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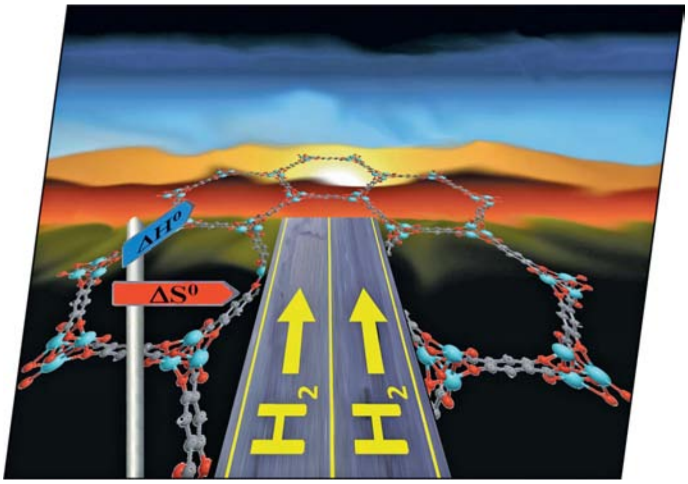
COVER PICTURE

The cover picture shows an allegoric representation of the dawning hopes of a hydrogen energy transition, which would alleviate the foreseeable shortage of fossil fuels for the transportation sector. Metal-organic frameworks (MOFs), represented by the honeycomb structure, have become a main focus in the current search for economically viable materials for hydrogen storage and delivery. The signpost at the left of the picture is a reminder that thermodynamics of the hydrogen uptake and delivery process is ruled by the corresponding enthalpy and entropy changes, which are shown to be interrelated. Both of these thermodynamic quantities have to be taken into account for intelligent design of hydrogen storage materials. Details are discussed in the article by C. O. Areán et al. on p. 1703ff.



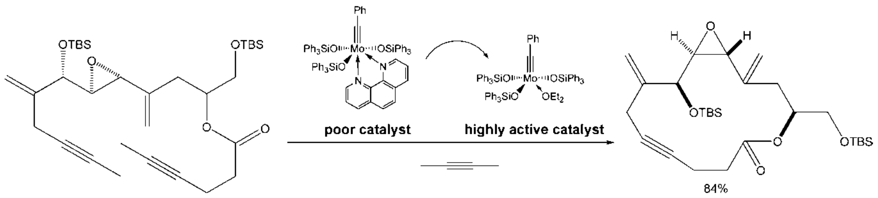
MICROREVIEW

Transition Metal Siloxides

C. Krempner* **1689–1698**

Role of Siloxides in Transition Metal Chemistry and Homogeneous Catalysis

Keywords: Siloxides / Silanes / Transition metals / Homogeneous catalysis / Metathesis



In this critical review, applications of well-defined transition metal siloxides as "single site" catalysts in homogeneous catalysis are highlighted. For example, $O{=}V(OSiPh_3)_3$ efficiently catalyzes atom-economic reactions of propargyl and allenic alcohols with imines or aldehydes. Alkylidyne complex $(Ph_3SiO)_3Mo{\equiv}CPh(ether)$ mediates the ring-closing alkyne metathesis of bis(alkynes) to biologically important products in high yields.

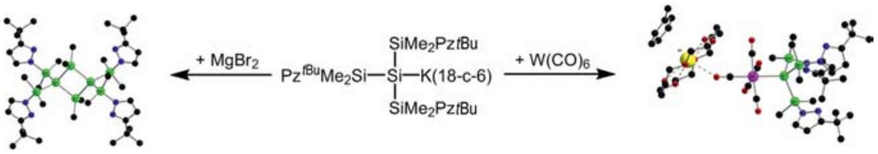
SHORT COMMUNICATION

Metal Silanides

B. McNerney, B. Whittlesey,
C. Krempner* **1699–1702**

Synthesis and Reactivity of New Pyrazolyl-Functionalized Potassium Silanides

Keywords: Silanes / Silanide / Tungsten / Nitrogen heterocycles



Easy synthetic access to pyrazolyl-functionalized neopentasilanes allowed for the preparation of the first stable pyrazolyl-substituted potassium silanides in high yields. These species are useful synthons for the synthesis of functionalized silyl tungsten carbonyl complexes and donor functionalized cyclotetrasilanes.

