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Contents

Regular Papers

Paul D. Smith, Thomas Gelbrich, Michael B. Hursthouse

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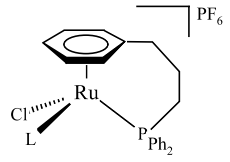
Cationic ruthenium(II) complexes containing a chelating η^1:η^6-phosphinoarene ligand; [RuCl(L)(PPh$_2$(CH$_2$)$_3$-η^6-C$_6$H$_5$)][PF$_6$] (L = P(OPh)$_3$, P(OMe)$_3$, PPh$_3$, PMe$_3$, NCMe, NC$_5$H$_5$)

Reactions of the ruthenium(II) complex [RuCl$_2$(PPh$_2$(CH$_2$)$_3$-η^6-C$_6$H$_5$)], containing a chelating η^1:η^6-phosphinoarene ligand, with NH$_4$PF$_6$, in the presence of a variety of neutral two-electron donor ligands, have yielded a series of new cationic complexes of the general formula [RuCl(L)(PPh$_2$-(CH$_2$)$_3$-η^6-C$_6$H$_5$)][PF$_6$] [L = P(OPh)$_3$, P(OMe)$_3$, PPh$_3$, PMe$_3$, NCMe, NC$_5$H$_5$]. In all cases ^{1}H- and ^{13}C{^{1}H}-NMR spectra were consistent with C_1 molecular symmetry at the ruthenium centre in solution. Assignment of the η^6-arene resonances has been achieved using a collection of 2D-NMR experiments, combined with a consideration of the relative magnetic anisotropic shielding and the *trans* influence effects attributed to the ligands L.



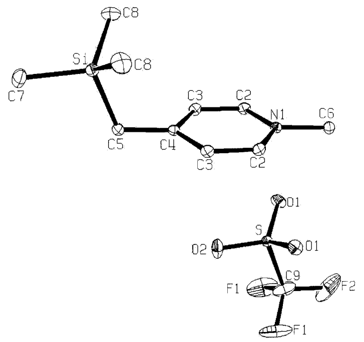
[L = P(OPh)$_3$, P(OMe)$_3$, PPh$_3$ PMe$_3$, NCMe, NC$_5$H$_5$]

Alan Happer, Janice N.G., Brett Pool, Jonathan White

J. of Organomet. Chem. 659 (2002) 10

Carbon–silicon hyperconjugation X-ray structural study of *N*-methyl-4-trimethylsilylmethylpyridinium triflate

Hyperconjugation between the CH$_2$–Si bond and the charged pyridinium π system in the *N*-methyl 4-trimethylsilylmethyl pyridinium ion, manifests in the crystal structure as lengthening of the CH$_2$–Si bond, shortening of the CH$_2$–C$_{ipso}$ bond and smaller but systematic effects on the C–C bond distances within the pyridinium ring.

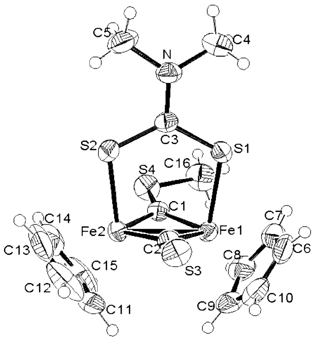


Vincenzo G. Albano, Silvia Bordoni, Luigi Busetto, Antonio Palazzi, Piera Sabatino, Valerio Zanotti

J. of Organomet. Chem. 659 (2002) 15

Dithiocarbamate derivatives of μ-thiocarbyne complexes: synthesis and X-ray molecular structure of [Fe$_2$(μ-CS)(μ-CSMe)(μ-S$_2$CNMe$_2$)Cp$_2$]

