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Journal of Organometallic Chemistry

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Contents

Regular Papers

A.A.O. Sarhan, T. Izumi

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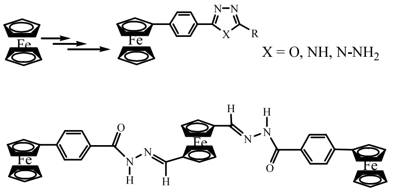
Design and synthesis of new functional compounds related to ferrocene bearing heterocyclic moieties
A new approach towards electron donor organic materials

The synthesis of heterocyclic systems incorporating more than one ferrocene unit was shown to be a facile and convenient route for the synthesis of new ferrocene-heterocycles.



Ming-Chang P. Yeh, Peng-Yu Sheu, Jin-Xuan Ho, Yi-Lin Chiang, Dai-Yu Chiu, U. Narasimha Rao

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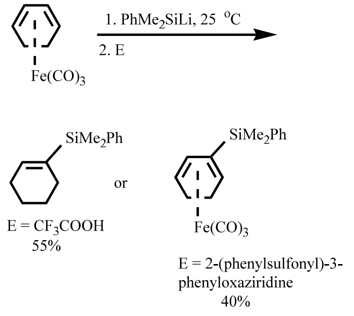
Addition reactions of lithiodimethylphenylsilane to (η^4-1,3-diene)-Fe(CO)$_3$ and (η^6-arene)Cr(CO)$_3$ complexes

Treatment of (η^4-cyclohexa-1,3-diene)Fe(CO)$_3$ complex with 1.2 equivalents of PhMe$_2$SiLi, followed by quenching reactive intermediates with CF$_3$COOH generates 1-dimethyl(phenyl)silylcyclohex-1-ene or with 2-(phenylsulfonyl)-3-phenyloxaziridine affords nucleophilic substituted iron–diene complexes. Additions of the silyl anion to (η^6-arene)Cr(CO)$_3$ and (η^6-cyclohepta-1,3,5-triene)Cr(CO)$_3$ complexes produce dienylsilanes after acid quenching.



Pietro Diversi, Marco Fontani, Melania Fuligni, Franco Laschi, Fabio Marchetti, Simona Matteoni, Calogero Pinzino, Piero Zanello

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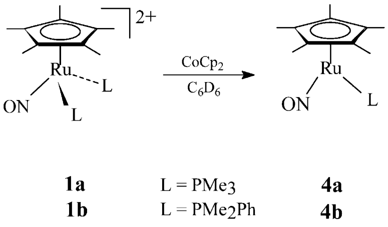
Reduction of the NO$^+$ ligand in 'half-sandwich' ruthenium derivatives

The electrochemical and chemical reduction of the ruthenium(II) nitrosyl dicationic [Ru(η^5-C$_5$Me$_5$)(NO)(L)$_2$] (BF$_4$)$_2$ (R = Me, L = PMe$_3$, **1a**; PMe$_2$Ph, **1b**; R = H, L = PPh$_3$, **2d**) and monocationic complexes [Ru(Me)Cp*(NO)(L)]BF$_4$ (Cp* = η^5-C$_5$Me$_5$, L = PMe$_3$, **3a**; PMe$_2$Ph, **3b**) has been studied by spectroscopic (IR, NMR, EPR) techniques. Chemical reduction is followed by the transformation of the intermediate leading to [Ru(η^5-C$_5$Me$_5$)(NO)(L)] (L = PMe$_3$, PMe$_2$Ph). The iridium nitrosyl complex [Ir(Me)$_2$Cp*(NO)]BF4 (**6**) was characterised structurally by X-ray diffraction.



