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Journal of Organometallic Chemistry

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Contents

Regular Papers

Erik Janes, Karl Heinz Dötz

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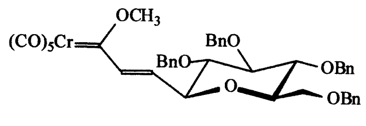
Organotransition metal modified sugars Part 23. Synthesis of vinylcarbene chromium complexes containing a *C*-monosaccharide ligand

Pentacarbonylmethoxy(methyl)carbene]-chromium undergoes a *trans*-selective aldol condensation with formyl glycosides to give *C*-glycosidic vinylcarbene complexes as a novel type of organometallic *C*-glycosides.



Mokhles M. Abd-Elzaher, Bernhard Weibert, Helmut Fischer

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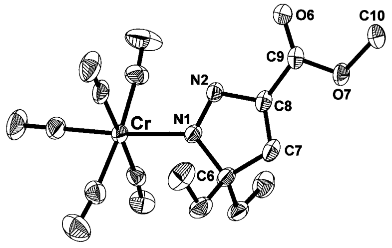
Addition of diazoalkanes to alkyne(pentacarbonyl) –chromium and –tungsten — formation of 3*H*-pyrazole complexes

Whereas alcohols, ynamines, and imines add to the vinylidene tautomer of the equilibrium terminal alkyne(pentacarbonyl) complex/vinylidene(pentacarbonyl) complex, diazoalkanes react with the alkyne tautomer giving 3*H*-pyrazole complexes, $[(CO)_5M-\overline{N{=}N-C(R){=}C(H)-C}(R^1)(R^2)]$.



Anna C. Hillier, Thomas Fox, Helmut W. Schmalle, Heinz Berke

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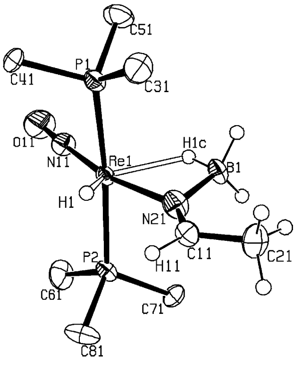
Borohydride reduction of a rhenium-bound acetonitrile: an example of a chelating iminoborane ligand at a low valent metal center

The reduction of acetonitrile by $[Bu_4N]BH_4$ at the rhenium(I) metal center in $ReCl_2(PMe_3)_2(CH_3CN)NO$ to afford $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (**2**) is reported. The coordinated iminoborane moiety is an intermediate in acetonitrile reduction. A mechanism is proposed for its formation. Further reaction with a hydride source ($LiBH_4$, $NaBH_4$, $LiHBEt_3$) results in replacement of chloride with hydride to give $ReH\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (**3**), together with varying proportions of $ReH_2(PMe_3)_3NO$ (**4**).



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H. Schmidt, Y. Shen, M. Leschke, Th. Haase, K. Kohse-Höinghaus, H. Lang

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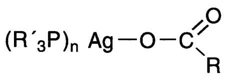
Phosphanstabilisierte Silber(I)–Carboxylate: Synthese und Verwendung in der Silber-CVD

The synthesis of complexes of type $[(R'_3P)_n$-AgOC(O)R] which can be used as precursors for the deposition of silver on TiN-coated SiO_2 wafers by the chemical vapour deposition process is described.



$(R'_3P)_n\,Ag-O-C(=O)R$

Youngjo Kim, John G. Verkade

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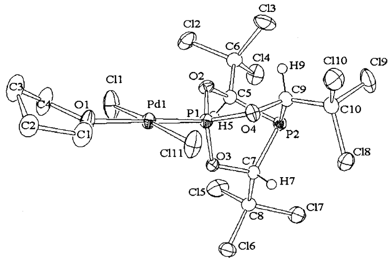
Synthesis and X-ray structure of palladium dichloride complexed with THF and 2,6,7-trioxa-3,5,8-tris(trichloromethyl)-1,4-diphosphabicyclo[2.2.2]octane

Palladium(II) dichloride containing both THF and the title bicyclic diphosphorus ligand **2** {i.e. $P[OCH(CCl_3)]_3P$} has been synthesized and characterized by spectroscopic methods including X-ray crystallography. This compound is the first example of a metal complex containing the novel ligand **2**. The X-ray structure of the complex reveals a virtually square-planar geometry around the palladium with *trans* oriented chlorine atoms and with **2** ligated by the PO_3 terminus.