The reaction of sodium dithiocarbamate [Me$_2$NCS$_2$]Na with the diiron carbyne cation [Fe$_2$(μ-CS){μ-C(SMe)}Cp$_2$(CO)$_2$]$^+$ (**1**) forms $[\mathrm{Fe}\overline{\mathrm{Fe}(\mu\text{-CS})\{\mu\text{-C(SMe)}}\overline{\mathrm{S}}\mathrm{C(S)NMe_2}\}\text{-}\mathrm{Cp(CO)}]$ (**2**) and [Fe$_2$(μ-CS)(μ-CSMe){μ-S$_2$CNMe$_2$}Cp$_2$] (**3**). The latter can be obtained either by photochemical irradiation of **2** or by reacting [Me$_2$NCS$_2$]$^-$ with the di-acetonitrile derivative [Fe$_2$(μ-CS)(μ-CSMe)(NCMe)$_2$Cp$_2$]$^+$(**1a**). The X-ray structure of **3** exhibits three bridging ligands and features a very short Fe–Fe interaction [2.453(1) Å].



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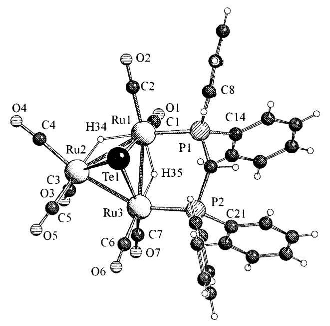
Martin Brandl, Henri Brunner, Helene Cattey, Yves Mugnier, Joachim Wachter, Manfred Zabel

J. of Organomet. Chem. 659 (2002) 22

Synthesis, reactivity and structures of ruthenium carbonyl clusters with telluride and hydride ligands

The reaction of $[Cp^*_2Nb(Te_2H)]$ (**1**) ($Cp^* = C_5Me_5$) with $[Ru_3(CO)_{12}]$ in boiling toluene gave $[Ru_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}Te)]$ (**2**), $[Ru_6(\mu_3\text{-}H)(CO)_{15}(\mu_3\text{-}Te)_3][Cp^*_2Nb(CO)_2]$ (**3**) and $[Ru_5(\mu_2\text{-}H)(CO)_{14}(\mu_4\text{-}Te)][Cp^*_2Nb(CO)_2]$ (**4**) along with already known $[Ru_4(CO)_{11}(\mu_4\text{-}Te)_2]$ (**5**). Electrochemical studies of **5** show this complex to be able to consume up to four electrons in reversible steps.

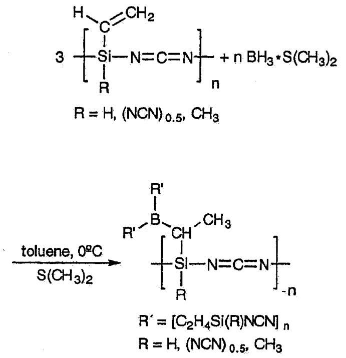


Markus Weinmann, Markus Hörz, Frank Berger, Anita Müller, Klaus Müller, Fritz Aldinger

J. of Organomet. Chem. 659 (2002) 29

Dehydrocoupling of tris(hydridosilylethyl)boranes and cyanamide: a novel access to boron-containing polysilylcarbodiimides

A novel procedure by dehydrocoupling of cyanamide and tris(hydridosilylethyl)boranes allows for the first time the synthesis of boron-modified polysilylcarbodiimides with adjustable nitrogen content, which are promising molecular precursors for ultrahigh temperature Si–B–C–N ceramics.

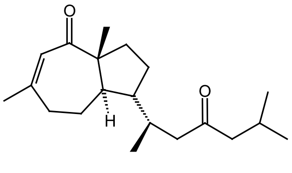


Branislav Horváth, Andrej Boháč, Marta Sališová, Eva Solčániová, Myron Rosenblum

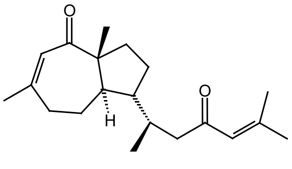
J. of Organomet. Chem. 659 (2002) 43

The synthesis of a hydroazulen-2-one skeleton-determination of the diastereoselectivity of [3+2] cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron with *E*/*Z*-η^1-(crotyl)Fp

The diastereoselectivity of [3+2] cycloaddition of tricarbonyl[(4,5,6,7-η)-2-methyltropone]iron (**2**) with an *E*,*Z* isomeric mixture of η^1-(crotyl)Fp (**4*E*/4*Z***) [Fp: $C_5H_5Fe(CO)_2$ or $CpFe(CO)_2$] has been studied. By this cyclopentaanulation, four stereogenic centres are formed. The reaction occurs regioselectively and stereoselectively.



