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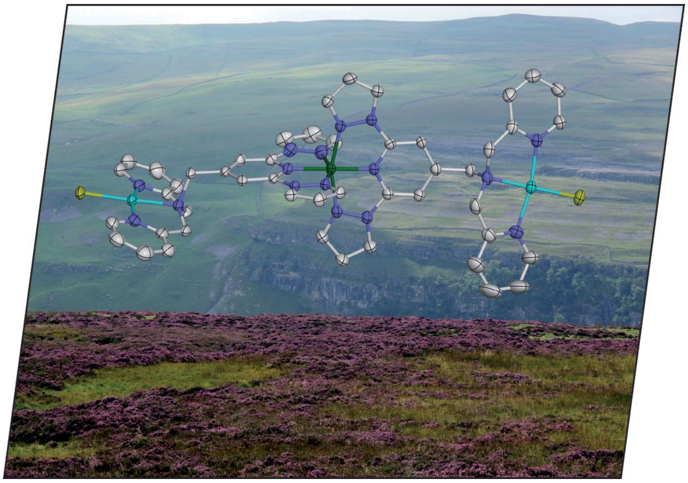
COVER PICTURE

The cover picture shows the crystal structure of a heteronuclear trimetallic complex of a "back-to-back" ligand superimposed on a view of the wild heather near Kettlewell in the Yorkshire Dales national park, near Leeds. The ligand contains two different metal-binding domains that can be sequentially metallated with high selectivity – there is no detectable exchange of metal ions between the domains of the ligand in solution. The iron(II) ion at the centre of the complex undergoes a spin transition on cooling, in solution and in the solid state. Details are discussed in the Short Communication by M. A. Halcrow et al. on p. 1007ff.



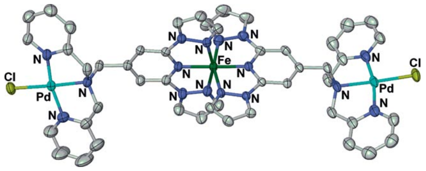
SHORT COMMUNICATION

Back-to-Back Ligands

C. A. Tovee, C. A. Kilner, S. A. Barrett, J. A. Thomas, M. A. Halcrow* **1007–1012**

A Back-to-Back Ligand with Dipyrazolylpyridine and Dipicolylamine Metal-Binding Domains

Keywords: Iron / Palladium / N ligands / Bridging ligands



The new ligand 4-bis(pyrid-2-ylmethyl)aminomethyl-2,6-bis(pyrazol-1-yl)pyridine (**L**) is metallated sequentially at its dipicolylamino and then its dipyrazolylpyridyl sites. The FeM_2 (M = Pd and Pt) complexes undergo gradual thermal spin transitions in the solid state and (when M = Pt) in solution.

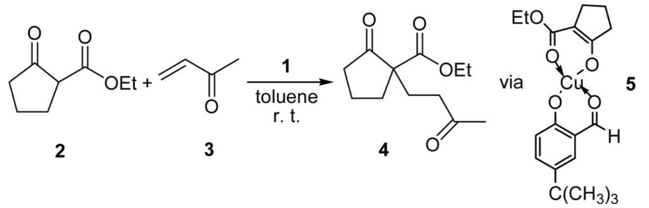
FULL PAPERS

Mechanism of Michael Reactions

E. Pérez, M. Moreno-Mañas, R. M. Sebastián, A. Vallribera,* A. Jutand* **1013–1019**

Mechanistic Insights into Copper-Catalyzed Michael Reactions

Keywords: Copper / Michael addition / Reaction mechanisms



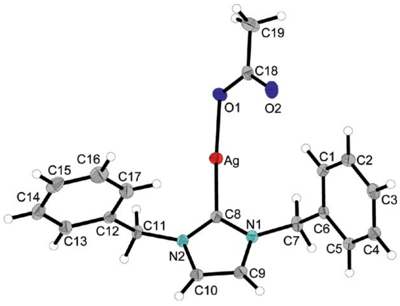
The rate and mechanism for the formation of the mixed complex [Cu(5-*t*Bu-Sal)(enolate-**2**)] (**5**) from the catalyst [Cu(5-*t*Bu-Sal)$_2$] (**1**) and the oxo ester **2** has been investigated. The complex **5** reacts with **3** in a rate-determining step to deliver the Michael product **4**.

