

## Contents

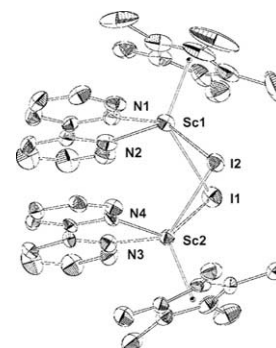
### Regular papers

**Karl A. Tupper, T. Don Tilley**

*J. Organomet. Chem.* 690 (2005) 1689

Synthesis and characterization of scandium complexes with reduced ligands: Crystal structures of Cp\*ScI<sub>2</sub>, [Cp\*ScI(bpy)]<sub>2</sub>, and [Cp\*ScCl(bpy)]<sub>2</sub>

The reaction of Cp\*ScI<sub>2</sub>(bpy) (3) with alkali metal-based reductants produced [Cp\*ScI(bpy)]<sub>2</sub> (5), a compound which features a strong  $\pi$ -stacking interaction between the bipyridine ligands. The chloride analog, [Cp\*ScCl(bpy)]<sub>2</sub> (7), was prepared from the reaction between Li<sub>2</sub>(dme)<sub>2</sub>bpy (6) and Cp\*ScCl<sub>2</sub>. Spectroscopic and crystallographic data indicate that the bipyridine ligands in 5 and 7 are reduced to their radical anion form.

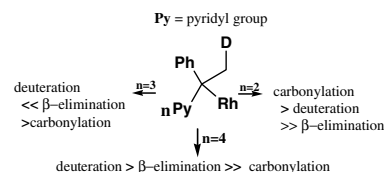


**Raffaello Lazzaroni, Roberta Settambolo, Silvia Rocchiccioli, Stefano Paganelli, Mauro Marchetti**

*J. Organomet. Chem.* 690 (2005) 1699

Evidence for formation and different evolution of tertiary rhodium alkyl intermediates under rhodium-catalyzed deuterio-(hydro)formylation of 1-(*n*-pyridyl)-1-phenylethenes

Rhodium catalyzed deuterio(hydro) formylation of the isomeric vinylidene substrates 1-(*n*-pyridyl)-1-phenylethenes with Rh/PPh<sub>3</sub> catalyst, at 80 °C and 100 atm, occurs via an almost exclusive formation of the tertiary alkyl rhodium intermediate which can  $\beta$ -eliminate, undergo migratory insertion or oxidative addition of deuterium in a different degree depending on the position of nitrogen atom.

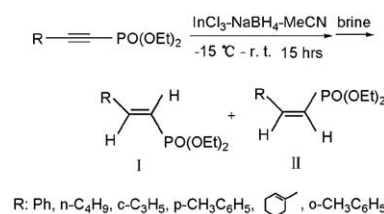


**Chunyan Wang, Yuanjiang Pan, Deyu Yang**

*J. Organomet. Chem.* 690 (2005) 1705

A novel stereoselective synthesis of (*E*)-2-arylvinyolphosphonates in InCl<sub>3</sub>-NaBH<sub>4</sub>-MeCN system

Hydroindation of arylalkynylphosphonates gives a intermediate which can be hydrolyzed to (*E*)-2-arylvinyolphosphonates in InCl<sub>3</sub>-NaBH<sub>4</sub>-MeCN system, a new and simple approach to (*E*)-2-arylvinyolphosphonates from (*E*)-2-arylkynylphosphonates has been developed, in which the InCl<sub>3</sub>-NaBH<sub>4</sub>-MeCN system was firstly employed in reduction of alkynylphosphonates successfully. A radical mechanism is proposed.