Reiswigin A



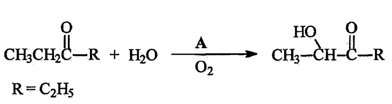
Reiswigin B

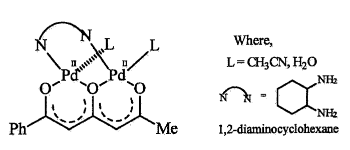
Arab K. El-Qisairi, Hanan A. Qaseer

J. of Organomet. Chem. 659 (2002) 50

Oxidation of ketone by palladium(II). α-Hydroxyketone synthesis catalyzed by a bimetallic palladium(II) complex

A bimetallic palladium(II) complex containing a triketone ligand and a bridging dinitrogen ligand oxidizes ketones in aqueous THF to α-hydroxyketone by an air oxidation.





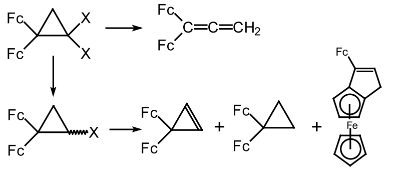
bimetallic catalyst, **A**

Elena I. Klimova, Marcos Martínez García, Tatiana Klimova, José M. Mendez Stivalet, Simón Hernández Ortega, Lena Ruíz Ramírez

J. of Organomet. Chem. 659 (2002) 56

3,3-Diferrocenylcyclopropene

Dehydrohalogenation of isomeric 2-chloro- and 2-bromo-1,1-diferrocenylcyclopropanes (Z- and E-isomers with respect to the 'bisecting' ferrocenyl substituent) under the action of Bu^{t}OK in DMSO afforded 3,3-diferrocenylcyclopropene. In solutions, this underwent facile opening of the small ring to give 3-ferrocenyl-1H-cyclopentaferrocene (~ 55%) and 1,1-diferrocenylpropene (15%). The spatial structure of Z-2-chloro-1,1-diferrocenylcyclopropane and 1,1-diferrocenylcyclopropane were elucidated by X-ray diffraction analysis of a single crystas.



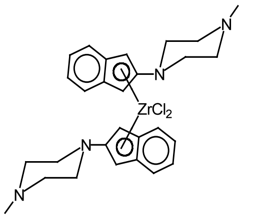
Fc = $C_5H_5FeC_5H_4$; X = Cl, Br

Markku Hämäläinen, Heikki Korpi, Mika Polamo, Markku Leskelä

J. of Organomet. Chem. 659 (2002) 64

Bis(2-N,N'-methylpiperazinoindenyl)zirconium dichloride. Crystal structure of bis(2-N,N'-methylpiperazinoindenyl)$ZrCl_2$

Synthesis of the title compound is described. The solid state structure, based on single crystal X-ray diffraction, shows that the compound has a nearly C_2-symmetric conformation. This amino-substituted zirconium metallocene catalyst and methylaluminoxane as a cocatalyst yield polyethylene with narrow molecular weight distribution and very high activity.

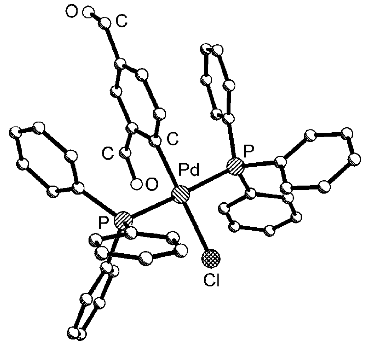


José M. Vila, Mª Teresa Pereira, Gemma Alberdi, Marta Mariño, Jesús J. Fernández, Margarita López Torres, Raquel Ares

J. of Organomet. Chem. 659 (2002) 67

Cyclometallated compounds of Pd(II): C=N to C=O conversion through acid hydrolysis. Crystal and molecular structures of [Pd{4-(CHO)$C_6H_3C(H)$=NCy}(Cl)$(PPh_3)_2$] and [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)$(PPh_3)_2$]

Cyclometallated palladium(II) derivatives undergo acid hydrolysis of the C=N double bonds to give compounds with one or two non-coordinated formyl groups on the metallated ring.