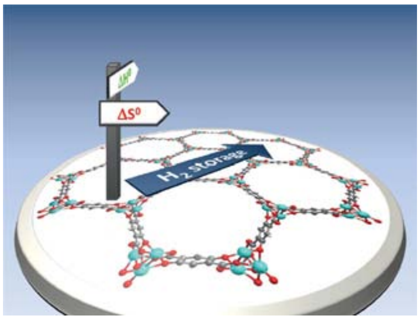
FULL PAPERS

Hydrogen Storage in Porous Solids

G. T. Palomino, C. P. Cabello,
C. O. Areán* **1703–1708**

Enthalpy–Entropy Correlation for Hydrogen Adsorption on MOFs: Variable-Temperature FTIR Study of Hydrogen Adsorption on MIL-100(Cr) and MIL-101(Cr)

Keywords: Hydrogen storage / Metal–organic frameworks / Physisorption / Thermodynamics



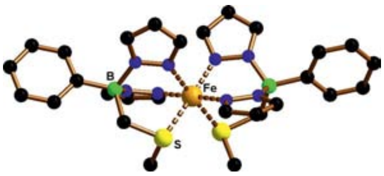
Variable-temperature infrared (VTIR) spectroscopy reveals an enthalpy–entropy correlation for hydrogen adsorption, which should facilitate intelligent design of MOFs and other porous hydrogen storage materials.

New Scorpionate Ligands

C. Reus, K. Ruth, S. Tüllmann, M. Bolte,
H.-W. Lerner, B. Weber,*
M. C. Holthausen,*
M. Wagner* **1709–1718**

Synthesis, Molecular Structure, and Physical Properties of the Complexes $[\{PhB(pz)_2(CH_2SMe)\}_2M]$ (M = Mn^{II}, Fe^{II}; pz = pyrazol-1-yl) Containing a Novel [*N*,*N*,*S*]-Heteroscorpionate Ligand

Keywords: N ligands / S ligands / Manganese / Iron / Scorpionates



With the synthesis of the [*N*,*N*,*S*] scorpionate $[PhB(pz)_2(CH_2SMe)]^-$, the homologous series of smoothly varying ligands $[PhB(pz)_x(CH_2SMe)_{3-x}]^-$ ($x = 0{-}3$) has been completed, and a gradual fine-tuning of key physical parameters (e.g. redox potentials, spin state, UV/Vis absorptions) is now possible by choice of the ligand with the best-suited donor set.

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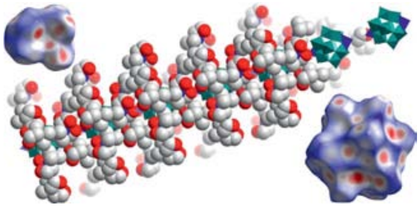
Hybrid Molecular Metal Oxides

A supramolecular organic–inorganic polyoxovanadate framework has been assembled using amphiphilic organic counterions as structure-directing agents. The heteropolyoxovanadate clusters aggregate into hydrogen-bonded chains, allowing the formation of hydrophobic cavities between the organic counterions. The use of theoretical Hirshfeld analysis of intermolecular interactions has been critically assessed. Combination with other crystallographic techniques allowed the evaluation of the dominating intermolecular interactions.



