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Contents

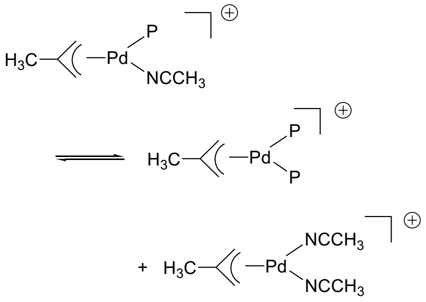
Regular Papers

Rosa M. Ceder, Carlos García, Arnald Grabulosa, Fatma Karipcin, Guillermo Muller, Mercè Rocamora, Mercè Font-Bardía, Xavier Solans

J. Organomet. Chem. 692 (2007) 4005

Synthesis and characterization of palladium(II) complexes with chiral aminophosphine ligands: Catalytic behaviour in asymmetric hydrovinylation. Crystal structure of *cis*-[$PdCl_2$(PPh-((*R*)-$NHCHCH_3Ph)_2)_2$]

Cationic Pd(II) complexes of type [Pd(η^3-2-$CH_3C_3H_4$)($NCCH_3$)P]BF_4 with chiral monodentate monoaminophosphines, $Ph_2P(NHR)$, and bisaminophosphines, $PhP(NHR)_2$, undergo a symmetrization reaction. The behaviour of each of the three species involved has been tested in the hydrovinylation catalytic reaction of styrene.

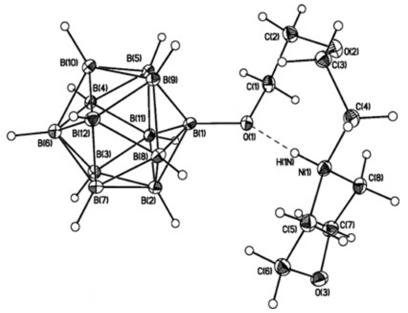


Andrey Semioshkin, Evgueniya Nizhnik, Ivan Godovikov, Zoya Starikova, Vladimir Bregadze

J. Organomet. Chem. 692 (2007) 4020

Reactions of oxonium derivatives of $[B_{12}H_{12}]^{2-}$ with amines: Synthesis and structure of novel B_{12}-based ammonium salts and amino acids

The reactions of cyclic oxonium derivatives of $[B_{12}H_{12}]^{2-}$ with various amines were studied. A series of novel B_{12}-species with ammonium group on the side chain was prepared. A structure of tetrabutylammonium-[2-(2-morpholinium-ethoxy)-ethoxy]-undecahydro-*closo*-dodecaborate was determined and the existence of intramolecular N–H···O–B bond was shown. Using these reactions, novel boronated piperazines and amino acids were synthesized.

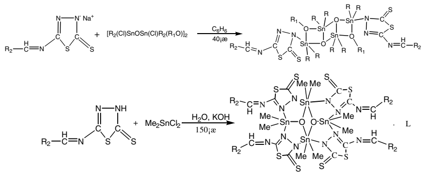


Chunlin Ma, Junshan Sun, Rufen Zhang, Daqi Wang

J. Organomet. Chem. 692 (2007) 4029

Self-assembly of organooxotin(IV) clusters with Schiff-base-containing-triazole from hydrolysis or solvothermal synthesis: Crystal structures, hydrogen bonds, C–H···π stacking and S···S interaction

The reactions of the diorganotin dichloride with the Schiff-base-containing-triazole ligand afford the following types: [$(Me_2Sn)_2O_2(Ln)]_2$ (n = 1, for **1**) [$(Me_2Sn)_2O(RO)(Ln)]_2$ (R = Et, n = 2, for **2**; R = Me, n = 3, for **3**), [(n-Bu_2-$Sn)_2O_2(Ln)]_2$ (n = 1, for **4**; n = 2, for **5**; n = 3, for **6**) and [$(Me_2Sn)_2Ln_2O]_2 \cdot L$ (n = 2; L = H_2O for **7**, L = CH_3OH for **8**). All the complexes were characterized by elemental analysis, IR, ^1H, ^{13}C and ^{119}Sn spectra analyses.



