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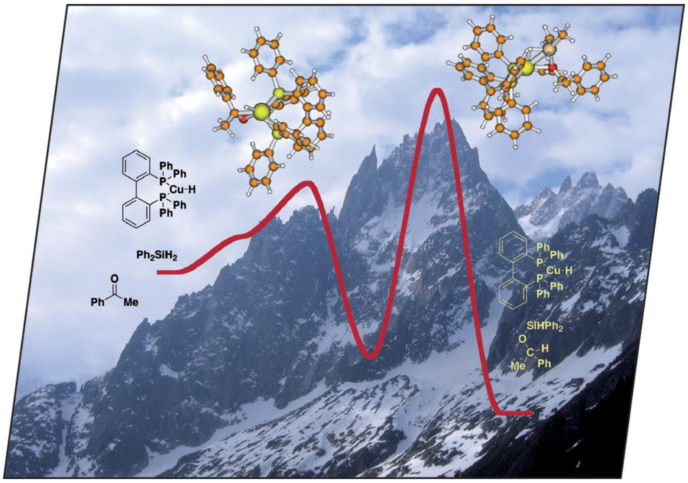
COVER PICTURE

The cover picture shows the Aiguille du Midi, Mont Blanc massif, France. The mechanism of the copper-catalyzed hydrosilylation of ketones has been determined by experimental mechanistic investigations and computational studies. The insertion of the ketone into the Cu–H bond was found to have a lower activation barrier than the reaction of the copper alkoxy intermediate with the silane that regenerates the Cu–H bond along with the silyl ether product, as shown in the picture. Details are discussed in the article by A. Dedieu, S. Bellemin-Laponnaz et al. on p. 529ff.



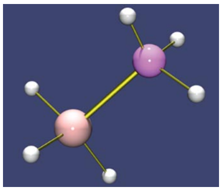
MICROREVIEW

Ammonia Borane

N. C. Smythe, J. C. Gordon* **509–521**

Ammonia Borane as a Hydrogen Carrier: Dehydrogenation and Regeneration

Keywords: Hydrogen storage / Dehydrogenation / Homogeneous catalysis / Transition metals / Ammonia borane



Ammonia borane (NH_3BH_3) is a potential hydrogen carrier for transportation applications. This Microreview focuses on recent results pertaining to its transition-metal-catalyzed dehydrogenation and the regeneration of ammonia borane “spent fuels”.

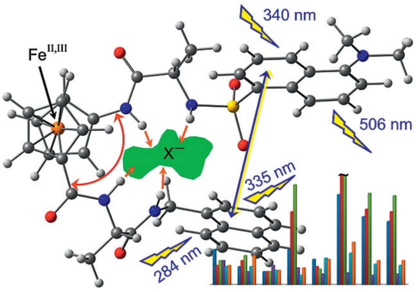
SHORT COMMUNICATION

Optical Sensors

D. Siebler, C. Förster,
K. Heinze* **523–527**

Molecular Multi-Wavelength Optical Anion Sensors

Keywords: Dyes / Ferrocenes / Fluorescence spectroscopy / Peptides / Optical molecular probes



Polychromatic fingerprinting of simple anions is achieved by employing neutral and charged multicolor fluorescent probes based on ferrocene-spaced dansyl and naphthyl groups. The double-dye receptors exhibit specific emission responses in the presence of anions X^- when excited at the absorption maxima of the dyes.

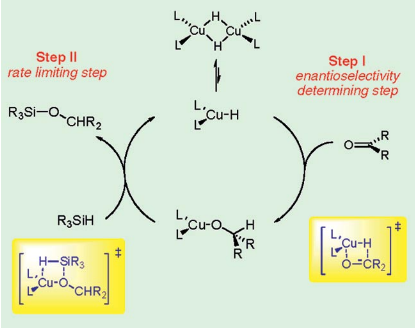
FULL PAPER

Hydrosilylation of Ketones

J.-T. Issenhuth, F.-P. Notter, S. Dagorne,
A. Dedieu,*
S. Bellemin-Laponnaz* **529–541**

Mechanistic Studies on the Copper-Catalyzed Hydrosilylation of Ketones

Keywords: Density functional calculations / Mechanistic studies / Asymmetric catalysis / Hydrosilylation / Copper



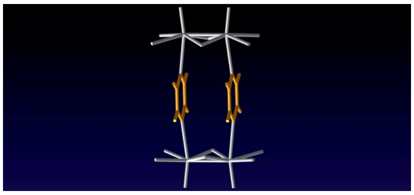
A detailed computational study (DFT/B3LYP) of the copper(I)-catalyzed hydrosilylation reaction is presented. The conclusions are supported by experimental mechanistic investigations (kinetic studies, kinetic isotope effect, isotope labeling).