NHC Silver Complexes

S. Patil, J. Claffey, A. Deally, M. Hogan, B. Gleeson, L. M. Menéndez Méndez, H. Müller-Bunz, F. Paradisi, M. Tacke* **1020–1031**

Synthesis, Cytotoxicity and Antibacterial Studies of *p*-Methoxybenzyl-Substituted and Benzyl-Substituted N-Heterocyclic Carbene–Silver Complexes

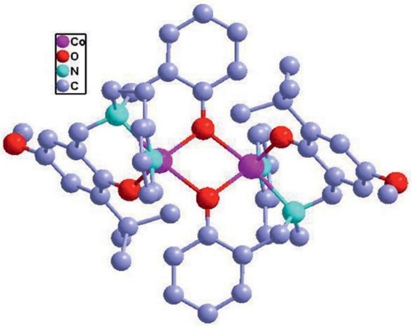
Keywords: Anticancer drug / Antibacterial drug / Silver / NHC / Caki-1 / Staphylococcus aureus / Carbenes



p-Methoxybenzyl- and benzyl-substituted N-heterocyclic carbene–silver acetate derivatives were synthesised by the reaction of appropriately substituted carbene precursors with silver acetate. The syntheses of six N-heterocyclic carbene–silver derivatives are reported along with structural discussion. Additionally, these compounds were tested for their anticancer and antimicrobial activity.

Metal-Coordinated Phenoxyl Radicals

Coulometrically generated two-electron oxidised forms of diphenoxido-bridged Co^{II} and Zn^{II} dimers authenticate the existence of metal-coordinated phenoxyl radical species. The electronic effect of *p*-methyl and *p*-methoxy substituents on the terminal phenolato ring and the effect of chelate ring size on the stability of the M^{II}-coordinated phenoxyl radical species has been systematically investigated.

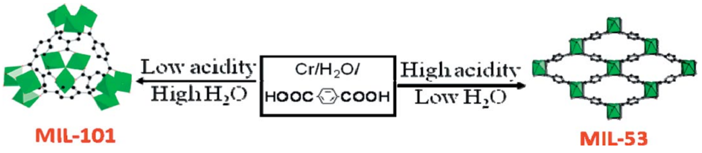


A. Mukherjee, F. Lloret,
R. Mukherjee* **1032–1042**

Diphenoxido-Bridged Co^{II} and Zn^{II} Complexes of Tripodal N_2O_2 Ligands: Stabilisation of M^{II}-Coordinated Phenoxyl Radical Species

Keywords: Dinuclear complexes / Cobalt / Zinc / Phenol / Tripodal ligands / Solid-state structures / Redox chemistry / Density functional calculations

Nanoporous Materials



Two chromium benzenedicarboxylates (MIL-101 and MIL-53) were synthesized, and the reaction conditions were optimized. MIL-101 is obtained preferentially in dilute solution and at low acidity, because the concentration of the Cr trimer is more important than the concentration of benzenedicarboxylate. On the contrary, MIL-53 is produced in concentrated solution at low pH, because of the rapid reaction.

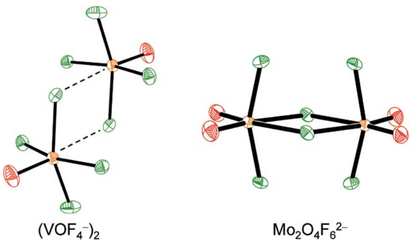
N. A. Khan, J. W. Jun,
S. H. Jhung* **1043–1048**

Effect of Water Concentration and Acidity on the Synthesis of Porous Chromium Benzenedicarboxylates

Keywords: Metal–organic frameworks / Hydrothermal synthesis / Chromium benzenedicarboxylates / Acidity / Water

Oxofluoro Complex Anion

1-Ethyl-3-methylimidazolium ($EMIm^+$) and *N*-butylpyridinium (BPy^+) salts of the VOF_4^- and $MoOF_5^-$ anions have been synthesized and characterized by physicochemical methods. The molecular geometries of the $(VOF_4^-)_2$ and $Mo_2O_4F_6^{2-}$ anions determined by single-crystal X-ray diffraction are also reported.