Aibing Xia, Mary Jane Heeg, Charles H. Winter

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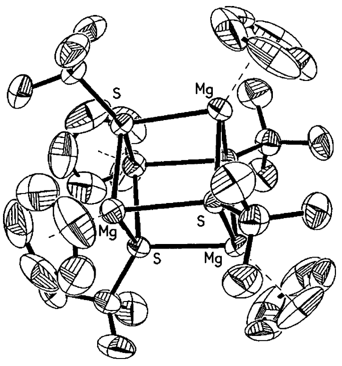
Synthesis and characterization of cyclopentadienyl thiolato complexes of magnesium

Treatment of magnesocene with alkanethiols in toluene affords the tetrameric thiolato complexes $[(\eta^5\text{-Cp})Mg(\mu_3\text{-SR})]_4$. Treatment of $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$ with tetrahydrofuran or 4-*tert*-butylpyridine afforded the dimeric complexes $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(L)]_2$. The molecular structures were determined by single crystal X-ray analyses.



Elena Lucenti, Elena Cariati, Claudia Dragonetti, Dominique Roberto

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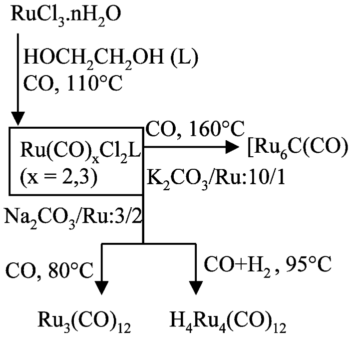
Reproducible high-yield syntheses of $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, and $[Ru_6C(CO)_{16}]^{2-}$ by a convenient two-step methodology involving controlled reduction in ethylene glycol of $RuCl_3 \cdot nH_2O$

$[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, and $[Ru_6C(CO)_{16}]^{2-}$ have been synthesized in reproducible high yields and under mild conditions (1 atm) by a two-step methodology involving (i) first carbonylation of $RuCl_3 \cdot nH_2O$ dissolved in ethylene glycol to give di- and tri-carbonyl ruthenium(II) species and (ii) addition of specific amounts of alkali carbonates and reductive carbonylation to give the desired ruthenium cluster.



Kesete Y. Ghebreyessus, John H. Nelson

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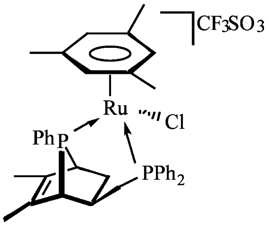
Conformationally rigid diphosphine arene–ruthenium(II) complexes as catalysts for transfer hydrogenation of ketones

Conformationally rigid complexes of the type $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Ru(P\text{–}P)Cl]CF_3SO_3$ (**3**) (where P–P is 2-diphenylphosphino-5,6-dimethyl-7-phenyl-7-phosphabicyclo-[2.2.1]hept-5-ene) were synthesized from $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)RuCl_2(DMPP)]$ (DMPP = 3,4-dimethyl-1-phenylphosphole) and diphenylvinylphosphine (DPVP) in the presence of $AgCF_3SO_3$. These complexes were found to be quite efficient catalysts for the transfer hydrogenation of ketones in 2-propanol in the presence of KOH.