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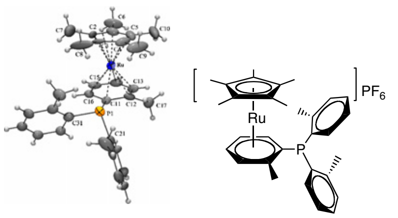
Helen Caldwell, Sheila Isseponi, Paul S. Pregosin, Alberto Albinati, Silvia Rizzato

J. Organomet. Chem. 692 (2007) 4043

Reactions of Ru(Cp*) complexes with P(o-tolyl)$_3$

Reaction of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) with P(o-tolyl)$_3$ affords [Ru(Cp*){(η^6-o-tolyl)P(o-tolyl)$_2$}](PF$_6$), in which the P-atom is not coordinated to the metal. Reaction of [Ru(Cp*)-(η^3-PhCHCHCH$_2$)(DMF)$_2$](PF$_6$)$_2$, with P(o-tolyl)$_3$ gives a mixture of the phosphonium salt, C$_6$H$_5$CH=CHCH$_2$P(o-tolyl)$_3$, and the dication [Ru(Cp*)(η^6-C$_6$H$_5$CH=CHCH$_2$P(o-tolyl)$_3$)](PF$_6$)$_2$.

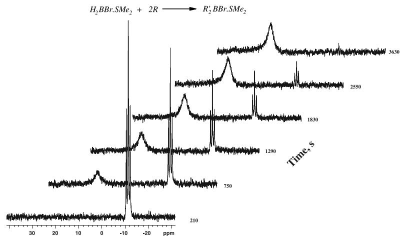


N. Xaba, D. Jaganyi

J. Organomet. Chem. 692 (2007) 4052

Change in mechanistic pathway of hydroboration: A detailed kinetic study of H$_2$BBr·SMe$_2$ and HBBr$_2$·SMe$_2$

^{11}B NMR kinetic array showing disappearance of H$_2$BBr·SMe$_2$ and formation of R′$_2$BBr·SMe$_2$.

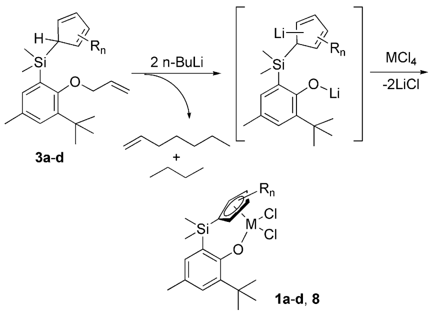


Hidenori Hanaoka, Takahiro Hino, Hiroshi Souda, Kazunori Yanagi, Yoshiaki Oda, Akio Imai

J. Organomet. Chem. 692 (2007) 4059

Synthesis and characterization of titanium and zirconium complexes with silicone-bridged phenoxycyclopentadienyl ligands

SiMe$_2$-bridged Cp-phenoxy titanium and zirconium complexes **1a**–**1d**, **8** were synthesized in high yields starting from allyl-protected phenolic ligands **3a**–**3d**, which were first treated with 2 equiv. of n-BuLi to selectively give the dilithium salt of the ligands along with 1-heptene, a coupling product of a protected allyl ether moiety and butyl anion. Addition of TiCl$_4$ to the resulting dilithium salts of the ligands in toluene afforded the complexes in good yields.