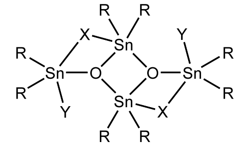


Jens Beckmann, Dainis Dakternieks, Fong Sheen Kuan, Edward R.T. Tiekink

J. of Organomet. Chem. 659 (2002) 73

A novel route for the preparation of dimeric tetraorganodistannoxanes

Reaction between polymeric diorganotin oxides $(R_2SnO)_n$ and saturated aqueous NH_4X can provide a facile route for synthesis of dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ for a range of R and X substituents.



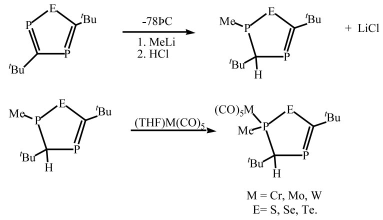
R = alkyl, aryl; X, Y = Hal, OH, OR, $OSiMe_3$, OOCR, $OSP(OR)_2$, NO_3, N_3, NCS, SH, $OReO_3$

**Monte L. Helm, Peter B. Hitchcock,
John F. Nixon, László Nyulászi,
Dénes Szieberth**

J. of Organomet. Chem. 659 (2002) 84

Synthetic, structural and theoretical studies on the new 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes, $P_2EC_2Bu^t_2(H)Me$, (E = S, Se, Te) and their [M(CO)$_5$] complexes (M = Cr, Mo, W)

The new 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes $P_2EC_2Bu^t_2(H)Me$, (E = S, Se, Te) are described as well as their η^1-$M(CO)_5$ complexes, of which, (E = S, M = W; E = Se, M = Cr, Mo, W) have been structurally characterised by single crystal X-ray diffraction studies. Theoretical calculations on isomers of the 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes, and the corresponding 2,3-dihydro-1*H*-1,2,4-triphosphole are also presented and discussed.

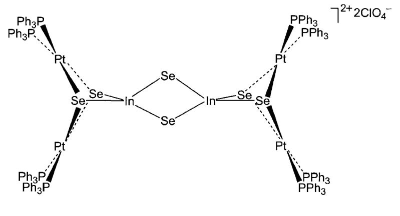


**Jeremy S.L. Yeo, Jagadese J. Vittal,
William Henderson, T.S. Andy Hor**

J. of Organomet. Chem. 659 (2002) 92

Nucleophilicity of the selenide ligands in $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$. Molecular assembly of a novel $\{In_2Pt_4Se_6\}$ core

The nucleophilicity of the selenide centres in $Pt_2(\mu\text{-}Se)_2(PPh_3)_4$ is exemplified in the isolation of a rare platinum–indium selenido aggregate, $\{[Pt_2(\mu_3\text{-}Se_2)_2(PPh_3)_4]_2In_2(\mu\text{-}Se)_2\}\{ClO_4\}_2$. X-ray crystallographic analysis revealed a hexametallic framework supported by a planar $\{In_2Se_2\}$ square sandwiched by two $\{Pt_2Se_2\}$ hinged butterfly moieties.