Liang-Fu Tang, Jian-Fang Chai, Shu-Bin Zhao, Ji-Tao Wang

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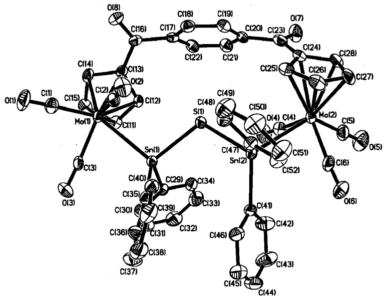
Tetranuclear heterodimetallic metallamacrocyles with M–Sn(IV) (M = Mo or W) bonds. Crystal structures of $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$ and $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2CH_2\}$

Treatment of tetranuclear complexes $p\text{-}[(Ph_2BrSn)(CO)_3MC_5H_4C(O)]_2C_6H_4$ with $Na_2S\cdot 9H_2O$ yielded novel metallamacrocyles $\{p\text{-}[(CO)_3MC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$. The reaction of $Na_2\{[p\text{-}(CO)_3MC_5H_4C(O)]_2C_6H_4\}$ with $CH_2(SnPh_2Br)$ also gave metallamacrocyclic complexes $\{p\text{-}[(CO)_3MC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2CH_2\}$ (M = Mo or W).



Slawomir Szumacher, Izabela Madura, Janusz Zachara, Antoni Ryszard Kunicki, Artur Cebulski, Lucjan Jerzykiewicz

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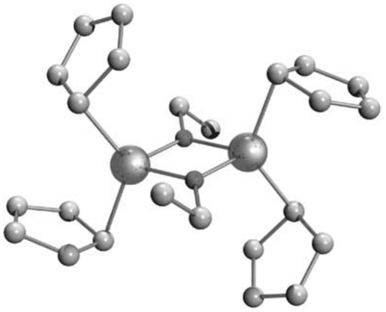
Influence of alkoxy ligands on the Cp–Al bonding mode in $[Cp_2Al\text{-}\mu\text{-}OR]_2$ from X-ray crystallographic and ^{27}Al-NMR spectroscopic solution studies

The dicyclopentadienylaluminium alkoxides of general formula $[Cp_2Al\text{-}\mu\text{-}OR]_2$ where R = Me, Et, *n*Bu, *i*Bu, CH_2*t*Bu, *s*Bu, CH_2Ph, C_6H_4-4-*t*Bu (**1**–**8**) were synthesised and structurally characterised by multinuclear NMR and compounds **2**, **5**, **6** by X-ray crystallography as well. The analysis of Cp–Al bond mode in dicyclopentadienylaluminium alkoxides regarding the steric demands of alkoxy groups was presented and the meaningful correlation between Cp ring-slippage and ^{27}Al-NMR chemical shifts was observed.



Bernd Wrackmeyer, Heidi E. Maisel, Wolfgang Milius, Moazzam H. Bhatti, Saqib Ali

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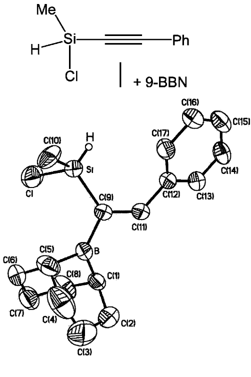
Hydroboration of alkyn-1-yl(methyl)silanes bearing functional substituents at silicon

In most cases, alkyn-1-yl(methyl)silanes $Me_2(H)Si\text{–}C{\equiv}C\text{–}R$, $Me(H)(Cl)Si\text{–}C{\equiv}C\text{–}R$, and $Me_2(Cl)Si\text{–}C{\equiv}C\text{–}R$ (R = Bu, ^{t}Bu, Ph, $SiMe_3$) react with 9-bora-bicyclo[3.3.1]nonane (9-BBN) by 1,2-*cis*-hydro-boration to give selectively alkenylsilanes with the boryl group in geminal position with respect to the silyl group bearing functional substituents. All products were characterised by NMR spectra (^{1}H-, ^{11}B-, ^{13}C- and ^{29}Si-NMR) in solution, and the molecular structures of two alkenes were determined by X-ray analysis.