Izabela Janowska, Janusz Zakrzewski, Keitaro Nakatani, Jacques A. Delaire, Marcin Palusiak, Marcin Walak, Henryk Scholl

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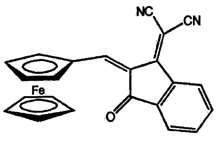
Ferrocenyl D-π-A chromophores containing 3-dicyanomethylidene-1-indanone and 1,3-bis(dicyanomethylidene)indane acceptor groups

The nonlinear optical properities of ferrocenyl D-π-A chromophores containing powerful3-dicyanomethylidene-1-indanone (**2**) and 1,3-bis(dicyanomethylidene)indane-based acceptor group (**3**) have been measured by the EFISH technique at 1.907 μm. The X-ray crystallographic study of 1 and 2 revealed significant distortions of the structure of the ferrocene moieties due to the contribution of a charge-separated η6-fulvene mesomeric form and important steric effects. The cyclic voltammetry data showed an anodic shift of the Fe(II)/Fe(III) oxidation potentials of **2** and **3** (in comparison to those of ferrocenecarboxaldehyde (**4**) and 2-(ferrocenylmethylidene)-1,3-indandione (**5**) and an approximately additive effect of the substitution of one or two carbonyl oxygens in **5** by the $C(CN)_2$ group.



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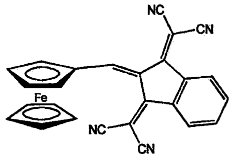

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Uwe Herzog, Horst Borrmann

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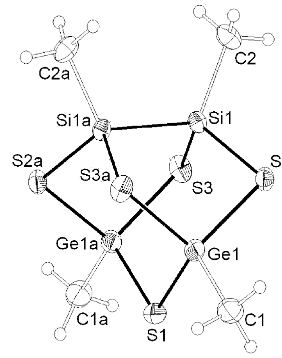
Heteronoradamantanes $Me_2Si_2(RM)_2E_5$ (RM = MeGe, PhSn; E = S, Se)

The reaction of a 1:2 molar mixture of 1,2-$Si_2Me_2Cl_4$ and $MeGeCl_3$ with H_2S/NEt_3 yielded $Me_2Si_2(MeGe)_2S_5$ (**1**), the first mixed silicon–germanium chalcogenide with a noradamantane-like structure, while the treatment of a 1:2 mixture of 1,2-$Si_2Me_2Cl_4$ and $PhSnCl_3$ with Li_2Se resulted in the formation of the first silicon- and tin-containing noradamantane $Me_2Si_2(PhSn)_2Se_5$ (**2**). Both compounds have been characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, ^{77}Se and ^{119}Sn). The molecular structure of **1** is reported.



Richard A. Varga, John E. Drake, Cristian Silvestru

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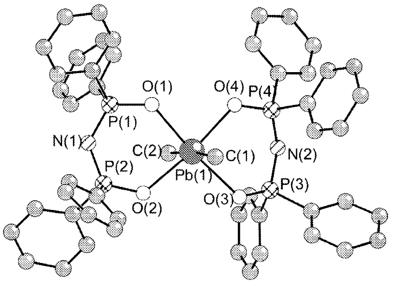
Organolead(IV) derivatives of oxophosphorus ligands.
X-ray structures of monomeric $R_2Pb[(OPPh_2)_2N]_2$ (R = Me, Ph) and tetrameric $[Me_3Pb(O_2PPh_2)]_4$

New organolead(IV) derivatives of phosphorus ligands were prepared and were characterized by IR and multinuclear NMR spectroscopy. The molecular structures of $R_2Pb[(OPPh_2)_2N]_2$ (R = Ph, Me) were determined by single-crystal X-ray diffraction. In both compounds the imidodiphosphinato ligands act as monometallic biconnective units, resulting in a *spiro*-bicyclic system with *six-membered* PbO_2P_2N rings. The coordination geometry around the metal atom is distorted octahedral, with C–Pb–C angles close to 180°. The crystal of the trimethyllead(IV) phosphinate contains discrete tetrameric units, $[Me_3Pb(O_2PPh_2)]_4$, with bridging phosphinato ligands, thus resulting in a *sixteen-membered* $Pb_4O_8P_4$ inorganic ring. The coordination geometry at lead atoms is distorted trigonal bipyramidal, with oxygen atoms in *trans* positions.