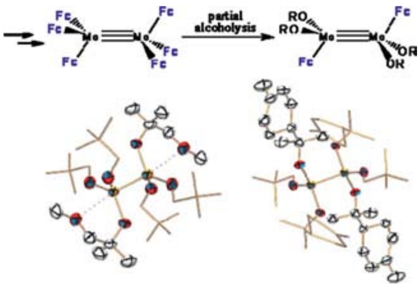
M. Grabau, J. Forster, K. Heussner, C. Streb* 1719–1724

Synthesis and Theoretical Hirshfeld Analysis of a Supramolecular Heteropolyoxovanadate Architecture

Keywords: Vanadium / Polyoxometalates / Supramolecular chemistry / Hirshfeld surface analysis / Self-assembly / Crystal engineering

Molybdenum Alkoxides

Additional functionalities (Fc) in the alkoxide ligands have been introduced in homo- and heteroleptic, triply bonded dimolybdenum alkoxides. The obtained alkoxides show interesting spectroscopic and structural features in comparison to their homoleptic analogues. They represent potential starting materials for immobilization on supports and synthesis of organic-inorganic hybrid materials.



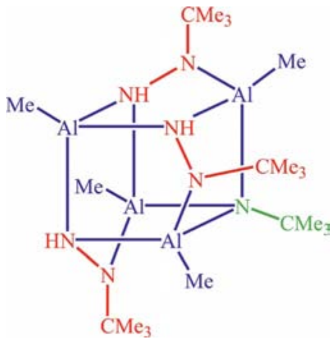
S. Krackl, J.-G. Ma, Y. Aksu, M. Driess* 1725–1732

Facile Access to Homo- and Heteroleptic, Triply Bonded Dimolybdenum Hexaalkoxides with Unsaturated Alkoxide Ligands

Keywords: Multiple bonds / O ligands / Heteroleptic alkoxides / Anisotropy / Molybdenum

Aluminum Hydrazide Cages

The two adjacent donor atoms of the hydrazine ligand give rise to unique coordination behavior that favours the formation of heterocyclic or cage-like metal hydrazides. Novel cage compounds were obtained by the thermolysis of trialkylaluminum hydrazine adducts. Their structures may be derived from Al_4N_4 heterocubanes or from a type of norbornane skeleton.



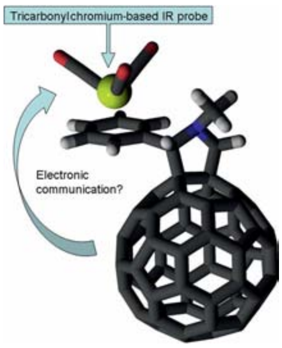
W. Uhl,* E. Hagemeier, M. Layh, B. Rezaeirad, J. Kösters, E.-U. Würthwein, N. Ghavtadze, W. Massa 1733–1743

From *tert*-Butylhydrazine Adducts of AlR_3 (R = Me, CMe_3) to Oligonuclear AlN Cage Compounds – Evidence for a Hydrazine Twist Across an Al_3 Triangle

Keywords: Aluminum / Hydrazines / Cage compounds / Nitrides

Fullerene Redox States

Methods to attach a tricarbonylchromium-based IR probe to C_{60} have been evaluated. A new C_{60}-tricarbonylchromium complex was successfully prepared via 1,3-dipolar cycloaddition. This compound was characterized by cyclic voltammetry and IR-based electrochemistry; the latter suggests communication between the two electroactive moieties. Furthermore, the redox state of the fullerene can be determined by IR spectroscopy.



C.-H. Andersson, G. Berggren, S. Ott, H. Grennberg* 1744–1749

Synthesis and IR Spectroelectrochemical Studies of a [60]Fulleropyrrolidine-(tricarbonyl)chromium Complex: Probing C_{60} Redox States by IR Spectroscopy

Keywords: Fullerenes / Chromium / IR spectroscopy / Cyclic voltammetry / Redox chemistry / Electrochemistry

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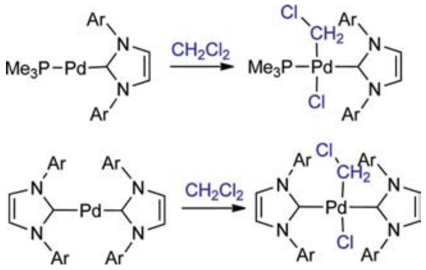
CONTENTS

Oxidative Addition

J.-H. Lee, H.-T. Jeon,
Y.-J. Kim,* K.-E. Lee, Y. O. Jang,
S. W. Lee 1750–1761

Facile Oxidative Addition of Organic Halides to Heteroleptic and Homoleptic Pd^0–N-Heterocyclic Carbene Complexes