Kannan Raghuraman,
Setharampattu S. Krishnamurthy,
Munirathinam Nethaji

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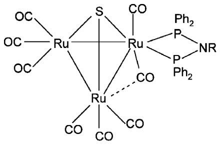
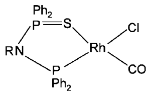
Late transition metal complexes derived from diphosphazane monosulfide ligands: X-ray crystal structures of $[Ru_3(\mu\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN((S)\text{-}{*}CHMePh)PPh_2\text{-}\kappa^2P,P\}]$ and $[Rh(CO)Cl\{Ph_2PN((S)\text{-}{*}CHMePh)P(S)Ph_2\}\text{-}\kappa^2P,S]$
Part 16. Organometallic chemistry of diphosphazanes

The reactions of diphosphazane monosulfides with $[Ru_3(CO)_{12}]$ result in the desulfurisation of the ligands to yield sulfido monocapped triruthenium clusters. Rhodium(chloro)(carbonyl) and palladium and platinum chloride chelate complexes of diphosphazane monosulfides have also been synthesized and structurally characterized.



R = (S)-*CHMePh (3)
R = CHMe$_2$ (4)



R = (S)-*CHMePh (5),
R = CHMe$_2$ (6)

Anthony G. Avent, Peter B. Hitchcock,
G. Jeffery Leigh, Maria Togrou

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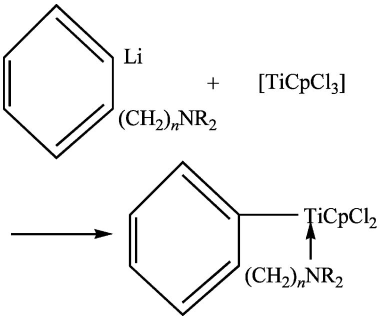
The lithiation of arylamines and the preparation of cyclopentadienyltitanium(IV) arylaminate complexes

Replacement of bromine in $1,2\text{-}C_6H_4Br\text{-}[(CH_2)_nNR_2]$ ($n = 1$ or 2, R = alkyl substituents) using butyl lithium can be quite clean, yielding tetrameric lithium compounds. These relatively unstable compounds can be used to make new titanium derivatives, and they also potentiate vanadium(II) to dinitrogen uptake, though these products have not been characterised.



Peter B. Hitchcock, G. Jeffery Leigh,
Maria Togrou

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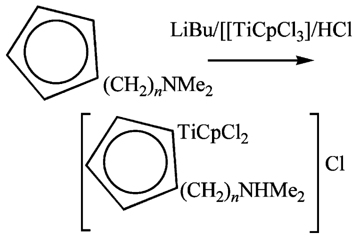
Synthesis of titanium(IV) (cyclopentadienylalkyl)aminate complexes

The cyclopentadienylaminates generated in situ do not potentiate vanadium(II) to dinitrogen uptake. They and their hydrochlorides can form adducts with compounds of titanium(IV), in which they appear to be monodentate.



Gwion J. Harfoot, Brian K. Nicholson

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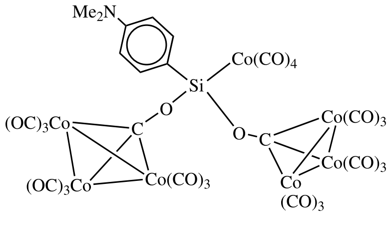
Anomalous reaction of an aryl silane with $Co_2(CO)_8$; characterisation of $Me_2NC_6H_4Si[Co(CO)_4][OCCo_3(CO)_9]_2$

Reaction of $Me_2NC_6H_4SiH_3$ with $Co_2(CO)_8$ gives $Me_2NC_6H_4Si[Co(CO)_4][OCCo_3(CO)_9]_2$ with a mixture of Si–Co and Si–O bonds.



Mala Nath, Sandeep Pokharia, George Eng, Xueqing Song, Ashok Kumar

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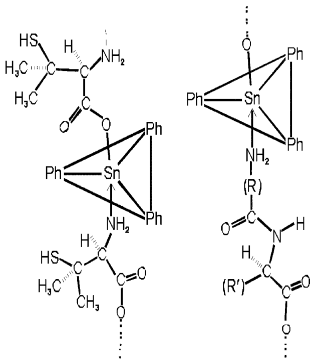
Comparative study of structure–activity relationship of di- and tri-organotin(IV) derivatives of amino acid and peptides

The reactions of di- and tri-organotin(IV) with D-penicillamine, L-carnosine and triglycine afforded various five-coordinate complexes depending upon reaction conditions. All the complexes have a distorted trigonal bipyramidal environment around tin with intermolecular association through H-bonding. Some of the complexes show good anti-inflammatory and cardiovascular activities.



