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Contents

Regular Papers

Matthias Tamm, Bernd Dreßel, Kim Baum, Thomas Lügger, Tania Pape

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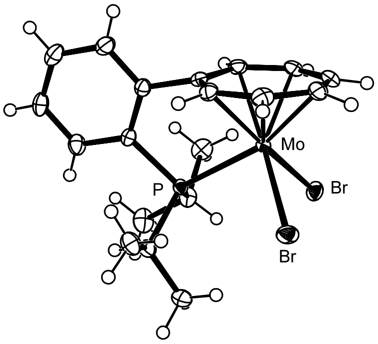
Synthesis and structural characterization of molybdenum complexes with linked cycloheptatrienyl–phosphane ligands

Chelate complexes with linked cycloheptatrienyl–phosphane ligands can be readily prepared from the *P*-functionalized cycloheptatriene derivative [2-(cyclohepta-2,4,6 - trienyl)phenyl]diisopropylphosphane. The properties and X-ray crystal structures of several 18- and 17-electron cycloheptatrienyl–molybdenum complexes containing the $[(o\text{-}{}^{i}Pr_2P\text{–}C_6H_4\text{–}\eta^7\text{-}C_7H_6)Mo\text{-}(P\text{–}Mo)]$ moiety are reported. These compounds are versatile starting materials for the preparation of cycloheptatrienyl complexes for applications in homogeneous transition metal catalysis.



Evgenii P. Talsi, Jan L. Eilertsen, Martin Ystenes, Erling Rytter

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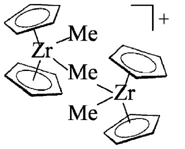
^{1}H-NMR spectroscopic study of cationic intermediates in solvent and oil constituents of the catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene

Using ^{1}H-NMR spectroscopy, mutual transformations and stability of cationic complexes $[(Cp_2ZrMe)_2(\mu\text{-Me})]^+[B(C_6F_5)_4]^-$ (**1**), $[Cp_2ZrMe^+\cdots B(C_6F_5)_4^-]$ (**2**) and $[Cp_2Zr(\mu\text{-Me})_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**3**) formed in catalytic systems $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ and $Cp_2ZrMe_2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ in benzene were studied both in the solution and in the oil deposit formed whenever the total zirconocene concentration is high enough. It was shown that at high zirconocene concentrations, the decay rate of complexes **1** and **2** in the oil constituent of the reaction mixture is at least a factor ten lower than that in the solvent.



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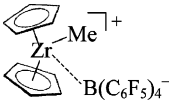

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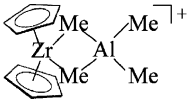


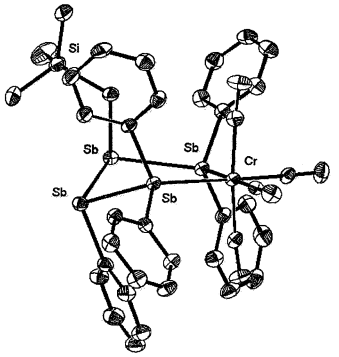
3

Hans Joachim Breunig, Ioan Ghesner, Mihaiela Emilia Ghesner, Enno Lork

J. of Organomet. Chem. 677 (2003) 15

Syntheses and coordination chemistry of di-, tri-, and tetrastibanes, $R_2Sb(SbR')_nSbR_2$ ($n = 0, 1, 2$)

Antimony chain compounds, ${}^{t}Bu_2Sb(SbMe)_nSb{}^{t}Bu_2$ [$n = 0,1,2$], $Mes_2Sb(SbPh)_n\text{-}SbMes_2$ [$n = 1,2$] and complexes with chain ligands, $[(CO)_5Cr]_2(Me_2Sb)_2$, $[Cr(CO)_4(Me_2\text{-}Sb(SbR)_2SbMe_2)]$, $[Cr(CO)_4(Ph_2Sb\text{–}SbPh\text{–}SbR\text{–}SbPh_2)]$ ($R = CH_2SiMe_3$) are reported.



