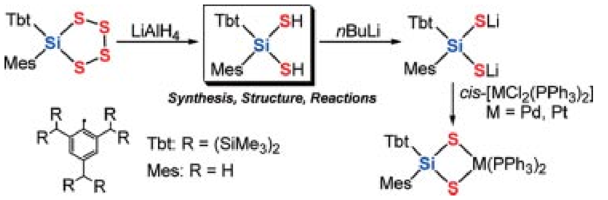


S. Zartilas, N. Kourkoumelis, S. K. Hadjikakou,* N. Hadjiliadis,* P. Zachariadis, M. Kubicki, A. Yu. Denisov, I. S. Butler .... 1219−1224

A New Silver(I) Aggregate Having an Octagonal Ag_4S_4 Core Where μ_3-S Bonding Interactions Lead to a Nanotube Assembly that Exhibits Quasiaromaticity

Keywords: Bioinorganic chemistry / Silver / Aromaticity / Nanotubes

Silanedithiol



An overcrowded silanedithiol was synthesized as an air- and moisture-stable crystalline compound by the reaction of the corresponding tetrathiasilolane with $LiAlH_4$. The reaction of dilithium silanedithiolate, which was generated by the reaction of silanedithiol with *n*-butyllithium, with *cis*-$[MCl_2(PPh_3)_2]$ (M = Pd, Pt) afforded the corresponding silanedithiolato complexes quantitatively.

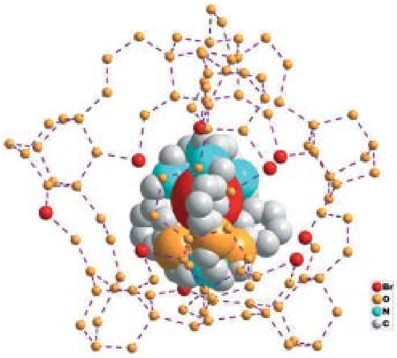
T. Tanabe, N. Takeda, N. Tokitoh* .... 1225−1228

First Structural Characterization of Silanedithiol and Its Application toward the Synthesis of Silanedithiolato Complexes

Keywords: Silanedithiol / Silanedithiolato complexes / Silaneselenol / Group 10 transition metal complexes / X-ray crystallography

Water Clusters

Adamantanoid water clusters H-bonded to bromide ions and other water molecules form a cage-like structure. Bromide-encapsulated aza cryptands reside within this cage to form a host-within-a-host-like structure. This adamantanoid water decamer is remarkably similar to that of cubic ice (I_c).



M. C. Das, P. K. Bharadwaj* .... 1229−1232

Molecular Ice with Hybrid Water−Bromide Network around a Cryptand with a Bromide Ion Included in the Cavity to Form a Host-within-a-Host-Like Structure

Keywords: Anion binding / Cryptands / Hydrogen bonds / Water chemistry / X-ray diffraction

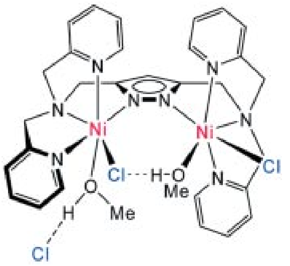
FULL PAPERS

Hydrogen Bonding

F.-M. Nie, G. Leibeling, S. Demeshko, S. Dechert, F. Meyer* 1233–1239

Intra- and Intermolecular H···Cl–Ni Bonding Patterns in a Series of Highly Preorganized Dinuclear Nickel(II) Complexes

Keywords: Nickel / Dimetallic complexes / Hydrogen bonds / Pyrazolate ligands / Magnetic properties



Various Cl···H–O hydrogen-bonding motifs are identified in a series of pyrazolato-based dinickel complexes, where either the H-donor (MeOH or H_2O) or the H-acceptor (chlorido) or both are bound to a nickel ion.

Heterodimetallic Complexes

Z.-H. Ni, L. Zheng, L.-F. Zhang, A.-L. Cui, W.-W. Ni, C.-C. Zhao, H.-Z. Kou* 1240–1250

Cyanido-Bridged Dimetallic Complexes Derived from Manganese(III) Schiff Bases and Pentacyanidonitrosylchromate(I): Synthesis, Crystal Structure and Magnetic Properties

Keywords: Cyanide ligands / Bridging ligands / Magnetic properties / Manganese / Schiff-base ligands

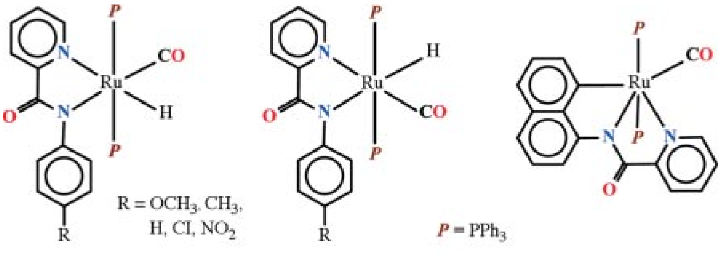
Four types of cyanido-bridged complexes derived from the $[Cr(CN)_5(NO)]^{3-}$ anion and Mn^{III} Schiff-base cations have been synthesized with trinuclear, 1D chain or 2D layered molecular structures. Antiferromagnetic $Mn^{III}-Cr^{I}$ coupling has been exclusively observed in these complexes.