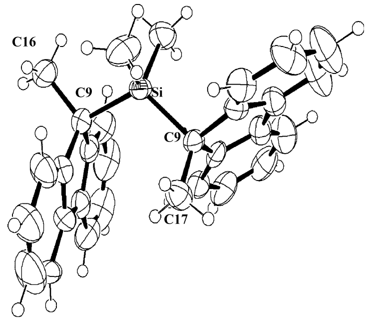


**Gabriela Cretiu, Luminita Silaghi-Dumitrescu, Ioan Silaghi-Dumitrescu,
Jean Escudié, Alfredo Toscano,
Simon Hernandez, Raymundo Cea-Olivares**

J. of Organomet. Chem. 659 (2002) 95

Difluorenylsilane derivatives, a class of compounds exhibiting strong intra- and intermolecular C–H···π interactions. Crystal and molecular structures of bis(9-methylfluoren-9-yl)dimethylsilane and (9-methylfluoren-9-yl)(fluoren-9-yl) dimethylsilane

The crystal and molecular structures of difluorenyl(dimethyl)silanes $Me_2Si(CR'R_2)(CR''R_2)$ (R′, R″ = H, Me; CR_2 = fluorenyl) have been determined by X-ray diffraction and compared with the conformations available in the gas phase. They exhibit intramolecular and intermolecular C–H···π interactions. MO calculations support the existence of these intramolecular interactions and correlate well with the temperature dependent proton NMR spectra.

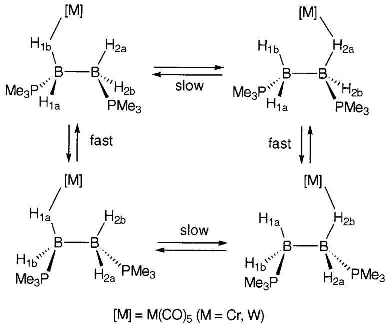


**Mamoru Shimoi, Kinji Katoh,
Yasuro Kawano, Goji Kodama,
Hiroshi Ogino**

J. of Organomet. Chem. 659 (2002) 102

Fluxional behavior of chromium and tungsten complexes of monodentate bis(trimethylphosphine)diborane(4), $[M(CO)_5(\eta^1\text{-}B_2H_4\cdot 2PMe_3)]$ (M = Cr, W):
A model case for alkane–metal complexes

The fluxional behavior of Group 6 metal complexes of monodentate bis(trimethylphosphine)diborane(4), $[M(CO)_5(\eta_1\text{-}B_2H_4\cdot 2PMe_3)]$ (M = Cr, W), was studied by NMR spectroscopy. They show two fluxional processes in solution: one is the very rapid exchange of the coordinated B*H* atom with the geminal hydrogen atom, and the other one is rather slow exchange with the vicinal hydrogens. This behavior embodies the fluxionality predicted for the ethane complex, $[W(CO)_5(\eta_1\text{-}C_2H_6)]$.

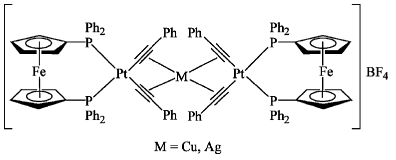


Wai-Yeung Wong, Guo-Liang Lu, Ka-Ho Choi

J. of Organomet. Chem. 659 (2002) 107

Synthesis, characterization and structural studies of new heterometallic alkynyl complexes of platinum and Group 11 metals with chelating bis(diphenylphosphino)ferrocene ligand

The synthesis, characterization and molecular structures of some dppf-stabilized mixed-metal alkynyl complexes of platinum and Group 11 metals are addressed. The crystal structures of $[\{Pt(dppf)(C\equiv CPh)_2\}_2M]BF_4$ (M = Cu, Ag) are reported.

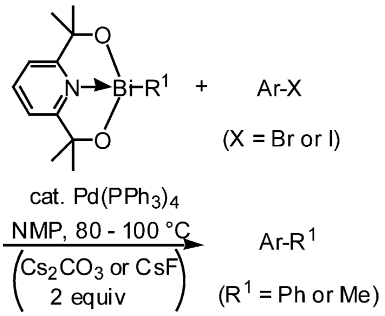


Maddali L.N. Rao, Shigeru Shimada, Osamu Yamazaki, Masato Tanaka

J. of Organomet. Chem. 659 (2002) 117

Cross-coupling reaction of organobismuth dialkoxides with aryl bromides and iodides catalyzed by $Pd(PPh_3)_4$

Organobismuth compounds bearing 2,6-pyridinedimethoxide ligand efficiently reacted with aryl bromides and iodides in the presence of $Pd(PPh_3)_4$ and Cs_2CO_3 or CsF.