Molybdenum Complexes

B. Modec,* M. Šala, R. Clérac 542–553

Pyrazine-Assisted Dimerization of Molybdenum(V): Synthesis and Structural Characterization of Novel Dinuclear and Tetranuclear Complexes

In Mo^V coordination compounds, pyrazine acts either as a monodentate or a bidentate bridging ligand. In the highly symmetrical, rectangular tetraanion $[(Mo_2O_4X_4)_2(Pyz)_2]^{4-}$ (X = Cl, Br), two $\{Mo_2O_4\}^{2+}$ building blocks are doubly bridged by bidentate pyrazine ligands.



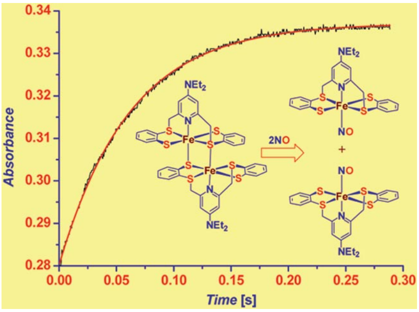
Keywords: Molybdenum / Polynuclear complexes / Molecular building units / N ligands / Magnetic properties

Synthetic Nitrogenase Models

S. Y. Shaban, R. van Eldik* 554–561

Mechanistic Information on the Reversible Binding of NO to Mono- and Dinuclear Fe^{II} Complexes of a Biomimetic S_4N Ligand

A structural and mechanistic study on the binding of NO to mono- and dinuclear Fe^{II} complexes of a biomimetic S_4N ligand has been performed. The results indicate that steric and electronic effects control the rate but not the nature of the substitution mechanism by which NO coordinates to the selected complexes.



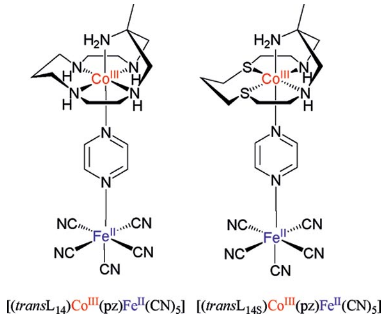
Keywords: Biomimetics / Kinetics / Nitrogen oxides / [FeS] core / Nitrogenases

Co/Fe Mixed-Valence Compounds

P. V. Bernhardt, M. Martínez,* C. Rodríguez 562–569

Outer-Sphere Redox Reactions Leading to the Formation of Discrete Co^{III}/Fe^{II} Pyrazine-Bridged Mixed-Valence Compounds

The outer-sphere redox reaction of $[Co^{III}XL]^{n+}$ [L = $(N)_5$ ligand, X = Cl, OH, H_2O] with $[Fe^{II}(CN)_5(pyrazine)]^{3-}$ has been studied from a kinetic and mechanistic perspective. The redox-triggered formal substitution process parallels that observed for the reaction already studied with the $[Fe^{II}(CN)_6]^{4-}$ reductant. A *Class II* mixed-valence compound is produced when L is an encapsulating pentadentate macrocycle.

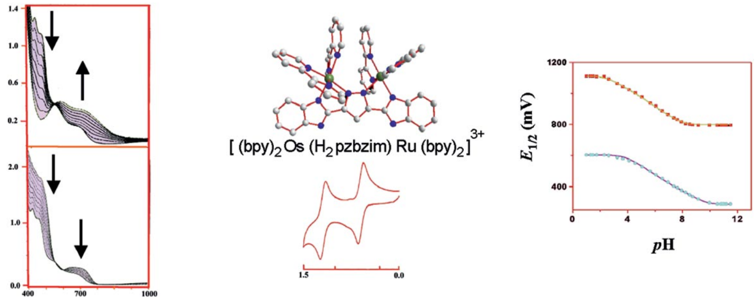


Keywords: Redox chemistry / Mixed-valent compounds / Reaction mechanisms / Cobalt / Iron