Keywords: Palladium / Oxidative addition / N-Heterocyclic carbenes / Halides / Heteroleptic complexes



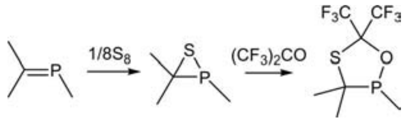
Facile oxidative additions of various organic halides as well as small alkyl halides such as dichloromethane and chloroform toward heteroleptic PMe_3–NHC–Pd^0 (NHC = *N*-heterocyclic carbene) complexes or homoleptic bis(NHC)–Pd^0 complexes were examined.

Thiaphosphirane

K. V. Turcheniuk, A. B. Rozhenko,
I. V. Shevchenko* 1762–1767

Synthesis and Some Chemical Properties of a $1,2\lambda^3\sigma^3$-Thiaphosphirane

Keywords: Phosphorus / Phosphaalkenes / Heterocycles / Ylides / Density functional calculations



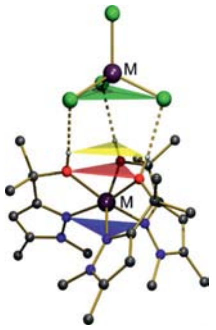
A rare example of the addition of sulfur to a phosphaalkene double bond leading to a $1,2\lambda^3,\sigma^3$-thiaphosphirane ring has been found. Hexafluoroacetone does not oxidize the three-valent phosphorus atom but adds to the P–S bond to form the previously unknown $1,4,2\lambda^3,\sigma^3$-oxathiaphospholane heterocyclic system.

Amino Alcohols

C. K. Seubert, Y. Sun, Y. Lan,
A. K. Powell, W. R. Thiel*....... 1768–1775

From a Simple Pyrazole-Derived 1,2-Amino Alcohol to Mono- and Multinuclear Complexes by Tailoring Hydrogen Bond Patterns

Keywords: Coordination chemistry / Hydrogen bonds / N ligands / Multinuclear complexes / Magnetic properties / Amino alcohols



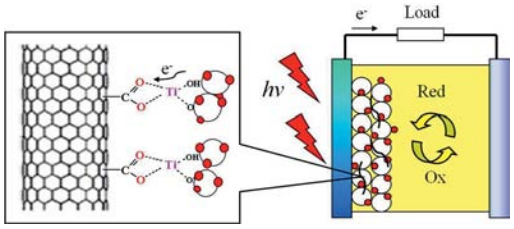
The hydroxy group of 2-[(1,5-dimethyl)pyrazol-3-yl]propan-2-ol, coordinated to transition metal sites, allows the formation of hydrogen bonds in the periphery of the complexes.

Dye-Sensitized Solar Cells

W. Guo, Y. Shen, L. Wu, Y. Gao,
T. Ma* 1776–1783

Performance of Dye-Sensitized Solar Cells Based on MWCNT/$TiO_{2-x}N_x$ Nanocomposite Electrodes

Keywords: Solar cells / Metal oxynitrides / Carbon / Nanotubes / Semiconductors / Nanostructures

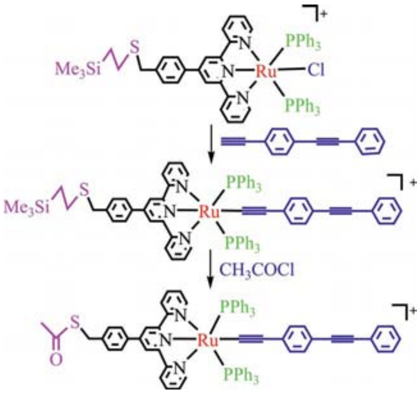


To enhance electron transport and charge collection efficiency, fibrous-type MWCNT fibrils were introduced into $TiO_{2-x}N_x$ and TiO_2 photoelectrodes to fabricate dye-sensitized solar cells. The role played by MWCNTs was systemically investigated. This paper also discusses electron lifetime, electron transport, and charge collection efficiency in DSCs based on MWCNT/TiO_2 and MWCNT/$TiO_{2-x}N_x$ electrodes.