Joy L. Morgan, Amar H. Flood, Keith C. Gordon, Brian H. Robinson, Jim Simpson

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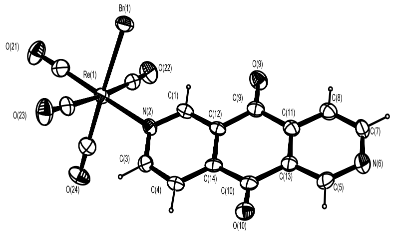
Rhenium carbonyl complexes of 2,6-diazaanthracene-9,10-dione(daad): spectroelectrochemistry of $BrRe(CO)_4daad$

Structural and spectroelectrochemical data are reported for the rhenium complex of daad, $BrRe(CO)_4daad$, **2**, and its radical anion, $\mathbf{2}^{\bullet -}$. $XRe(CO)_4daad$, $XRe(CO)_3(daad)_2$, $[XRe(CO)_3daad]_n$ (X = Br, Cl) were also identified.



Ramaswamy Murugavel,
Nallasamy Palanisami, Ray J. Butcher

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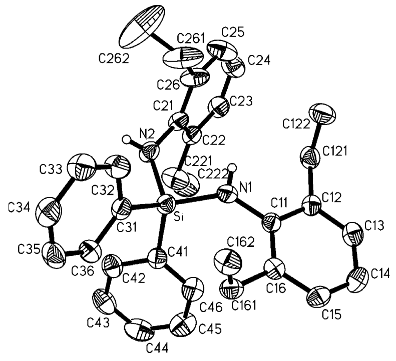
Synthesis, characterization and structures of diphenyldiaminosilanes bearing bulky substituents on nitrogen

Aminosilanes bearing bulky substituents on nitrogen centers, [(ArNH)$_2$SiPh$_2$] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), 2,4,6-Me$_3$C$_6$H$_2$ (**2**), 2,6-Et$_2$C$_6$H$_3$ (**3**)), are accessible in good yields by the addition of dichlorodiphenylsilane to the corresponding monolithiated substituted aniline. The molecules have a C_s symmetry due to the large steric crowding and the two N–H protons are approximately *trans* to each other.



Chang Bo Shim, Young Heui Kim,
Bun Yeoul Lee, Dong Mok Shin,
Young Keun Chung

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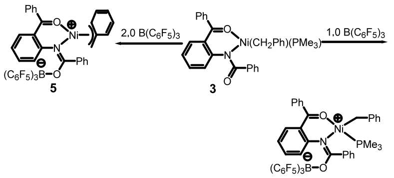
N-(2-Benzoylphenyl)benzamido nickel(II) complexes and polymerization reactivity

[*N*-(2-Benzoylphenyl)benzamido-κ^2*N,O*](η^1-benzyl)(trimethylphosphine)Ni(II) (**3**) is prepared. When **3** is treated with one or two equivalent(s) of B(C$_6$F$_5$)$_3$, one obtains a zwitterionic complex, [PhC(O)–C$_6$H$_4$–N=C(Ph)OB(C$_6$F$_5$)$_3$ - κ^2*N,O*]Ni(η^1 - CH$_2$C$_6$H$_5$)-(PMe$_3$) (**4**) or [PhC(O)–C$_6$H$_4$–N=C(Ph)-OB(C$_6$F$_5$)$_3$-κ^2*N,O*]Ni(η^3-CH$_2$C$_6$H$_5$) (**5**), respectively. Solid structures of **4** and **5** were determined by X-ray crystallography. When ethylene is added to **5**, low molecular weight polyethylene is obtained.