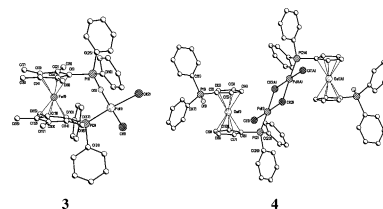


**Oleg V. Gusev, Tat'yana A. Peganova, Alexander M. Kalsin, Nikolai V. Vologdin, Pavel V. Petrovskii, Konstantin A. Lyssenko, Aleksei V. Tsvetkov, Irina P. Beletskaya**

*J. Organomet. Chem.* 690 (2005) 1710

Palladium (II) complexes with mono-oxide 1, 1'-bis(diphenylphosphino)metallocene ligands [Fe( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>P{O}-Ph<sub>2</sub>)] and [Os( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P{O}-Ph<sub>2</sub>)]

The monoxides [Fe( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>-Me<sub>4</sub>P{O}Ph<sub>2</sub>)] (**1**) and [Os( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P{O}Ph<sub>2</sub>)] (**2**) have been prepared by treatment of the corresponding diphosphines with CCl<sub>4</sub> and methanol. The **1** and **2** react with [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>] to give dichlorides [Fe( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>-Me<sub>4</sub>P{O}Ph<sub>2</sub>)}PdCl<sub>2</sub>] (**3**) and [Os( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P{O}Ph<sub>2</sub>)}PdCl(μ-Cl)]<sub>2</sub> (**4**) with  $\kappa^2$ -P,O and  $\kappa^1$ -P chelated ligands, correspondingly. The **3** and **4** were tested in catalytic amination and Suzuki type reactions of *p*-bromotoluene to show moderate activity.

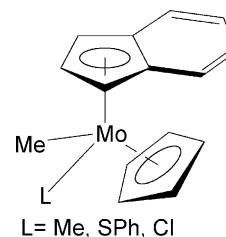


**Isabel S. Gonçalves, Carla A. Gamelas, Cláudia C.L. Pereira, Carlos C. Romão**

*J. Organomet. Chem.* 690 (2005) 1718

Synthesis and reactivity of mixed-ring indenyl complexes of molybdenocene

The complex [IndCpMo(NCMe)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> provides a suitable entry to the synthesis of IndCpMoX<sub>2</sub> (X = Br, Me) and [IndCpMo( $\kappa^2$ -BPz<sub>4</sub>)]BF<sub>4</sub>. Asymmetric complexes like IndCpMoCl(Me), [IndCpMoCl(Me)]-BF<sub>4</sub> and IndCpMo(SPh)(Me) were also prepared. These mixed ring indenyl complexes were characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy, and examined by cyclic voltammetry.

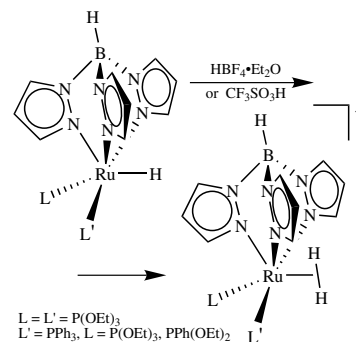


**Gabriele Albertin, Stefano Antoniutti, Marco Bortoluzzi, Gianluigi Zanardo**

*J. Organomet. Chem.* 690 (2005) 1726

Synthesis and reactivity of hydride and dihydrogen complexes of ruthenium with tris(pyrazolyl)borate and phosphite ligands

The synthesis of classical and non-classical ruthenium (II) mixed-ligand hydride complexes RuHTpL(PPh<sub>3</sub>) and [Ru( $\eta^2$ -H<sub>2</sub>)TpL(PPh<sub>3</sub>)]<sup>+</sup> with phosphite and tris(pyrazolyl)borate is described. Vinylidene [RuTp{C=C(H)R}L(PPh<sub>3</sub>)]BPh<sub>4</sub> and allenylidene [RuTp{C=C=CR1R2}L(PPh<sub>3</sub>)]-BPh<sub>4</sub> complexes were also prepared by allowing  $\eta^2$ -H<sub>2</sub> derivatives to react with the appropriate HC≡CR and HC≡CC(OH)-R1R2 alkynes.

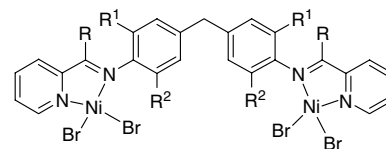


**Suyun Jie, Dongheng Zhang, Tianzhu Zhang, Wen-Hua Sun, Jiutong Chen, Qing Ren, Dongbing Liu, Gang Zheng, Wei Chen**

*J. Organomet. Chem.* 690 (2005) 1739

Bridged bis-pyridinylimino dinickel(II) complexes: Syntheses, characterization, ethylene oligomerization and polymerization

A series of dinickel(II) complexes bearing 4,4'-methylene-bis(2,6-disubstituted aniline) were synthesized and characterization by IR, microanalysis and X-ray diffraction. In the presence of MAO, these complexes displayed good catalytic activities for ethylene polymerization and oligomerization.