Terpyridine–Thiol Complexes

H.-M. Wen, D.-B. Zhang, L.-Y. Zhang, L.-X. Shi, Z.-N. Chen* **1784–1791**

Efficient Synthetic Approaches To Access Ruthenium(II) Complexes with 2-(Trimethylsilyl)ethyl- or Acetyl-Protected Terpyridine–Thiols



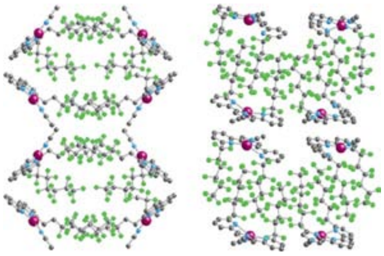
A series of thiol-functionalized terpyridines with protective groups, such as acetyl (Ac), 2-(trimethylsilyl)ethyl (TMSE), and *tert*-butyl (*t*Bu), together with the corresponding ruthenium(II) complexes were synthesized, and feasible synthetic approaches were thus established.

Keywords: Electrochemistry / Ligand design / Ruthenium / Synthetic methods / Thiol / Tridentate ligands

Fluorous Copper Complexes

V. Madhu, Y. Diskin-Posner, R. Neumann* **1792–1796**

Copper(I) Complexes of Bipyridine and Terpyridine with Fluorous Tails and the Formation of Crystalline Materials with Fluorous Layers



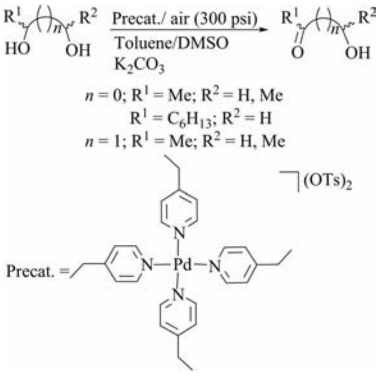
Copper(I) complexes of bipyridine (Y-shaped trigonal planar) and terpyridine (tetrahedrally distorted square-planar) with fluorous tails showed crystal packing with segregation of the aromatic units and the fluorous tails. Layered structures that are tilted in two different dimensions as well as “herring bone” structures with accordion-like fluorous layers were observed.

Keywords: Ligand effects / Stacking interactions / Fluorous compounds / Copper / Electron-deficient compounds

Aerobic Diol Oxidation

L. Bettucci, C. Bianchini, J. Filippi, A. Lavacchi, W. Oberhauser* **1797–1805**

Chemoselective Aerobic Diol Oxidation by Palladium(II)–Pyridine Catalysis



Neutral and cationic palladium(II) complexes with pyridine ligands were synthesized and employed as catalyst precursors for the aerobic K_2CO_3-assisted oxidation of unprotected diols to chemoselectively give hydroxy ketones. Within the series of catalyst precursors studied, the bis-cationic compound [Pd(4-EtPy)$_4$](OTs)$_2$ (Py = pyridine, OTs = *p*-toluenesulfonate) emerged as the most promising.

Keywords: Oxidation / Palladium / N ligands / Chemoselectivity / Diols

Solar Cell Sensitizers

P. G. Bomben, K. D. Thériault, C. P. Berlinguette* **1806–1814**

Strategies for Optimizing the Performance of Cyclometalated Ruthenium Sensitizers for Dye-Sensitized Solar Cells

A series of tris-heteroleptic cyclometalated ruthenium sensitizers have been developed for dye-sensitized solar cell applications. Each metal complex contains two 2,2′-bipyridine ligands, one bearing anchoring groups, and an anionic cyclometalating ligand. Cell performance is shown to be dominated by the ground-state oxidation potentials of the complexes.