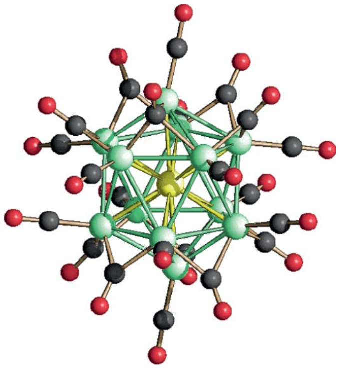
T. Kanatani, K. Matsumoto,
R. Hagiwara* **1049–1055**

Syntheses and Physicochemical Properties of Low-Melting Salts Based on VOF_4^- and $MoOF_5^-$, and the Molecular Geometries of the Dimeric $(VOF_4^-)_2$ and $Mo_2O_4F_6^{2-}$ Anions

Keywords: Ionic liquids / Fluorides / Vanadium / Molybdenum / Structure elucidation

Metal Carbonyl Clusters

The $[H_{3-n}Ni_{12}(\mu_{12}\text{-}Ga)(CO)_{22}]^{n-}$ (n = 2, 3) and $[Ni_{14.3}(\mu_{12}\text{-}Ga)(CO)_{24.3}]^{3-}$ icosahedral clusters were obtained by treating $[Ni_6(CO)_{12}]^{2-}$ with $GaCl_3$ in dichloromethane under a nitrogen atmosphere; they represent the first metal carbonyl clusters containing a gallium atom as interstitial heteroelement.



C. Femoni, M. C. Iapalucci,* G. Longoni,
S. Zacchini **1056–1062**

Icosahedral Ga-Centred Nickel Carbonyl Clusters: Synthesis and Characterization of $[H_{3-n}Ni_{12}(\mu_{12}\text{-}Ga)(CO)_{22}]^{n-}$ (n = 2, 3) and $[Ni_{14.3}(\mu_{12}\text{-}Ga)(CO)_{24.3}]^{3-}$ Anions

Keywords: Cluster compounds / Carbonyl ligands / Nickel / Gallium / Hydrides

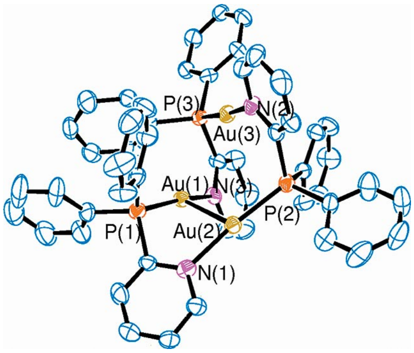
CONTENTS

Gold Catalysts

C. Khin, A. S. K. Hashmi,*
F. Rominger 1063–1069

Gold(I) Complexes of P,N Ligands and Their Catalytic Activity

Keywords: Transition metals / Gold / Lewis acids / N ligands / P ligands / Cations



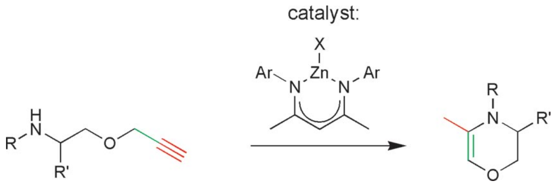
If P,N ligands are used for the preparation of gold(I) catalysts, the catalytic activity is reduced. A structure showing coordination to the additional nitrogen when forming a new trimeric structure could be identified as a mode of catalyst deactivation.

Zn Catalysts for Hydroaminations

M. Biyikal, K. Löhnwitz, N. Meyer,
M. Dochnahl, P. W. Roesky,*
S. Blechert* 1070–1081

β-Diketiminate Zinc Complexes for the Hydroamination of Alkynes

Keywords: Alkynes / Cyclization / β-Diketiminates / Hydroamination / Zinc



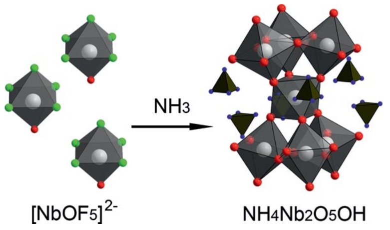
A series of electronically and sterically modified β-diketiminate zinc complexes has been investigated as catalysts for the intramolecular hydroamination of non-activated alkynes. They show high catalytic activity in conjunction with the cocatalyst $[PhNMe_2H][SO_3CF_3]$.

Nanocrystalline Pyrochlores

S. N. Britvin,* O. I. Siidra, A. Lotnyk,
S. V. Krivovichev,
W. Depmeier 1082–1088

Niobate and Tantalate Pyrochlores: Soft Synthesis by the Fluoride Route

Keywords: Niobium / Tantalum / Sol–gel processes / Nanostructures / Ion exchange



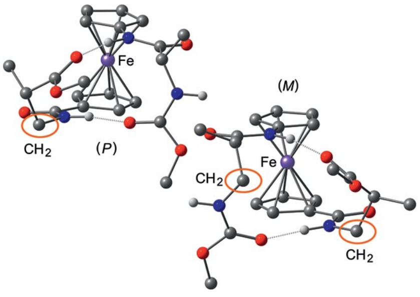
A new soft and industrially applicable method of synthesis of nanocrystalline pyrochlores $A(Nb,Ta)_2O_5(OH,F)(nH_2O)$ (A = NH_4, K, Rb, Cs) is described.