Shoken Nagao, Hidetake Seino, Masanobu Hidai, Yasushi Mizobe

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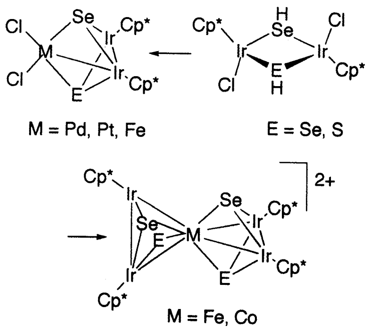
Syntheses of a series of trinuclear MIr_2 or pentanuclear MIr_4 bimetallic bis(selenido) and selenido–sulfido clusters (M = Pd, Pt, Fe, Co) from diiridium μ-bis(hydroselenido) and μ-hydroselenido–hydrosulfido complexes $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(\mu\text{-}SeH)(\mu\text{-}EH)]$ (E = Se, S)

A series of trinuclear and pentanuclear bis(selenido) or selenido–sulfido clusters containing $Ir_2M(\mu_3\text{-}Se)(\mu_3\text{-}E)$ (M = Pd, Pt, Fe) or $Ir_4M(\mu_3\text{-}Se)_2(\mu_3\text{-}E)_2$ (M = Fe, Co) cores has been derivatized from diiridium complexes $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(\mu\text{-}SeH)(\mu\text{-}EH)]$ (E = Se, S).

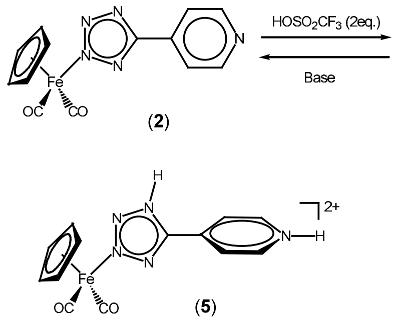


Antonio Palazzi, Stefano Stagni, Simona Selva, Magda Monari

J. of Organomet. Chem. 669 (2003) 135

Synthesis and reactivity of a new Fe(II) 5-(4-pyridyl)-tetrazolate complex and X-ray structure of its doubly protonated derivative.

The synthesis and the spectroscopic characterization (IR; ^1H- and ^{13}C-NMR) of the new complex $[CpFe(CO)_2(N_4C{-}C_5H_4N)]$ (**2**) is reported. The reactivity of **2** toward electrophilic species is also discussed. Complex **2** reacts with two equivalents of triflic acid to afford the diprotonated complex **5**, whose structural characterization is described.



Kazuya Kubo, Motohiro Nakano, Hatsue Tamura, Gen-etsu Matsubayashi, Masami Nakamoto

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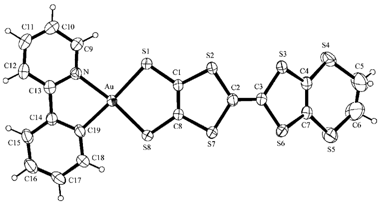
Preparation and oxidation of polarized Au(III) complexes having both the *C*-deprotonated-2-phenylpyridine (ppy) and a sulfur-rich dithiolate ligand and X-ray crystal structure of $[Au(\eta^2\text{-}C,N\text{-ppy})(\eta^2\text{-}S,S\text{-}C_8H_4S_8)]\cdot 0.5DMF$

Polarized Au(III) complexes having both the *C*-deprotonated-2-phenylpyridine (ppy) and a sulfur-rich ditholate ligand, $[Au(ppy)(C_8H_4S_8)]$ and $[Au(ppy)((C_{10}H_{21})_2C_6S_8)]$ were prepared. The X-ray crystal structure of the former complex was clarified. They exhibit first oxidation potentials of −0.06 to +0.20 V (vs. Ag/Ag^+) due to the dithiolate ligand-centered oxidation. These complexes were reacted with iodine or TCNQ to afford the oxidized $[Au(ppy)(C_8H_4S_8$ or $(C_{10}H_{21})_2C_6S_8)]^{n+}$ $(0.5 \leq n < 1)$ species containing the I_3^- ion or the $TCNQ^{\bullet -}$ radical anion, which exhibited electrical conductivities of 2.0×10^{-2}–4.0×10^{-2} S cm^{-1} measured for compacted pellets at room temperature.