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**Vera I. Maslennikova, Olga S. Serkova,
Larisa K. Vasyanina,
Konstantin A. Lyssenko,
Mikhail Yu. Antipin, Eduard E. Nifantyev**

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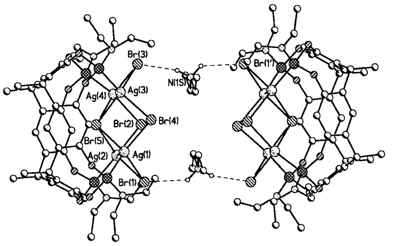
First heterobimetallic complexes of phosphocavitands

The synthesis and characterisation were described for tetranuclear phosphocavitand complexes **4**, where each phosphorus atom is coordinated to the silver atom, and tetranuclear heterobimetallic phosphocavitand complexes **6**, in which only three phosphorus atoms are coordinated to silver and the fourth phosphorus atom is coordinated to molybdenum.

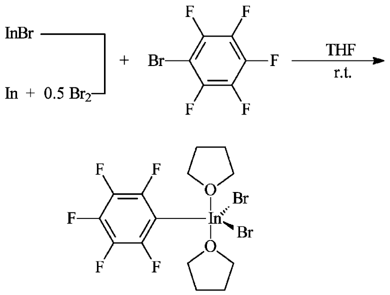


Wieland Tyrra, Mathias S. Wickleder

J. of Organomet. Chem. 677 (2003) 28

On the chemistry of fluoroorgano derivatives of Group 13 elements
Part 3. Syntheses of pentafluorophenylindium dibromide, $In(C_6F_5)Br_2 \cdot 2D$ ($D = THF, C_5H_5N$), and related compounds—single crystal structure analyses of $In(C_6F_5)Br_2 \cdot 2THF$ and $In(acac)Br_2 \cdot 2THF$

The title compound is formed according to the above equation. Subsequent reactions gave compounds such as $In(C_6F_5)_3 \cdot DMAP$ and $In(acac)Br_2 \cdot 2THF$.

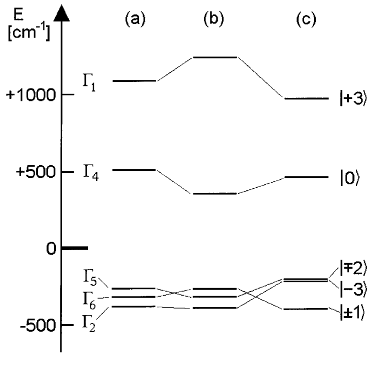


**Hanns-Dieter Amberger, Hauke Reddmann,
Hans H. Karsch, Volker W. Graf,
Changtao Qian, Bing Wang**

J. of Organomet. Chem. 677 (2003) 35

Zur Elektronenstruktur metallorganischer Komplexe der f-Elemente LVI. Parametrische Analyse der Kristallfeld-Aufspaltungsmuster pseudo-trigonal-bipyramidal koordinierter O- und P-donorfunktionalisierter Ethylcyclopentadienyl-Komplexe des Neodym(III)

The absorption spectra of pseudo trigonal bipyramidally coordinated $Nd(\eta^5\text{-}C_5H_4CH_2CH_2OMe)_3$ (**1**) and $Nd(\eta^5\text{-}C_5H_4CH_2CH_2PMe_2)_3$ (**2**) have been measured at room and low temperatures. From the spectra obtained, truncated crystal field (CF) splitting patterns of these compounds are derived, and simulated by fitting the parameters of a phenomenological Hamiltonian. For 55 and 53 assignments, respectively, reduced r.m.s. deviations of 31 and 23 cm^{-1} are achieved for complexes **1** and **2**. The parameters derived allow the estimation of the crystal field strength experienced by the Nd^{3+} central ions of compounds **1** and **2**, the insertion of these complexes into truncated empirical nephelauxetic and relativistic nephelauxetic series, and the setup of their experimentally-based non-relativistic and relativistic molecular orbital schemes in the f range.