Ferrocene Bioconjugates

M. Č. Semenčić, K. Heinze,* C. Förster,
V. Rapić* 1089–1097

Bioconjugates of 1′-Aminoferrocene-1-carboxylic Acid with (*S*)-3-Amino-2-methylpropanoic Acid and L-Alanine

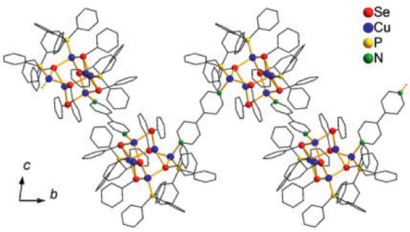
Keywords: β-Amino acids / Conformation analysis / Density functional calculations / Hydrogen bonds / Metallocenes



Formal CH_2 insertion in bioconjugates composed of 1′-aminoferrocene-1-carboxylic acid (Fca) and alanine Boc-Ala-Fca-Ala-OCH_3 gives Fca conjugates with the β-amino acid (*S*)-3-amino-2-methylpropanoic acid (Aib). "L-Ala–to–(*S*)-β-Aib mutations" exert ferrocene helix inversion and (de-)stabilize the secondary structure, depending on the "mutation site", as shown by NMR, CD and IR spectroscopy and DFT calculations.

1-D Cluster Polymers

Depending on the phosphane used reactions of copper(I) acetate with $PhSeSiMe_3$ in the presence of 4,4′-bipyridine lead to the formation of different one-dimensional coordination polymers. In the case of $[Cu_6(SePh)_6(PPh_3)_3(4,4'\text{-bpy})]$ hexanuclear selenolato-bridged clusters are linked by 4,4′-bipyridine forming a zigzag chain.



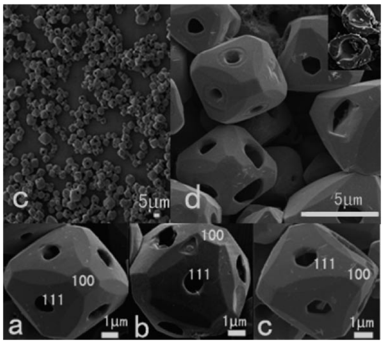
M.-L. Fu, D. Fenske, B. Weinert, O. Fuhr* .... 1098−1102

One-Dimensional Coordination Polymers Containing Polynuclear (Selenolato)copper Complexes Linked by Bipyridine Ligands

Keywords: Copper / Selenium / Coordination polymers / X-ray diffraction / UV/Vis spectroscopy

Microcages

The controllable synthesis of Cu_2O microcrystals with distinctive morphologies, including porous hollow microspheres, octahedral microcages, and microcrystals with truncated corners and edges and octahedral microcrystals, was accomplished. These structures can be fine-tuned by varying reaction temperature, reaction time, and concentration.

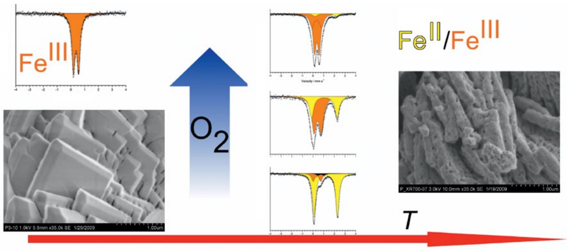


W. Zhang, L. Shi,* K. Tang, S. Dou .... 1103−1109

Controllable Synthesis of Cu_2O Microcrystals via a Complexant-Assisted Synthetic Route

Keywords: Synthesis design / Crystal growth / Microcages / Photochemistry / Hydrothermal synthesis

Solid-State Decomposition



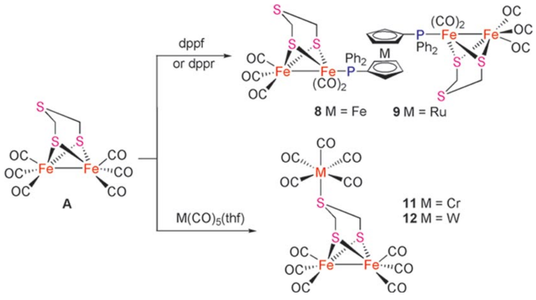
The reductive formation of FeC_2O_4 during thermal solid-state decomposition of $Fe_2(C_2O_4)_3{\cdot}4H_2O$ proceeds in an oxidative atmosphere. The observable amount of the Fe^{2+} cations depends on the access of oxygen to the sample volume. Preservation of the precursor morphology encourages disproportionation/synproportionation/re-disproportionation processes during the decomposition in an inert atmosphere.