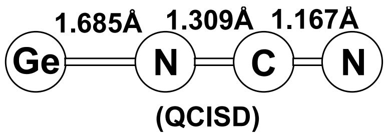


Mingjae Huang, Ming-Der Su

J. of Organomet. Chem. 659 (2002) 121

A theoretical study of linear germacyanogen isomers

MP2, B3LYP, and QCISD computational results suggest that the order of stability of the acyclic germacyanogens is GeNCN > GeNNC > NGeCN > NGeNC.

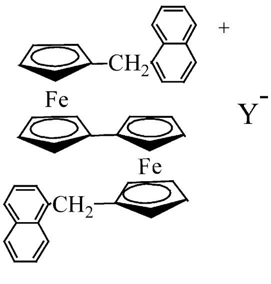


Teng-Yuan Dong, Bor-Ruey Huang, Shie-Ming Peng, Gene-Hsiang Lee, Michael Y. Chiang

J. of Organomet. Chem. 659 (2002) 125

Effects of counterions on intramolecular electron transfer in 1′,1‴-dinaphthylmethylbiferrocenium cation: structural, Mössbauer and EPR characteristics

An amazing change in the Mössbauer characteristics results when the I_3^- anion of the mixed-valence 1′,1‴-dinaphthylmethylbiferrocenium triiodide is replaced by the BF_4^- anion and PF_6^- anion. The change from I_3^- to BF_4^- lead to a change of ~170 K in the temperature at which the mixed-valence 1′,1‴-dinaphthylmethylbiferrocenium cation transfers electron slower than the Mössbauer time scale. The relatively minor perturbations caused by the crystallinity and counterions have pronounced effects on the magnitude of electron-transfer rate.



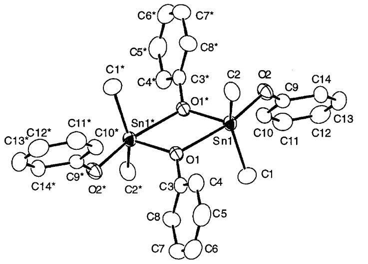
Y = I_3, BF_4, PF_6

Hiroyuki Yasuda, Jun-Chul Choi, Sang-Chul Lee, Toshiyasu Sakakura

J. of Organomet. Chem. 659 (2002) 133

Structure of dialkyltin diaryloxides and their reactivity toward carbon dioxide and isocyanate

The structure and reactivity of dialkyltin diaryloxides, $R_2Sn(OAr)_2$, were investigated. The solid state structure of $Me_2Sn(OAr)_2$ determined by X-ray crystallography was aryloxo-bridged dinuclear, while $R_2Sn(OAr)_2$ in solution easily dissociated upon dilution. Neither carbon dioxide nor carbon disulfide reacted with $R_2Sn(OAr)_2$, whereas isocyanate readily reacted to produce aryl carbamates.



Harry Adams, Laurence V.Y. Guio, Michael J. Morris, Fiona A. Wildgoose

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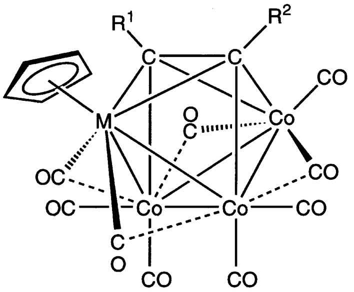
Rational synthesis of tricobalt-molybdenum and -tungsten butterfly clusters with alkyne ligands

The reaction of $[CoM(\mu\text{-}R^1C{\equiv}CR^2)(CO)_5\text{-}Cp]$ (M = Mo, W) with dicobalt octacarbonyl in refluxing toluene provides a rational synthesis of the tetranuclear clusters $[Co_3M(\mu_4\text{-}R^1C_2R^2)(CO)_9Cp]$.