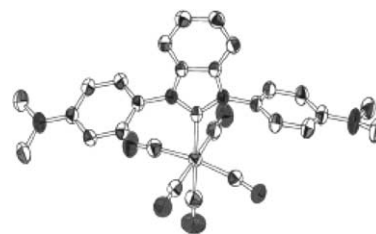


**Hidehiro Sakurai, Koichi Sugitani,  
Toshiyuki Moriuchi, Toshikazu Hirao**

*J. Organomet. Chem.* 690 (2005) 1750

Synthesis and oxidation of (benzimidazolylidene)Cr(CO)<sub>5</sub> complexes

A series of (benzimidazolylidene)Cr(CO)<sub>5</sub> complexes were synthesized and characterized by X-ray crystal structural analysis. Chemical oxidation with (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>-NSbCl<sub>6</sub> afforded the complex with the spin delocalized on the benzimidazolide moiety.

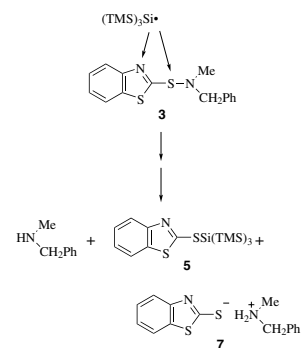


**Vladimir T. Varlamov, Carla Ferreri,  
Chrysostomos Chatgililoglu**

*J. Organomet. Chem.* 690 (2005) 1756

The reaction of benzothiazole sulfenamide with (TMS)<sub>3</sub>SiH: An example of degenerate-branched chain process

The radical initiated reaction of **3** with (TMS)<sub>3</sub>SiH gave benzylmethylamine and thiosilane **5** as main products together with salt **7** as by-product. The amine obtained in a quantitative yield can arise from two independent routes of (TMS)<sub>3</sub>Si· radical attack on **3**. The minor attack on the ring affords 2-mercaptobenzothiazole that can act as a catalyst for the major route during the reaction course and then gives the salt **7** with amine. The reaction is a rare example of a radical chain-branching process and the origin of autocatalysis is discussed in some details.

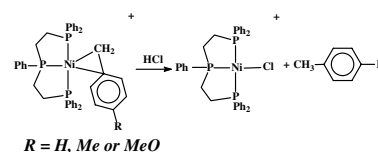


**Valerie Autissier, Ellie Brockman,  
William Clegg, Ross W. Harrington,  
Richard A. Henderson**

*J. Organomet. Chem.* 690 (2005) 1763

Synthesis of [Ni(η<sup>2</sup>-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R-4){PPh(CH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}]<sup>+</sup> (R = H, Me or MeO) and protonation reactions with HCl

The complexes [Ni(η<sup>2</sup>-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>R-4)(triphos)]BPh<sub>4</sub> {R = H, Me or MeO; triphos = PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>} have been prepared and structurally characterised. These complexes react with anhydrous HCl in MeCN to form [NiCl(triphos)]<sup>+</sup> and the substituted toluene. Kinetic studies suggest a mechanism involving initial rapid protonation at the nickel, followed by intramolecular proton migration from nickel to carbon to yield the products.

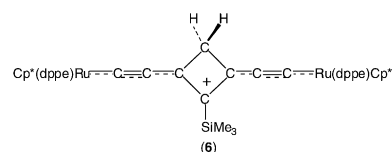


**Michael I. Bruce, Benjamin G. Ellis,  
Brian W. Skelton, Allan H. White**

*J. Organomet. Chem.* 690 (2005) 1772

Further chemistry of ruthenium butatrienylidene complexes

Crystallographically characterised complexes Ru{C≡CC(O)Me}(dppe)Cp\* (3), [Ru{C≡CC(=NH<sub>2</sub>)Me}(dppe)Cp\*]PF<sub>6</sub> (4), [{Ru(dppe)Cp\*}<sub>2</sub>{μ-C≡CC(OMe)=CHCMe=C-C=}]PF<sub>6</sub> (5), and the bis(ethynyl)cyclobutenylidene [{Ru(dppe)Cp\*}<sub>2</sub>{μ-C≡CC<sub>4</sub>H<sub>2</sub>(SiMe<sub>3</sub>)C≡C}]PF<sub>6</sub> (6) have been obtained from the putative butatrienylidene intermediate [Ru(=C=C=C=CH<sub>2</sub>)(dppe)Cp\*]<sup>+</sup>.