Youval Shvo, Revital Green

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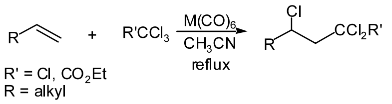
Addition of α-polyhalides to olefins under mild reaction conditions, catalyzed by Mo(CO)$_6$

Addition of α-polyhalides to the double bond in acyclic, and cyclic alkenes, as well as dienes, was carried out under mild condition using Mo(CO)$_6$ as efficient catalyst. The reaction solvent was refluxing acetonitrile, thus generating the reactive species in situ at low temperature. 1,5-cyclooctadiene gave a bicyclic addition product. A catalytic cycle with mechanistic implication has been proposed.



Jingyang Niu, Mingxue Li, Jingping Wang

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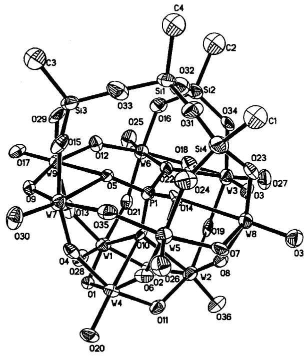
Organosilyl derivatives of trivacant tungstophosphate of general formula α-A-[PW$_9$O$_{34}$(RSiO)$_3$(RSi)]$^{3-}$
Synthesis and structure determination by X-ray crystallography

In the presence of NBu$^n_4$Br acting as phase-transfer reagent, organosilicon trichloride RSiCl$_3$ reacts in acetonitrile with the trivacant tungstophosphate sodium salt β-A-Na$_8$H[PW$_9$O$_{34}$]·24 H$_2$O to give hybrid organosilyl polyoxotungstate derivatives α – A – [NBu$^n_4$]$_3$[PW$_9$O$_{34}$(RSiO)$_3$(RSi)] (R = C$_2$H$_3$ or CH$_3$). Their crystal structures are determined by X-ray single crystal diffraction analysis.



Kathrin Junge, Günther Oehme, Axel Monsees, Thomas Riermeier, Uwe Dingerdissen, Matthias Beller

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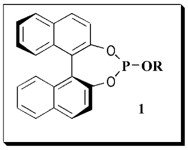
Synthesis of new chiral monodentate aminophosphinites and their use in catalytic asymmetric hydrogenations

A general synthesis of chiral 4-amino-4,5-dihydro-3H-dinaphthophosphepines **5a–f** is described.



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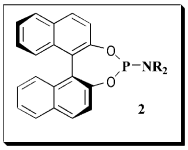

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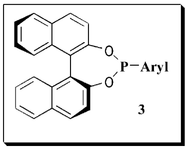

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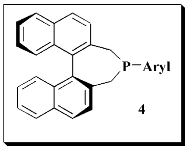

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John J. Esteb, Mandy Bergeron, Carol N. Dormady, James C.W. Chien, Marvin D. Rausch

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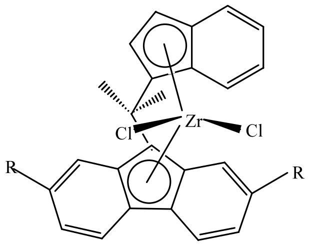
Novel C_1 symmetric zirconocenes containing substituted fluorenyl moieties for the polymerization of olefins

Four new asymmetric *ansa*-metallocenes containing a 2,7-disubstituted fluorenyl moiety and an indenyl moiety have been synthesized and studied as catalyst precursors for the polymerization of ethylene and propylene in the presence of methylaluminoxane (MAO).



R = 2,4,6-trimethylphenyl,
2,6-dimethylphenyl,
2-tolyl,
benzyl

Paromita Debroy, Sujit Roy

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Synthesis of ferrocenes with ene-terminus via water-promoted Barbier-like carbonyl allylation using bimetallic copper(II)/tin(II) reagent

γ-Regiospecific allylation of formylferrocene **1** and 1,1′-bis-formylferrocene **2** with allyl and substituted allyl bromides in the presence of stannous chloride dihydrate and catalytic cupric chloride in dichloromethane-water (1:1) afford the corresponding ferrocenyl dienes, homoallylic alcohols or oxa-bridged [3]ferrocenophanes depending on the substrate.