Ruthenium Complexes

S. Nag, R. J. Butcher, S. Bhattacharya* 1251–1260

N-(Aryl)picolinamide Complexes of Ruthenium: Usual Coordination and Strategic Cyclometalation

Keywords: Picolinamide ligands / Ruthenium complexes / Cyclometalation



1-R **2-R** **3**

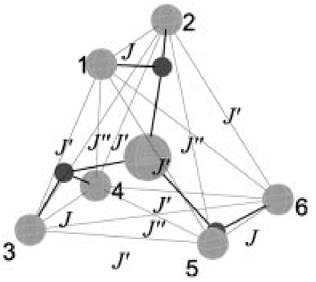
Reaction of $[Ru(PPh_3)_2(CO)_2Cl_2]$ with five *N*-(4-*R*-phenyl)picolinamides in the presence of a base affords two geometrical isomers (**1-R** and **2-R**) on N–H activation. A similar reaction with *N*-(naphthyl)picolinamide affords complex **3** on additional C–H activation.

Single-Molecule Studies

Y.-Q. Zhang,* C.-L. Luo 1261–1267

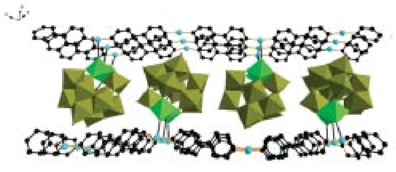
A Theoretical Study of the Nearest Cu···Cu Antiferromagnetic Exchange Coupling Interactions in $[LaCu_6]$ and $[YCu_6]$

Keywords: Magnetic properties / Density functional calculations / Broken symmetry / Single-molecule studies

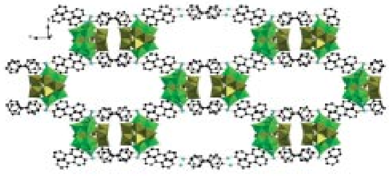


Calculation of the exchange coupling interactions between the nearest Cu^{II} centers in complexes $[LaCu_6]$ and $[YCu_6]$ show that the Cu···Cu antiferromagnetic interactions increase with a decrease of the ionic radius of the central La^{III} and Y^{III} and the stronger antiferromagnetic interactions between the nearest Cu^{II} centers in $[LaCu_6]$ than in $[YCu_6]$ are not due to the central La^{III} but the structure.

Modified Keggin Polyoxometalates



1



2

Fully oxidized Keggin $SiMo_{12}$ and SiW_{12} anions as polydentate pendant ligands covalently bonded to a multitrack Cu(bipy) chain(s) through linearly arrayed terminal and bridging oxygen atoms of the M_3O_{13} triad(s) are reported for the first time. Compound **1** has a tri-chain 1D "zipper" structure, and **2** a di-chain 2D net-texture structure.

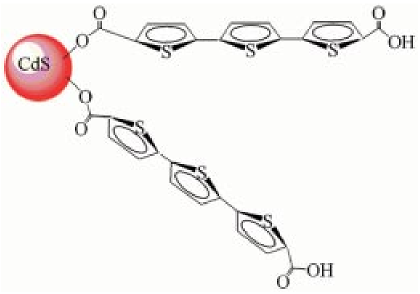
J. Sha, J. Peng,* H. Liu, J. Chen, B. Dong, A. Tian, Z. Su .... **1268−1274**

Keggin POMs Modified by Bonding to Multitrack Cu(bipy) Chains through Linearly Arrayed Terminal and Bridging Oxygen Atoms of the M_3O_{13} Triad

Keywords: Polyoxometalates / N ligands / Copper / Organic−inorganic hybrids

Organic−Inorganic Nanoparticles

To improve the electronic communication between nanocrystal semiconductors and conjugated molecules, we have prepared CdS-bound oligothiophenes. In such a design, the two components are in intimate contact and electron transfer is not altered by the presence of insulating surfactants.



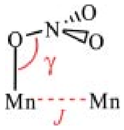
T. Antoun, R. Brayner, S. Al terary, F. Fiévet, M. Chehimi, A. Yassar* .... **1275−1284**

Facile Synthesis of Oligothiophene-Capped CdS Nanoparticles

Keywords: Nanoparticle synthesis / Oligothiophenes / Photovoltaics / Conjugated polymers / Nanostructures

Magneto-Structural Correlations

The magnetic properties of dinuclear Mn^{III} complexes with a $[Mn_2O(RCOO)_2]^{2+}$ core could be sensitive to the type and orientation of the monodentate ligand coordinated to the manganese ions.



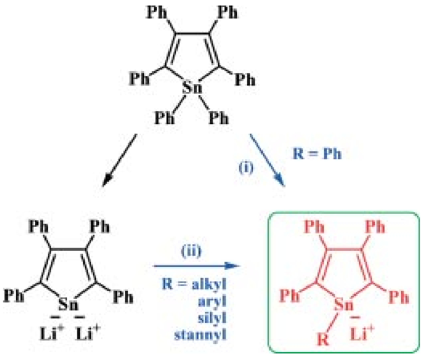
G. Fernández, M. Corbella*, G. Aullón, M. A. Maestro, J. Mahía ...... **1285−1296**

New Dinuclear Mn^{III} Compounds with 2-MeC_6H_4COO and 2-FC_6H_4COO Bridges − Effect of Terminal Monodentate Ligands (H_2O, ClO_4^- and NO_3^-) on the Magnetic Properties

Keywords: Manganese / Magnetic properties / Ligand effects

Stannole Anions

Methods for the preparation of stannole anions are described: (i) the reduction of hexaphenylstannole with the proper amount of lithium, and (ii) the reaction of the stannole dianion with various halogen reagents. NMR studies on the stannole anions and their reactions are also reported.



R. Haga, M. Saito,* M. Yoshioka .... **1297−1306**

Synthesis and Reactions of Stannole Anions

Keywords: Anions / Aromaticity / Lithium / Metallacycles / Tin