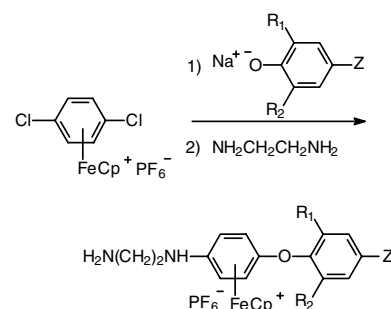


**Joulia Smirnova, Lars Engman,  
Carl-Magnus Andersson, Johan Malm**

*J. Organomet. Chem.* 690 (2005) 1784

An organoiron approach to thyroid hormone analogues

Various approaches to thyroid hormone analogues based on sequential substitution of cationic cyclopentadienyl(1,4-dichlorobenzene)iron(II) complexes with phenoxide/thiophenoxide and hydroxide/amine were studied.

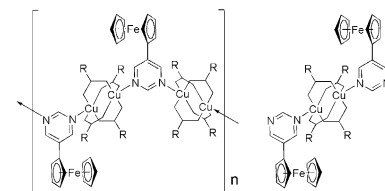


**Ryo Horikoshi, Kazuya Okazawa,  
Tomoyuki Mochida**

*J. Organomet. Chem.* 690 (2005) 1793

Preparation and structures of copper(II) and zinc(II) complexes with 5-ferrocenylpyrimidine: Structural variation derived from flexible coordination ability of the ligand and metal ions

5-Ferrocenylpyrimidine (FcPM) reacted with copper(II) carboxylates and zinc(II) salts to produce coordination polymers  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{FcPM})]_n$  and  $[\text{Cu}_2(\text{C}_5\text{H}_{11}\text{COO})_4(\text{FcPM})]_n \cdot n\text{CH}_3\text{CN}$ , and three discrete complexes with various M:L stoichiometries,  $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{FcPM})_2]$ ,  $[\text{Zn}(\text{NO}_3)_2(\text{FcPM})_3]$ , and  $[\text{Zn}(\text{SCN})_2(\text{FcPM})_2] \cdot 0.5\text{H}_2\text{O}$ .



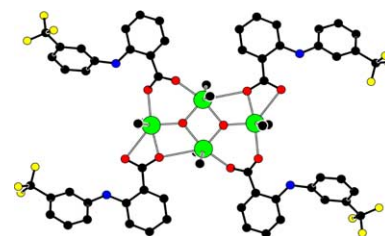
**Dimitra Kovala-Demertzi, Vaso N. Dokorou,  
Jerry P. Jasinski, Adam Opolski,  
Joanna Wiecek, Maria Zervou,  
Mavroudis A. Demertzis**

*J. Organomet. Chem.* 690 (2005) 1800

Organotin flufenamates: Synthesis, characterization and antiproliferative activity of organotin flufenamates

Three novel flufenamates  $[\text{Me}_2(\text{flu})\text{SnO-Sn}(\text{flu})\text{Me}_2]_2$  (**1**),  $[\text{Bu}_2(\text{flu})\text{SnOSn}(\text{flu})\text{Bu}_2]_2$  (**2**) and  $[\text{Bu}_2\text{Sn}(\text{flu})_2]$  (**3**) have been prepared and structurally characterized by means of

vibrational and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$ ) spectroscopy. Based on spectroscopic data, dimeric tetraorganostannoxanes are proposed for **1** and **2**, and monomeric hexacoordinate structure for **3**, respectively. The crystal structure of **1** was determined by X-ray crystallography. This structure is self-assembled via  $\pi \rightarrow \pi$  and C-H  $\rightarrow \pi$  stacking interactions. Flufenamic acid and flufenamates **2** and **3** were evaluated for antiproliferative activity in vitro. Among the compounds tested **2** and **3** exhibited high cytotoxic activity against the cancer cell line A549 (non-small cell lung carcinoma).