Yulia G. Budnikova, Tatyana V. Gryaznova, Oleg G. Sinyashin, Sergey A. Katsyuba, Tatyana P. Gryaznova, Mikhail P. Egorov

J. Organomet. Chem. 692 (2007) 4067

Germylene complexes of tungsten pentacarbonyls W(CO)$_5$=GeCl$_2$ and W(CO)$_5$=Ge=W(CO)$_5$, Electrochemical synthesis and quantum-chemical computations

Convenient synthetic route to prepare the germylene complexes of tungsten pentacarbonyls, W(CO)$_5$=GeCl$_2$ and W(CO)$_5$=Ge=W(CO)$_5$, electrochemically is developed. Combined quantum-chemical/IR spectroscopic approach is used for identification of the synthesized compounds. Good agreement between theoretical and experimental spectra can be regarded as one of the proofs of their supposed structures.

$$\mathrm{W(CO)_6} + 2e \xrightarrow[-\mathrm{CO}]{} [\mathrm{W(CO)_5}]^{2-}$$

$$[\mathrm{W(CO)_5}]^{2-} \xrightarrow[(1:1)]{\mathrm{GeCl_4}} \mathrm{(CO)_5W{=}GeCl_2} + 2\mathrm{Cl}^-$$

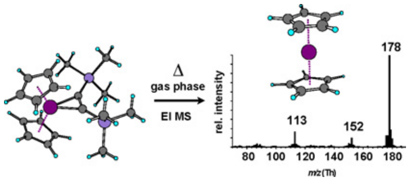
$$[\mathrm{W(CO)_5}]^{2-} \xrightarrow[(2:1)]{\mathrm{GeCl_4}} \mathrm{(CO)_5W{=}Ge{=}W(CO)_5} + {} + 4\mathrm{Cl}^-$$

Miroslav Polášek, Jiří Kubišta

J. Organomet. Chem. 692 (2007) 4073

Bis(η^5-cyclopentadienyl)titanium(II) in the gas phase: Mass spectrometric and computational study of the structure and reactivity

Bis(η^5-cyclopentadienyl)titanium(II), titanocene, was generated in the gas phase by a thermolysis of the titanocene complex with bis(trimethylsilyl)acetylene. Structure and reactivity of this elusive compound was characterized by means of mass spectrometric methods and density functional theory calculations.

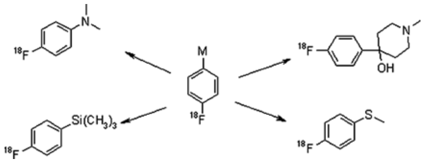


Johannes Ermert, Thomas Ludwig, René Gail, Heinz H. Coenen

J. Organomet. Chem. 692 (2007) 4084

[^{18}F]Fluorophenyl organometallics as intermediates of no-carrier-added ^{18}F-fluoroarylation reactions

Studies of the synthesis and synthetic potential of no-carrier-added 4-[^{18}F]fluorophenyl compounds of lithium, sodium and magnesium. The ^{18}F-fluoroarylation was verified with examples of aryl-carbon, -silicon, -sulphur, and -nitrogen bond formation with radiochemical yields of 20–25% related to the starting radioactivity of [^{18}F]fluoride.

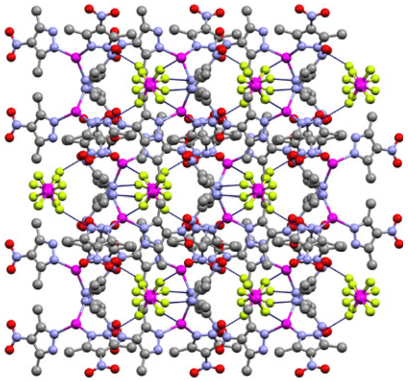


Paloma Ovejero, M. José Mayoral, Mercedes Cano, José A. Campo, José V. Heras, Elena Pinilla, M. Rosario Torres

J. Organomet. Chem. 692 (2007) 4093

The 3,5-dimethyl-4-nitropyrazole ligand in the construction of supramolecular networks of silver(I) complexes

New ionic silver(I) compounds based on the 3,5-dimethyl-4-nitropyrazole (Hpz^{NO_2}) ligand have been prepared looking for predictable molecular assemblies. Hydrogen-bonds and/or coordinative, $\pi\cdots\pi$ and/or non-conventional hydrogen-bond interactions have been used in designing polymers or supramolecular arrays. Herein the structures of the compounds $[Ag(Hpz^{NO_2})_2][BF_4]$, $[Ag(Hpz^{NO_2})_3][SbF_6]$ and $[Ag(Hpz^{NO_2})_3][PO_2F_2]\cdot Hpz^{NO_2}$ are described analysing the influence of factors as the metal coordination environment, the counteranion and the NO_2 substituent on the final architectures.