Proton-Coupled Electron Transfer

S. Baitalik,* S. Dutta, P. Biswas, U. Flörke, E. Bothe, K. Nag* 570–588

Structural, Spectroscopic, and Proton-Coupled Electron-transfer Behavior of Pyrazolyl-3,5-bis(benzimidazole)-Bridged Homo- and Heterochiral $Ru^{II}Ru^{II}$, $Os^{II}Os^{II}$, and $Os^{II}Ru^{II}$ 2,2′-Bipyridine Complexes



Using pyrazole-3,5-bis(benzimidazole) ($H_3pzbzim$) as the bridging ligand, physicochemical studies, including proton-coupled electron-transfer reactions and spectroelectrochemistry, were carried for the $Ru^{II}Ru^{II}$, $Os^{II}Os^{II}$, and $Ru^{II}Os^{II}$ complexes $[(bpy)_2M^{II}(H_2pzbaim)M'^{II}(bpy)_2]^{3+}$ and $[(bpy)_2M^{II}(pzbaim)M'^{II}(bpy)_2]^{+}$obtained as their homochiral and heterochiral diastereomers.

Keywords: Ruthenium / Osmium / Electrochemistry / Electron transfer / Bridging ligands

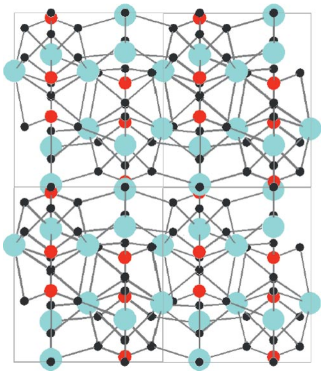
CONTENTS

Solid Oxide Electrolytes

T. Kharlamova,* S. Pavlova, V. Sadykov,
M. Chaikina, T. Krieger, A. Ishchenko,
Y. Pavlyukhin, S. Petrov,
C. Argirusis 589–601

Mechanochemical Synthesis of Fe-Doped Apatite-Type Lanthanum Silicates

Keywords: Lanthanum / Silicates / Doping / Mechanical activation / Topochemistry



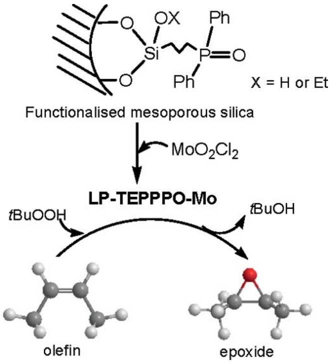
Rapid formation of apatite-type silicate by a topotactic acid–base reaction in the course of milling is favored by the structural similarities of La_2O_3, $La(OH)_3$, and apatite, whereas an appreciable amount of water in the reaction space can result in a dissociative mechanism of interaction. Incorporation of a dopant into the apatite during milling involves the intermediate amorphous silicate formation.

Mesostructured Epoxidation Catalyst

A. Castro, J. C. Alonso, P. Neves,
A. A. Valente,* P. Ferreira* 602–607

Dioxomolybdenum(VI) Epoxidation Catalyst Supported on Mesoporous Silica Containing Phosphane Oxide Groups

Keywords: Molybdenum / P ligands / Mesoporous materials / Homogeneous catalysis / Epoxidation / Ionic liquids



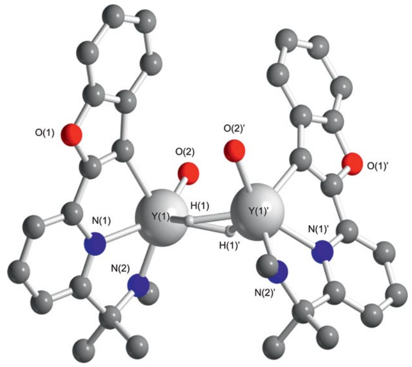
A mesostructured hybrid material (LP-TEPPPO-Mo) prepared by anchoring $[MoO_2Cl_2]$ to mesoporous silica functionalised with phosphane oxide spacer ligands: catalytic performance in the epoxidation of olefins with *t*BuOOH, at 55 °C, in comparison with the complex $[MoCl_2(O)_2\{OP(CH_2CH_3)(Ph)_2\}_2]$ without a co-solvent or dissolved in an ionic liquid.