Keywords: Ruthenium / Electrochemistry / Dyes / Sensitizers / Solar cells

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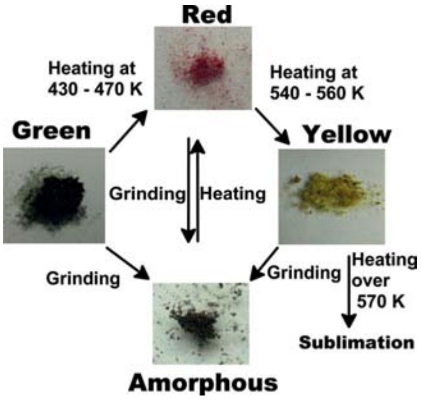
Platinum Complex Polymorphs

Y. Nishiuchi, A. Takayama, T. Suzuki, K. Shinozaki* **1815–1823**

💻 A Polymorphic Platinum(II) Complex: Yellow, Red, and Green Polymorphs and X-ray Crystallography of [Pt(fdpb)Cl] [Hfdpb = 1,3-Bis(5-trifluoromethyl-2-pyridyl)benzene]

Keywords: Luminescence / Polymorphism / Phase transitions / Stacking interactions / Crystal engineering



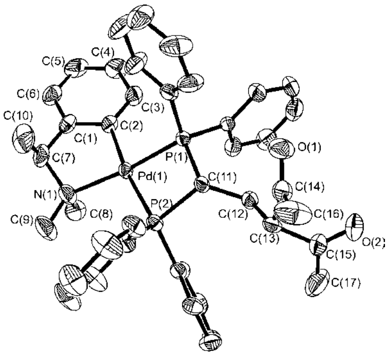
Polymorphs of a platinum(II) complex were prepared, and their crystal structures were clarified by X-ray crystallography. Mechanical grinding changed the polymorphs from the crystalline to the amorphous phase. Heating caused the transition between the amorphous and the crystal phase and the crystal–crystal transformations of the green form to the red from and of the red form to the yellow form.

Chiral Palladacycles

R. Mosteiro, A. Fernández,* D. Vázquez-García, M. López-Torres, A. Rodríguez-Castro, N. Gómez-Blanco, J. M. Vila,* J. J. Fernández **1824–1832**

Cyclometallated Palladium Diphosphane Compounds Derived from the Chiral Ligand (*S*)-PhCH(Me)NMe$_2$. Michael Addition Reactions to the Vinylidene Double Bond

Keywords: Palladium / Palladacycles / Phosphane ligands / Chiral ligands / Michael addition



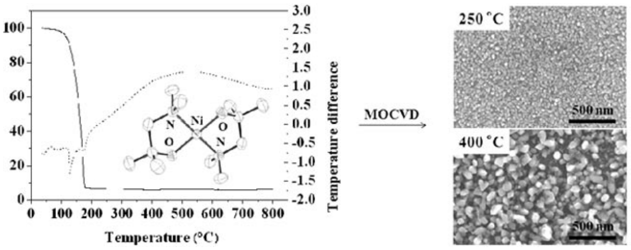
Chiral palladacycles were prepared from ligand **1**. Those that involve the functionalized diphosphane vdpp may give complexes that bear more than one stereogenic center, which originate after the Michael addition to the vinylidene double bond.

Precursors for Ni Thin Films

S. H. Yoo, H. Choi, H.-S. Kim, B. K. Park, S. S. Lee, K.-S. An, Y. K. Lee, T.-M. Chung, C. G. Kim* **1833–1839**

💻 Synthesis and Characterization of Nickel(II) Aminoalkoxides: Application to Molecular Precursors for MOCVD of Ni Thin Films

Keywords: Nickel / N,O ligands / Chemical vapor deposition / Thin films



New Ni^{II} aminoalkoxide precursors, Ni(dmamp)$_2$ (**1**), Ni(deamp)$_2$ (**2**), and Ni(emamp)$_2$ (**3**), for preparing Ni thin films were synthesized and characterized. Thermal properties of **1**–**3** show high volatility.

By MOCVD, **1** gave both hexagonal-phase (250 °C) and cubic-phase thin films (400 °C). A reaction pathway was proposed for **1** in which Ni is formed by γ-elimination and then reductive elimination.

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* Author to whom correspondence should be addressed.

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