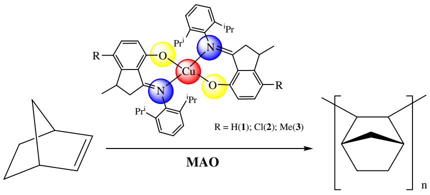


Guangrong Tang, Yue-Jian Lin, Guo-Xin Jin

J. Organomet. Chem. 692 (2007) 4106

Syntheses, structures and catalytic activity of copper(II) complexes with hydroxyindanimine ligands

Copper(II) complexes with hydroxyindanimine ligands have been synthesized, characterized and used as catalysts for the vinyl polymerization of norbornene in the presence of methylaluminoxane (MAO) as co-catalyst in moderate activities.

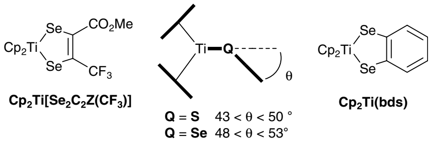


Olivier Jeannin, Mitsushiro Nomura, Marc Fourmigué

J. Organomet. Chem. 692 (2007) 4113

Structural flexibility of titanocene diselenolene complexes: Combined structural and VT NMR investigations

Based on structural and variable-temperature NMR data, a comparative investigation of five different Cp_2Ti(diselenolene) complexes shows the evolution of the static and dynamic properties associated with the folding of the $TiSe_2C_2$ metallacycle along the Se···Se hinge. Larger folding angles and $\Delta G_c^{\ddagger}$ activation energies for the folding process are associated with the most electron rich diselenolenes (bds, ddds), when compared with those bearing electron-withdrawing CO_2Me or CF_3 substituents.

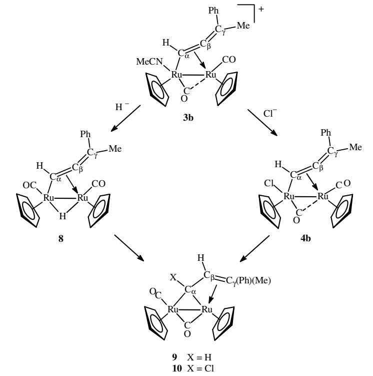


Selby A.R. Knox, Fabio Marchetti

J. Organomet. Chem. 692 (2007) 4119

Additions and intramolecular migrations of nucleophiles in cationic diruthenium μ-allenyl complexes

Hydride and halide anions readily replace the acetonitrile ligand in the diruthenium μ-allenyl complex **3b**. The hydride can successively migrate to the C_α carbon of the allenyl moiety, and then to C_β, affording **9** as the most stable product. The μ-vinyl-chlorocarbene adduct **10** is believed to be formed from **4b** by chloride migration to C_α and hydrogen migration from C_α to C_β.

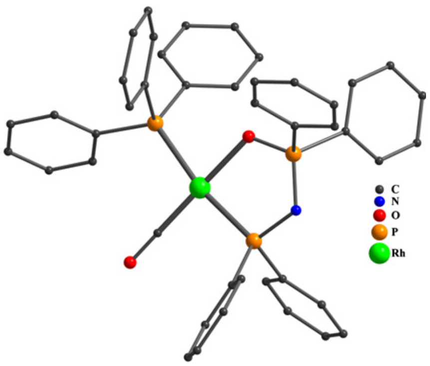


Konstantinos A. Chatziapostolou, Kalliopi A. Vallianatou, Alexios Grigoropoulos, Catherine P. Raptopoulou, Aris Terzis, Ioannis D. Kostas, Panayotis Kyritsis, Georgios Pneumatikakis