Jens Beckmann, Dainis Dakternieks, Andrew Duthie, Naomi A. Smith

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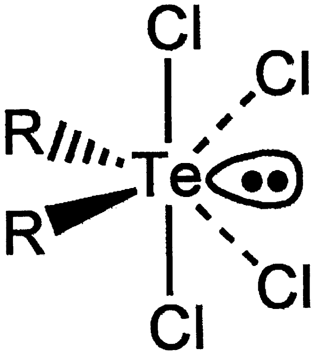
Secondary bonding in *para*-substituted diphenyltellurium dichlorides (p-$XC_6H_4)_2$-$TeCl_2$ (X = H, Me, MeO) probed by ^{125}Te MAS NMR spectroscopy. Crystal and molecular structure of (p-$MeC_6H_4)_2TeCl_2$

^{125}Te MAS NMR sheilding anisotropy (SA) was used to study the supramolecular structures of diorganotellurium dichlorides (p-$XC_6H_5)_2TeCl_2$ (X = H, Me, MeO). The anisotropy (ξ) and asymmetry (η) were found to be more sensitive to structural changes than the isotropic chemical shift (δ_{iso}).



Alan R. Bassindale, Yuri I. Baukov, Moheswar Borbaruah, Simon J. Glynn, Vadim V. Negrebetsky, David J. Parker, Peter G. Taylor, Robert Turtle

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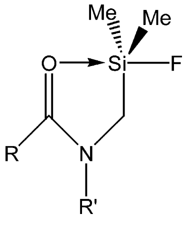
Modelling nucleophilic substitution at silicon using solution ^{19}F-NMR chemical shift, $^1J_{Si-F}$ and $^2J_{C-F}$ coupling constant data of pentacoordinate silicon compounds. Correlation with other magnetic nuclei and X-ray structures

Solution $^1J_{Si-F}$ and $^2J_{C-F}$ NMR coupling constant and ^{19}F-NMR chemical shift data have been analysed for a series of pentacoordinate silyl monofluoride complexes used to model nucleophilic substitution at silicon. Patterns in the data reveal strong correlations between both coupling constants and ^{19}F-NMR chemical shifts and the degree of substitution displayed by each.



Amparo Caubet, Concepción López, Xavier Solans, Mercè Font-Bardía

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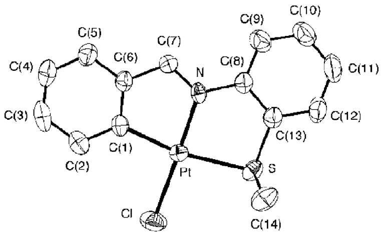
Synthesis, characterisation and study of the first luminescent platinum(II) compound with a $[C,N,S]^-$ terdentate ligand. X-ray crystal structure of $[Pt\{C_6H_4-CH=N-(C_6H_4-2\text{-}SMe)\}Cl]$

A comparative study of the reactivity of ligand $C_6H_5-CH=N-(C_6H_4-2\text{-}SMe)$ with *cis*-$[PtCl_2(DMSO)_2]$ or *cis*-$[PtCl_2(PhCN)_2]$ is reported. These studies have allowed us to prepare and characterise the novel, cycloplatinated compound $[Pt\{C_6H_4-CH=N-(C_6H_4-2\text{-}SMe)\}Cl]$ containing a terdentate $[C,N,S]^-$ group. Studies based on its spectroscopic properties as well as its reactivity versus PPh_3 are described.