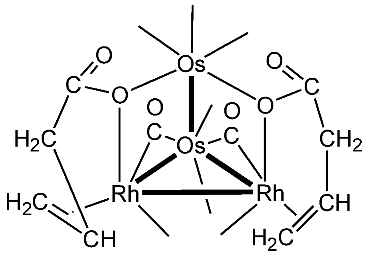


Jasmine Po-Kwan Lau, Wing-Tak Wong

J. of Organomet. Chem. 659 (2002) 151

Reactivity of osmium–rhodium mixed-metal cluster $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ towards vinyl containing ligands

Reactivity of mixed-metal cluster $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**), towards vinyl containing ligands is reported. Catalytic alkene isomerization by **1** is also observed.

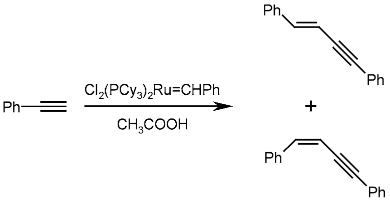


Karen Melis, Dirk De Vos, Pierre Jacobs, Francis Verpoort

J. of Organomet. Chem. 659 (2002) 159

Acid controlled alkyne dimerisation initiated by a Ru–carbene precursor

The Grubb's catalyst $Cl_2(PR_3)_2Ru{=}CHPh$ (**1**) is an excellent precursor for the dimerisation of phenylacetylene. Thermal treatment and addition of two equivalents of phenylacetylene to complex **1** generate a new Ru–vinylidene complex **3**. Complex **3** catalyses a selective product formation for *trans*-tail-to-tail enynes. Surprisingly, addition of acetic acid enhances the yield and the reaction rate dramatically and reverses the stereoselectivity to the formation of *Z*-isomers.

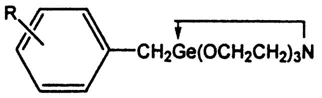


Edmunds Lukevics, Luba Ignatovich, Tatyana Shul'ga, Olga Mitchenko, Sergey Belyakov

J. of Organomet. Chem. 659 (2002) 165

Synthesis, molecular structure and biological activity of bromobenzylgermatranes

The new series of benzylgermatranes, R = H (**I**), 2-Br (**II**), 3-Br (**III**), 4-Br (**IV**) has been obtained to study the influence of a substituent position on coordination of the germanium atom, the values of bond angles and neurotropic activity. The intramolecular donor–acceptor bond N → Ge in benzylgermatranes (2.175–2.219 Å) is shorter than that in tolylgermatranes (2.212–2.230 Å). Biological investigations have demonstrated that all benzylgermatranes (**I**–**IV**) are low toxic compounds ($LD_{50} > 1000$ mg kg^{-1}) with high anaesthetic and anti-Corazol activity. Benzylgermatranes **I**, **III** and **IV** improve memory processes and completely prevent animals from RA caused by electroshock.

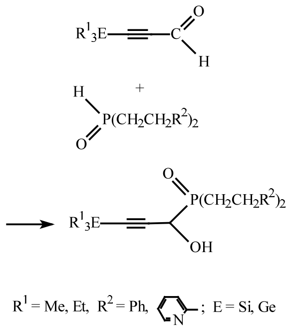


Nina K. Gusarova, Aelita M. Reutskaya, Nina I. Ivanova, Alevtina S. Medvedeva, Maria M. Demina, Peter S. Novopashin, Andrei V. Afonin, Alexander I. Albanov, Boris A. Trofimov

J. of Organomet. Chem. 659 (2002) 172

Regioselective addition of secondary phosphine oxides to 3-(trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals

Silicon- and germanium-containing acetylenic phosphine oxides with hydroxyl groups are easily prepared in quantitative yield by the reaction of 3-(trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals with secondary phosphine oxides.