J. Organomet. Chem. 692 (2007) 4129

Synthesis and characterization of new Rh^I complexes bearing CO, PPh_3 and chelating *P*,*O*- or *Se*,*Se*-ligands: Application to hydroformylation of styrene

Complexes containing electron rich Rh^I centres and bearing (cod), CO, PPh_3 and *P*,*O*- or *Se*,*Se*-ligands have been synthesized, structurally and spectroscopically characterized and applied as catalysts for the hydroformylation of styrene. Complexes which contain the *P*,*O*-ligand, forming a five-membered ring with Rh, exhibit the best catalytic activity.

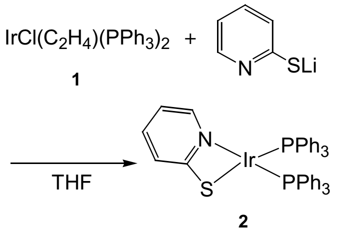


Kenichi Ogata, Akinori Toyota

J. Organomet. Chem. 692 (2007) 4139

Iridium(I) complex of chelating pyridine-2-thiolate ligand: Synthesis, reactivity, and application to the catalytic *E*-selective terminal alkyne dimerization via C–H activation

An iridium(I) complex bearing a chelate-coordinated pyridine-2-thiolate ligand $[Ir(\eta^2\text{-}SNC_5H_4)(PPh_3)_2]$ (**2**) was prepared by the reaction of $[IrCl(C_2H_4)(PPh_3)_2]$ (**1**) with $Li[SNC_5H_4]$. On the treatment of **2** with various substrates, iridium(III) complexes were formed. Complex **2** catalyzed dimerization of terminal alkynes leading to enynes (**7**) with high *E*-selectivity via C–H bond activation.

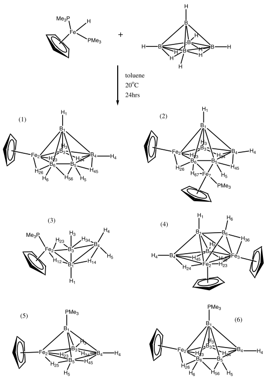


Malcolm L.H. Green, John B. Leach, Malcolm A. Kelland

J. Organomet. Chem. 692 (2007) 4147

Formation of ferraboranes from pentaborane(9) or $BH_3 \cdot$ thf and an electron-rich cyclopentadienyl iron phosphine hydride

$[(\eta^5\text{-}C_5R_5)Fe(PMe_3)_2H]$ (R = H, Me) can be made in good yields in a simple one-pot reaction between $FeCl_2$, PMe_3, C_5R_5H (R = H, Me) and Na/Hg in thf. Reaction of $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ with pentaborane(9) gives the known metallaborane $[(\eta^5\text{-}C_5H_5)$-*nido*-2-$FeB_5H_{10}]$ (**1**) in improved yield as well as the new metallaboranes $[(\eta\text{-}C_5H_5)$-*nido*-2-$FeB_5H_8\{\mu\text{-}5,6\text{-}Fe(\eta^5\text{-}C_5H_5)(PMe_3)(\mu\text{-}6,7\text{-}H)\}]$ (**2**), $[(\eta\text{-}C_5H_5)(PMe_3)$-*arachno*-2-$FeB_3H_8]$ (**3**), $[(\eta^5\text{-}C_5H_5)_2$-capped-*nido*-2,3-$Fe_2B_4H_8]$ (**4**), $[(\eta^5\text{-}C_5H_5)$-*nido*-2-$FeB_4H_7(PMe_3)]$ (**5**) and $[(\eta^5\text{-}C_5H_5)$-*nido*-2-$FeB_5H_8(PMe_3)]$ (**6**).