Yttrium-Alkyl-Hydrido Complexes

L. Luconi, D. M. Lyubov, C. Bianchini,
A. Rossin, C. Faggi, G. K. Fukin,
A. V. Cherkasov, A. S. Shavyrin,
A. A. Trifonov,*
G. Giambastiani* 608–620

Yttrium-Amidopyridinate Complexes: Synthesis and Characterization of Yttrium-Alkyl and Yttrium-Hydrido Derivatives

Keywords: Amidopyridinate / Yttrium / Hydrides / Metathesis / Ethylene / Polymerization



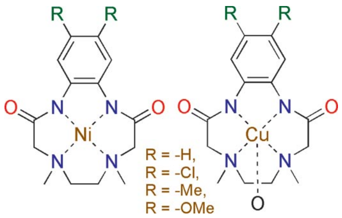
Yttrium-alkyl complexes that feature 6-aryl or heteroaryl-substituted amidopyridinate ligands quantitatively undergo intramolecular sp^2 C–H bond activation. A selective σ-bond metathesis at the residual Y–C(alkyl) bond generates binuclear yttrium-hydrido complexes.

Electronic Effects

S. K. Sharma, G. Hundal,
R. Gupta* 621–636

The Effect of Ligand Architecture on the Structure and Properties of Nickel and Copper Complexes of Amide-Based Macrocycles

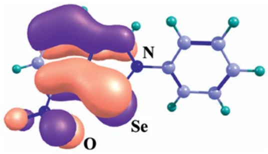
Keywords: Nickel / Copper / Macrocyclic ligands / Electrochemistry / Oxidation



The present work demonstrates the influence of electron-donating and electron-withdrawing substituents on the structural, chemical and redox properties of nickel and copper complexes in a set of 12-membered macrocyclic ligands. The well-characterized Ni^{II} and Cu^{II} complexes undergo one-electron oxidation to generate Ni^{III} and Cu^{III} species in a square-planar environment.

Stable Selenenium Cations

Reactions of *N*-[*n*-butyl-(3-nitrobenzylimino)]phenyl selenide with sulfuryl chloride and bromine result in the formation of selenenium cations with halide counter anions. The ionization of the Se–halide bond is mainly attributed to the high charge on selenium and delocalization of the p-electrons on selenium in the five-membered heterocyclic ring. The high GPx-like activities of selenenium cations are due to the formation of corresponding selenoxides.

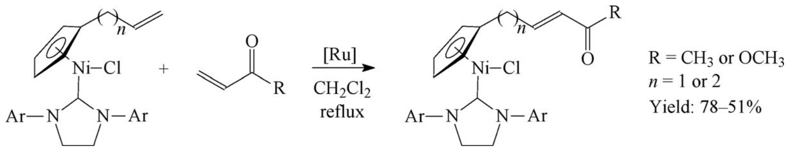


V. P. Singh, H. B. Singh,*
R. J. Butcher **637–647**

Stable Selenenium Cations: Unusual Reactivity and Excellent Glutathione Peroxidase-Like Activity 💻

Keywords: Selenenium / Selenium / Glutathione peroxidase / Ebselen / Enzyme models / Density functional calculations

Cross-Metathesis in a Complex



The novel complexes [(RC$_5$H$_4$)Ni(X)(NHC)], which contain NHC ligands bearing two different N-substituents, are synthesized and fully characterized. Complexes with R = (CH$_2$)$_n$CH=CH$_2$ (n = 1 or 2) undergo chemoselective cross-metathesis with α,β-unsaturated carbonyl compounds in the presence of the second-generation Grubbs catalyst. The new complexes efficiently polymerize styrene or phenylacetylene.

W. Buchowicz,* W. Wojtczak,
A. Pietrzykowski, A. Lupa,
L. B. Jerzykiewicz, A. Makal,
K. Woźniak **648–656**

Synthesis, Structure, and Polymerization Activity of Cyclopentadienylnickel(II) N-Heterocyclic Carbene Complexes: Selective Cross-Metathesis in Metal Coordination Spheres 💻

Keywords: Nickel / Carbene ligands / Metathesis / Homogeneous catalysis / Polymerization

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* Author to whom correspondence should be addressed.

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