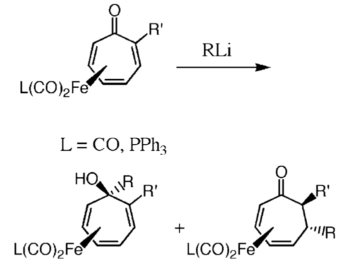


Yoann Coquerel, Jean-Pierre Deprés, Andrew E. Greene, Christian Philouze

J. of Organomet. Chem. 659 (2002) 176

Addition of organolithium compounds to tricarbonyl(tropone)iron complexes: experimental and structural studies

The regioselectivity (1,2 vs. 1,4) in the nucleophilic addition of organolithium reagents to tropone(tricarbonyl)iron complexes has been studied and found to be correlated with the relative hardness of the nucleophile (HSAB principle). X-ray structures of several 1,2 and 1,4 adducts are reported.



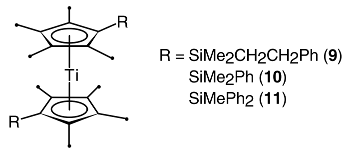
Ratio 1,2 : 1,4 addition = 100 : 0 to 0 : 100

Lenka Lukešová, Michal Horáček, Petr Štěpnička, Karla Fejfarová, Róbert Gyepes, Ivana Císařová, Jiří Kubišta, Karel Mach

J. of Organomet. Chem. 659 (2002) 186

Synthesis and crystal structures of thermally stable titanocenes

Reduction of titanocene dichlorides $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$, where R = $SiMe_2CH_2CH_2Ph$ (**3**), $SiMe_2Ph$ (**4**), and $SiMePh_2$ (**5**) with magnesium in THF proceeds via the respective titanocene monochlorides $[TiCl(\eta^5\text{-}C_5Me_4R)_2]$ (**6**–**8**) to afford finally the thermally stable titanocenes, $[Ti(\eta^5\text{-}C_5Me_4R)_2]$ (**9**–**11**). As revealed by X-ray crystallography, titanocenes **9** and **11** possess bent metallocene structures with the cyclopentadienyl rings tilted at an angle of 9.8(1) and 14.4(2)°, respectively.



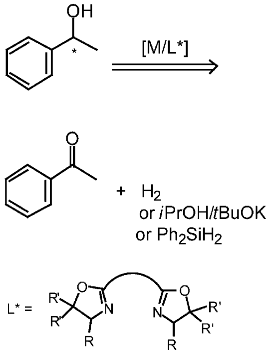
cyclopentadienyl-ring tilt: **9**, 9.8(1); **11**, 14.4(2)°.

Montserrat Gómez, Susanna Jansat, Guillermo Muller, Michel C. Bonnet, Jérémy A.J. Breuzard, Marc Lemaire

J. of Organomet. Chem. 659 (2002) 197

Catalytic reduction of acetophenone with transition metal systems containing chiral bis(oxazolines)

Ru-, Ir- and Rh-chiral bis(oxazoline) systems have been tested in the acetophenone catalytic reduction, giving good activities and moderate selectivities for two carbon spacer ligands. NMR studies of Ru complexes with seven-membered metallic rings showed two main isomers in solution (ca. 3/1 ratio), in agreement with PM3(tm) calculations.



Pradeep Mathur, Chimalakonda Srinivasu, Moawia O. Ahmed, Vedavati G. Puranik, Shubhangi B. Umbarkar

J. of Organomet. Chem. 659 (2002) 207

Reactivity studies of monoacetylide species towards chalcogen-bridged mixed-metal clusters:
Synthesis and characterisation of $[(\eta^5\text{-}C_5H_5)_2Fe_2RuM_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)\text{-}C(Ph)C\}]$ (M = Mo, W; E = S, Se) and $[(\eta^5\text{-}C_5H_5)_2Fe_2Ru_2M_2(CO)_9(\mu_3\text{-}E)_2\{\mu\text{-}CCPh\}_2]$ (M = W, E = S, Se)

Reaction of $[Fe_2Ru(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se) with $[(\eta^5\text{-}C_5H_5)M(CO)_3(C{\equiv}CPh)]$ (M = Mo, W) in refluxing toluene afforded two new types of mixed-metal clusters, which were characterised by IR and by ^1H- and ^{13}C-NMR spectroscopy. The crystal structures of one of each type were elucidated by single crystal X-ray diffraction studies.