**Christoph C. Karl, Stefan Joneleit,
Mokhles M. Abd-Elzaher,
Bernhard Weibert, Helmut Fischer**

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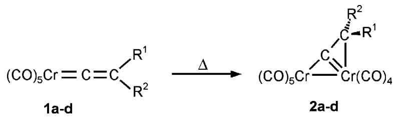
A unusual bridging mode of vinylidene ligands in nonacarbonyl(vinylidene)dichromium complexes

Thermolysis of the pentacarbonyl(vinylidene)chromium complexes **1a**–**d** ($C(R^1)R^2 = CMe_2$ (**a**), $C(CH_2)_5$ (**b**), C(Et)Me (**c**), $C({}^tBu)Me$ (**d**)) affords the binuclear, vinylidene-bridged nonacarbonyldichromium complexes **2a**–**d**. The solid-state structures of **2a** and **2d** prove the unusual $\mu\text{-}\eta^1,\eta^2\text{-}C{=}C(R^1)R^2$ bonding mode.



Ali Mechria, Claude Bavoux, Faouzi Bouachir

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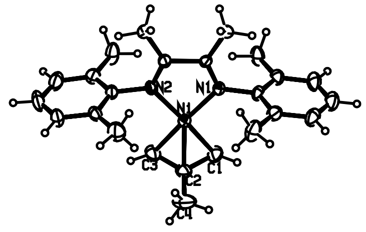
Cationic methallylnickel(II) complexes with α-diimine ligands: synthesis and X-ray structure

The α-diimine ligands Ar–N=C(R)C(R)=N–Ar react with $Ni(COD)_2$ (**2**) in the presence of methallyloxyphosphonium hexafluorophosphate $[CH_2{=}C(Me)CH_2{-}O{-}P(NMe_2)_3]^+ \cdot PF_6^-$ (**3**) to give new cationic methallyl complexes of nickel(II) with α-diimine ligands **4a** and **4b**.



Yongbao Zhu, Beth R. Cameron, Renato T. Skerlj

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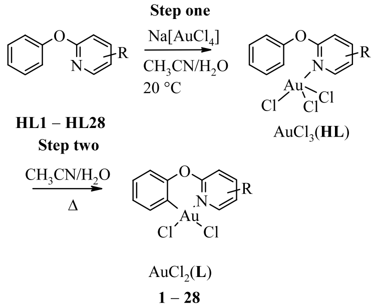
Cycloauration of substituted 2-phenoxypyridine derivatives and X-ray crystal structure of gold, dichloro[2-[[5-[(cyclopentylamino)carbonyl]-2-pyridinyl-κ*N*]oxy]phenyl-κ*C*]-, (*SP*-4-3)-

Direct cycloauration of substituted 2-phenoxypyridines (**HL**) was carried out in an CH_3CN/H_2O medium, leading to isolation of cycloaurated compounds $AuCl_2$(**L**) with alkyl, substituted alkyl, phenyl, halo, ester or amido substituted on the pyridine ligand.



R = alkyl, substuted alkyl, phenyl, halo, ester or amido group.

Elena N. Suslova, Aleksandr I. Albanov, Bagrat A. Shainyan

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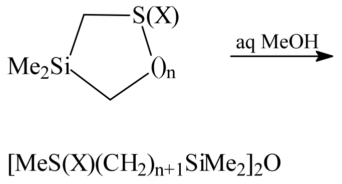
Synthesis and relative stability of five- and six-membered *S*-functional derivatives of 1,3-thiasilacycloalkanes

S-Functional derivatives of five- and six-membered 1,3-thiasilacycloalkanes, namely *S*-oxides, *S*,*S*-dioxides, sulfimides, and sulfonium salts were prepared and their solvolytic stability examined in protic media. The ease of the ring opening by the solvolytic Si–C$_\alpha$ bond cleavage depends on the *S*-functionality and on the ring size. The order of the stability for the five-membered compounds is: sulfimide < sulfoxide < salt < sulfone. For the six-membered analogs it is different: sulfonium salt < sulfimide < sulfoxide ≤ sulfone.



n = 1, 2; X = O, O_2, NSO_2Ph, Me.