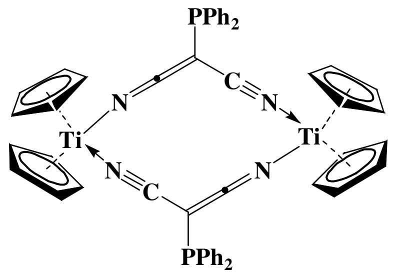


Yuriy A. Min'ko, Natalia V. Belina, Vyacheslav V. Sushev, Georgy K. Fukin, Mikhail P. Bubnov, Alexander N. Kornev

J. Organomet. Chem. 692 (2007) 4157

Binuclear titanium(III) complex derived from diphenylphosphanylmalononitrile, $[\mu^2(N,N')\text{-}Ph_2PC(CN)_2TiCp_2]_2$: Synthesis, structure and properties

$Ph_2P\text{–}CH(CN)_2$ reacts with Cp_2TiCl in the presence of triethylamine in THF to give air sensitive Ti(III) complex $[\mu^2(N,N')\text{-}Ph_2PC(CN)_2TiCp_2]_2$, which is centrosymmetric dimer in the solid state, containing nearly planar 12-member metallocycle. Solution of the complex exhibits anisotropic EPR spectrum (200 K); every spectral component contains splitting on a single phosphorus nucleus.

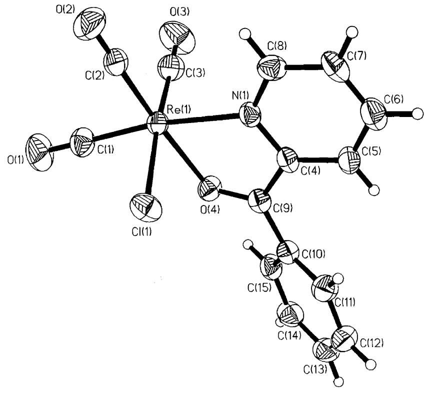


B. Machura, R. Kruszynski

J. Organomet. Chem. 692 (2007) 4161

A novel tricarbonyl rhenium complex of 2-benzoylpyridine – Synthesis, spectroscopic characterization, X-ray structure and DFT calculations

The reaction of $Re(CO)_5Cl$ with 2-benzoylpyridine (bopy) has been examined and a novel $Re(CO)_3^+$ tricarbonyl – *fac*-$[Re(CO)_3(bopy)Cl]$ – has been obtained. The compound has been studied by IR, UV–Vis spectroscopy and X-ray crystallography. The molecular orbital diagram of the tricarbonyl has been calculated with the density functional theory (DFT) method. The spin-allowed singlet–singlet electronic transitions of $[Re(CO)_3(bopy)Cl]$ have been calculated with the time-dependent DFT method, and the UV–Vis spectrum of the title compound has been discussed on this basis.

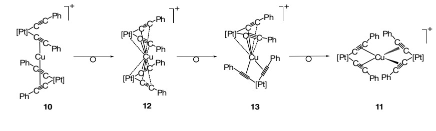


Heinrich Lang, Petra Zoufalá, Sami Klaib, Amaya del Villar, Gerd Rheinwald

J. Organomet. Chem. 692 (2007) 4168

Synthesis of di-, tri- and tetranuclear platinum(II) and copper(I) acetylide complexes

The synthesis and reaction behavior of heterobimetallic $\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2\}[Cu(N{\equiv}CMe)]BF_4$ (**I**) is described. On addition of *cis*-$[Pt](C{\equiv}CPh)_2$ to **I** trimetallic $\{[cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2]_2Cu\}BF_4$ is formed in a consecutive reaction sequence. The thereby observed intermediates could be characterized by single X-ray structure determinations.