P. Hermankova, M. Hermanek,* R. Zboril .... 1110−1118

Thermal Decomposition of Ferric Oxalate Tetrahydrate in Oxidative and Inert Atmospheres: The Role of Ferrous Oxalate as an Intermediate

Keywords: Solid-state reactions / Thermolysis / Redox chemistry / Synproportionation / Iron

Hydrogenase Models



A series of the structurally modified TDT-type model complexes **1**−**12** has been successfully prepared by substitution of the CO ligand and coordination at the central S atom of the parent complex **A**. Six crystal structures are reported.

L.-C. Song,* Q.-S. Li, Z.-Y. Yang, Y.-J. Hua, H.-Z. Bian, Q.-M. Hu .... 1119−1128

Synthesis and Characterization of Diiron Thiadithiolate Complexes Related to the Active Site of [FeFe]-Hydrogenases

Keywords: Bioinorganic chemistry / Transition metals / Enzyme models / Iron / Hydrogenases

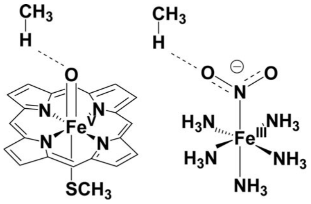
CONTENTS

Hydrocarbon Activation

R. Silaghi-Dumitrescu,
S. V. Makarov* .... 1129−1132

Hydrocarbon Oxygenation by Metal Nitrite Adducts: Theoretical Comparison with Ferryl-Based Oxygenation Agents

Keywords: Iron / Heme proteins / Oxygenation / Cytochromes / Redox chemistry



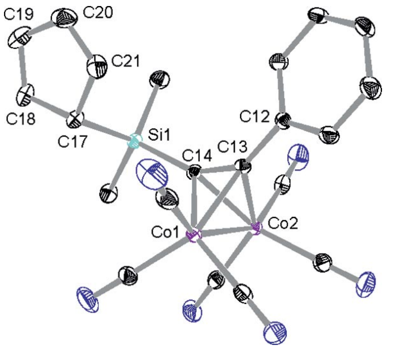
Ferric nitrite adducts mimic, to some extent, the oxygenating reactivity of high-valent iron centers such as heme compound I. The role of the redox potential in controlling oxygenation reactions with iron centers is revealed in this context to be by far the most important in comparison to factors such as the unusual electronic structure of the ferryl moiety.

Functional Alkynylsilanes

F. Hoffmann, J. Wagler,
G. Roewer* .... 1133−1142

💻 Selective Synthesis of Functional Alkynylmono- and -trisilanes

Keywords: Alkyne complexes / Alkynylsilanes / Cobalt / Molybdenum / Protecting groups



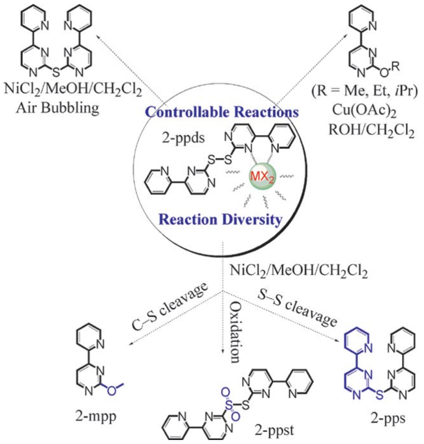
The selective synthesis of functional alkynylsilanes $RC\equiv C-(SiMe_2)_m-X$ ($m = 1, 3$) was investigated. Several alkynylsilanes and two of their transition-metal complexes were synthesized and characterized.

In Situ Metal-Promoted Reactions

H.-B. Zhu, L. Li, G. Xu,
S.-H. Gou* .... 1143−1148

💻 Reaction Diversity of the S−S Bond Promoted by Metal Coordination: From Discovery to Controllable Reactions

Keywords: Disulfides / Metal coordination / Oxidation / Cleavage reactions / Coordination modes



Promoted by metal coordination, the disulfide ligand of 2-ppds undergoes diverse in situ reactions, such as *S*-oxidation and C−S and S−S bond scission, which can be orientated towards one specific product under appropriate reaction conditions.

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* Author to whom correspondence should be addressed.

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