Fung-E Hong, Chin-Pei Chang, Hao Chang, Yi-Luen Huang, Yu-Chang Chang

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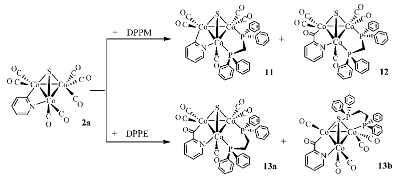
Reactions of sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) with diphosphine ligands and (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) towards diphenyl-2-pyridylphosphine

Treatment of sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) (**2a**) with bis(diphenylphosphino)methane (DPPM) or bis(diphenylphosphino)ethane (DPPE) under mild reaction condition gave DPPM or DPPE bridged complexes **11** and **12** or **13a** and **13b**. The X-ray structural analyses of **12** and **13b** revealed that carbonylation occurred at the Co–C(pyridyl) bond.



William J. Evans, Benjamin L. Davis, Gregory W. Nyce, Jeremy M. Perotti, Joseph W. Ziller

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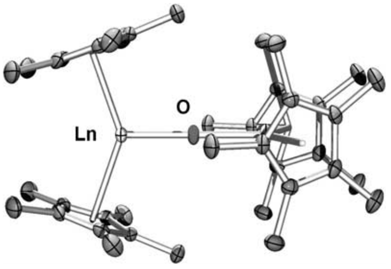
Structural studies of lanthanide and yttrium metallocene oxides

The high reactivity of the sterically crowded $(C_5Me_4R)_3Ln$ complexes has provided five new $[(C_5Me_4R)_2Ln]_2(\mu\text{-}O)$ complexes that have Ln–O–Ln angles between 173 and 180°. The effect of metal and cyclopentadienyl ring size on Ln–O bond distances and Ln–O–Ln angles in this class of complexes is presented.



Gantasala N. Srinivas, Liwen Yu, M. Schwartz

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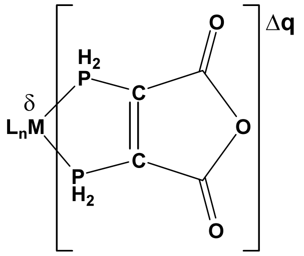
Theoretical determination of δ in $18+\delta$ organometallic complexes

The $18+\delta$ character ($\delta+\Delta q=1e$) of the 19e organometallic complexes (M = Co, Fe and Re) were studied using density functional theory methods. The δ values are estimated using computed IR frequencies as well as natural charges. The predicted δ values have shown that only 10–25% of the 19th electron is localized on the metal and the remaining charge is delocalized onto the chelating ligand.



Meritxell DelaVarga, Ramon Costa, Roser Reina, Alberto Núñez, Miguel Ángel Maestro, José Mahía

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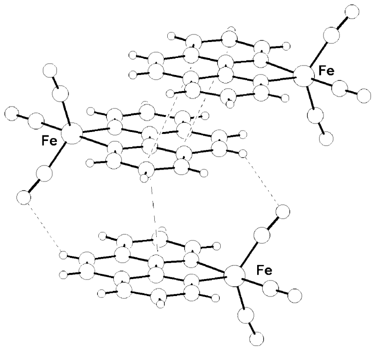
Iron carbonyl complexes of heterocyclic α-diimines: systematic synthesis, crystal structures of $[Fe(CO)_3(L)]$ and $[Fe_2(CO)_7(L)]$ (L = 2,2′-bipyridine and 1,10-phenantroline), and their AIM analysis