Antoni Solsona, Joan Suades, René Mathieu

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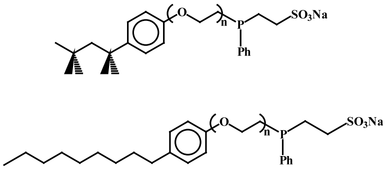
Hydridorhodium(I) complexes with amphiphilic polyether phosphines
NMR study and biphasic hydroformylation of 1-octene

The biphasic rhodium-catalysed hydroformylation of 1-octene with water-soluble amphiphilic phosphines with the general formula $4\text{-}(R)C_6H_4(OCH_2CH_2)_nP(Ph)CH_2$-$CH_2SO_3Na$ (R = 2,2,4,4-tetramethylbutyl, n-octyl, $\bar{n}$ = 1.4–11) was studied. Ligands with the shorter polyether chain led to the higher conversion. This result is ascribed to the ability of these ligands to increase metal concentration in the organic phase. The hydridorhodium(I) complexes with the amphiphilic phosphines were studied by NMR methods using related neutral ligands as model compounds.



Hsiu-Chi Liang, Ying-Yann Wu, Fang-Chu Chang, Pang-Yen Yang, Jhy-Der Chen, Ju-Chun Wang

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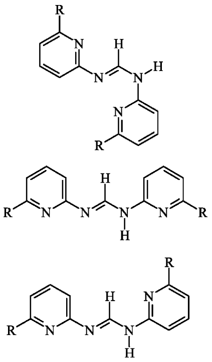
Synthesis and X-ray structures of some metal carbonyl complexes containing dipyridylformamidine ligands

Five metal carbonyl complexes of types $ReBr(CO)_3L$ (L = HDpyF, **1**; L = HDMepyF, **2**) and $M(CO)_4(L)$ (M = Mo, L = HDpyF, **3**; M = Mo, L = HDMepyF, **4**; M = W, L = HDMepyF, **5**) are reported, where HDpyF is *N*,*N′*-di(2-pyridyl)formamidine and HDMepyF is *N*,*N′*-di(6-methyl-2-pyridyl)formamidine, respectively. The neutral dipyridylformamidine ligands in **1** and **2** adopt the *s-cis-syn-s-cis* (top) and *s-trans-anti-s-trans* (middle) conformations, respectively, while those in complexes **3**–**5** adopt the *s-trans-anti-s-cis* (bottom) conformation.



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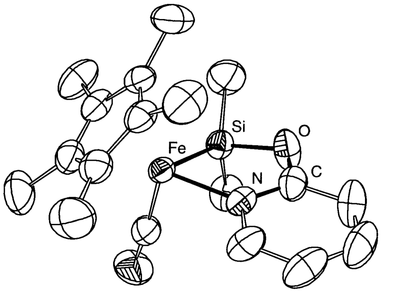
Synthesis, structure, and reactivity of novel iron(II) complexes with a five-membered chelate ligand $\kappa^2(Si,N)$-$SiMe_2O(2$-$C_5H_4N)$

Photolysis of $Cp'(CO)_2FeSiMe_2O(2$-$C_5H_4N)$ (**1**, $Cp' = \eta^5$-C_5H_5, η^5-C_5Me_5) afforded thermally stable complexes $Cp'(CO)Fe[\kappa^2(Si,N)$-$SiMe_2O(2$-$C_5H_4N)]$ (**2**), containing a five-membered chelate ring comprised of Fe, Si, O, C, and N. Studies on the reactions of **2** established that both Fe–Si bond and Fe–N bond in **2** are notably sturdy.



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The first example of a structurally characterized octahedral hydrotris(pyrazolyl)borate iron methyl complex

Visible light photolysis of the one-step prepared acetyl complex κ^3-$TpFe(CO)(PMe_3)(COMe)$ in toluene for 1 h afforded the first octahedral methyl-iron complex featuring the hydrotris(pyrazolyl)borate ligand $TpFe(CO)(PMe_3)Me$ in 80% yield. The latter has been fully characterized by conventional spectroscopies and by an X-ray diffraction analysis.