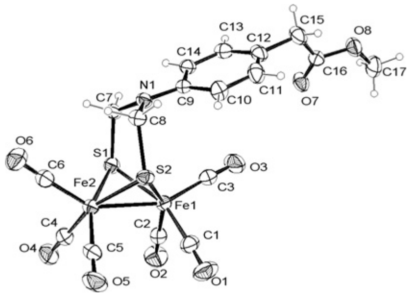
Notes

Vijendran Vijaikanth, Jean-François Capon, Frédéric Gloaguen, François Y. Pétillon, Philippe Schollhammer, Jean Talarmin

J. Organomet. Chem. 692 (2007) 4177

Carboxy-functionalized dithiolate di-iron complexes related to the active site of Fe-only hydrogenase

New carboxy-functionalized di-iron compounds have been synthesized by addition of dihalide derivatives $(XCH_2)_2R$ [X = Cl, R = $NC_6H_4CH_2CO_2CH_3$; X = Br, R = C_6H_3-COOH, $C_6H_3COON(COCH_2)_2$] to dinuclear anionic species $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$.

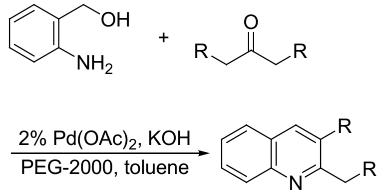


Chan Sik Cho, Wen Xiu Ren

J. Organomet. Chem. 692 (2007) 4182

A recyclable palladium-catalyzed modified Friedländer quinoline synthesis

2-Aminobenzyl alcohol undergoes oxidative cyclization with an array of ketones in toluene/poly(ethylene glycol) (PEG-2000) at 100 °C in the presence of a catalytic amount of $Pd(OAc)_2$ together with KOH to afford quinolines. The solidified palladium catalyst/PEG-2000 could be recovered and reused five times without any loss of catalytic activity.

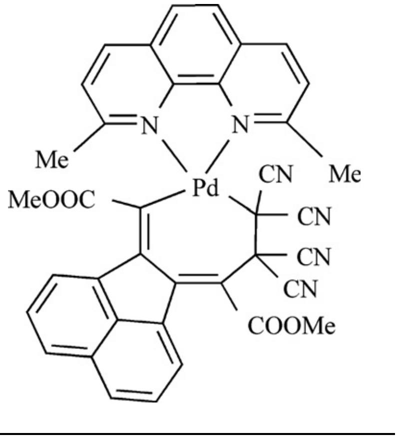


Luciano Canovese, Fabiano Visentin, Claudio Santo

J. Organomet. Chem. 692 (2007) 4187

The formation of a metallacycloheptadienyl intermediate in the reaction of palladacyclopentadienyl derivatives with tetracyanoethylene

The palladium(II) derivatives of the type **1** ($[Pd(LL')(C_4R_1R_2R_3R_4)]$ (LL′ = HNSPh:2-(phenylthiomethyl)-pyridine (**A**), BiPy: 2,2′-bipyridyl (**B**), DPPE: bis-diphenylphosphinoethane (**C**), NEOC: neocuproine (2,2′-dimethyl-*o*-phenanthroline) (**D**), $R_1 = R_4$ = COOMe, R_2, $R_3 = C_{10}H_6$ (**a**), $R_1 = R_3 = C_6H_5$, $R_2 = R_4$ = COOMe (**b**), $R_1 = R_2 = R_3 = R_4$ = COOMe (**c**)) react with the electron poor olefin tetracyanoethylene (TCNE) to yield under mild conditions the type **2** cycles $C_6(CN)_4$-$R_1R_2R_3R_4$ and the corresponding palladium(0) olefin derivative $[Pd(\eta^2\text{-TCNE})(LL')]$.



Virginie Riollet, Mostafa Taoufik, Jean-Marie Basset, Frédéric Lefebvre

J. Organomet. Chem. 692 (2007) 4193

Reactivity of silica-supported zirconium neopentyl fragments with trimethylphosphine and acetone: Formation of unexpected reaction products

$(\equiv SiO)_2ZrNp_2$ Neopentyl zirconium complexes grafted on silica react with trimethylphosphine leading to the formation of a surface alkylidene complex while mono- and tri-grafted complexes do not react. All complexes react with the enolic form of acetone, leading to a removal of all neopentyl ligands.