We investigated the reaction of $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ in tetrahydrofuran with 2,2′-bipyridine (bpy), 1,10-phenantroline (phen) and their commercial dimethyl derivatives. In all cases, mixtures containing both mono-iron $[Fe(CO)_3(NN)]$ and di-iron $[Fe_2(CO)_7(NN)]$ derivatives (NN = α-diimine) were obtained. A reaction mechanism is proposed to explain this behaviour. The crystal structures of compounds $[Fe(CO)_3(bpy)]$, $[Fe(CO)_3(phen)]$, $[Fe_2(CO)_7(bpy)]$ and $[Fe_2(CO)_7(phen)]$ at 173 K were described, and a comparative theoretical study was performed on them in order to determine the existence of Fe–Fe bond in the dinuclear complexes.



Zbigniew Grobelny

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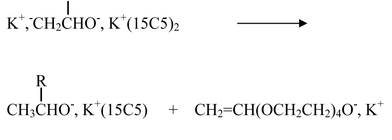
The behaviour of organopotassium intermediates derived from oxiranes under the influence of alkalide K^-, K^+(15-crown-5)$_2$

Organopotassium compounds are the intermediate products of K^-, K^+(15-crown-5)$_2$ reaction with monosubstituted oxiranes. A part of them opens the crown ether ring. Potassium tetraethylene glycoxide vinyl ether is one of the reaction products.



$$K^+,{}^-CH_2\overset{R}{C}HO^-, K^+(15C5)_2 \longrightarrow CH_3\overset{R}{C}HO^-, K^+(15C5) + CH_2{=}CH(OCH_2CH_2)_4O^-, K^+$$

Michael P. Coogan, Lisa S. Stanton, Thilo Walther

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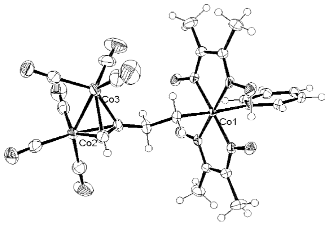
Dicobalt hexacarbonyl-3-butyn-1-yl cobaloxime: synthesis X-ray crystal structure and reactions of the first combined cobaloxime–dicobalt hexacarbonyl alkyne complex

Reaction of but-3-yn-1-ol *p*-toluene sulphonate with the nucleophile generated upon reduction of Co(DMGH)$_2$(Py) with sodium borohydride gives but-3-yn-1-yl cobaloxime. Treatment of this alkyne with dicobalt octacarbonyl gives the tricobalt mixed cobaloxime–cobalt carbonyl system but-3-yn-1-yl cobaloxime dicobalt hexacarbonyl, the first of its kind to be reported and crystallographically characterised.



Young Chul Won, Heon Yong Kwon, Bun Yeoul Lee, Young-Whan Park

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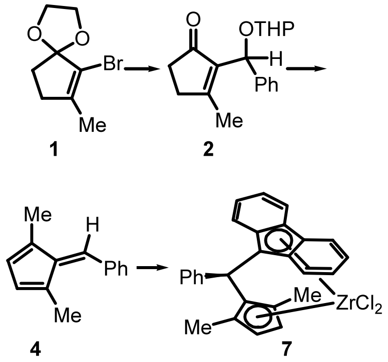
Fulvene having substituents only on 1-, 4-, and 6-positions: a key intermediate for novel *ansa*-metallocene complexes

A synthetic route for 1,4-dimethyl-6-phenylfulvene (**4**) and 1,4-dimethyl-6,6-diphenylfulvene (**5**), which are characteristic in that they have substituents only on 1-, 4-, and 6-positions, is developed and synthesis of an *ansa*-metallocene complex, [Ph(H)C(fluorenyl)(1,3-Me$_2$Cp)]ZrCl$_2$ (**7**), is demonstrated using **4**. Much higher comonomer incorporation in ethylene/1-hexene copolymerization and dramatic increase of molecular weight in 1-hexene polymerization are observed with **7** when the reactivity compared with that of the one not having methyl substituents, [Ph(H)C(fluorenyl)(Cp)]ZrCl$_2$.



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