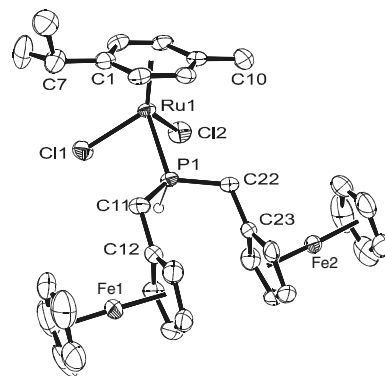


**Shadrick I.M. Paris, Frederick R. Lemke,  
René Sommer, Peter Lönnecke,  
Evamarie Hey-Hawkins**

*J. Organomet. Chem.* 690 (2005) 1807

Molecular structures of ruthenium half-sandwich complexes with primary and secondary phosphines:  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$  [ $p\text{-cymene} = 1\text{-Me-4-Pr}^t\text{C}_6\text{H}_4$ ;  $\text{PR}_3 = \text{PH}_2\text{Fc}$  (**1**),  $\text{PH}(\text{CH}_2\text{Fc})_2$  (**3**);  $\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$ ] were synthesized from  $[(p\text{-cymene})\text{RuCl}_2]_2$  and the corresponding phosphine and fully characterized by IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) spectroscopy. Molecular structures of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$  [ $\text{PR}_3 = \text{PH}_2\text{Fc}$  (**1**),  $\text{PH}_2\text{CH}_2\text{Fc}$  (**2**),  $\text{PH}(\text{CH}_2\text{Fc})_2$  (**3**)] are reported.

A series of air-stable half-sandwich complexes of general formula  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$  [ $p\text{-cymene} = 1\text{-Me-4-Pr}^t\text{C}_6\text{H}_4$ ;  $\text{PR}_3 = \text{PH}_2\text{Fc}$  (**1**),  $\text{PH}(\text{CH}_2\text{Fc})_2$  (**3**);  $\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$ ] were synthesized from  $[(p\text{-cymene})\text{RuCl}_2]_2$  and the corresponding phosphine and fully characterized by IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) spectroscopy. Molecular structures of  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$  [ $\text{PR}_3 = \text{PH}_2\text{Fc}$  (**1**),  $\text{PH}_2\text{CH}_2\text{Fc}$  (**2**),  $\text{PH}(\text{CH}_2\text{Fc})_2$  (**3**)] are reported.

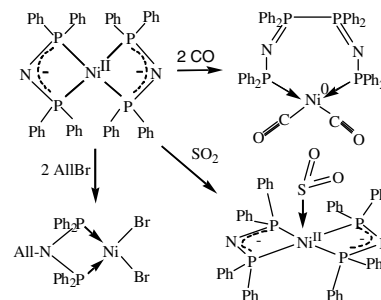


Vyacheslav V. Sushev, Alexander N. Kornev, Yuri A. Kurskii, Olga V. Kuznetsova, Georgy K. Fukin, Yulia H. Budnikova, Gleb A. Abakumov

*J. Organomet. Chem.* 690 (2005) 1814

Nickel(II) bis(diphenylphosphino)amide: Redox-coupling of dppa ligands in coordination sphere of Ni<sup>2+</sup> and some other properties

Interaction of nickel(II) bis(diphenylphosphino)diphenylamide {Ni(dppa)<sub>2</sub>} with carbon monoxide leads to the redox coupling of dppa ligands and formation of zero-valent nickel complex (CO)<sub>2</sub>Ni(Ph<sub>2</sub>P=N=PPh<sub>2</sub>—PPh<sub>2</sub>=NPPH<sub>2</sub>). Similar reaction with sulphur dioxide yields simple adduct (SO<sub>2</sub>)-Ni<sup>II</sup>[(PPh<sub>2</sub>)<sub>2</sub>N]<sub>2</sub>, while allyl bromide alkylate dppa ligand to form All-N(PPh<sub>2</sub>)<sub>2</sub>NiBr<sub>2</sub>. The electrochemical reduction of Ni(dppa)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> takes place in two steps: reversible one-electron and quasi-reversible three-electron step.

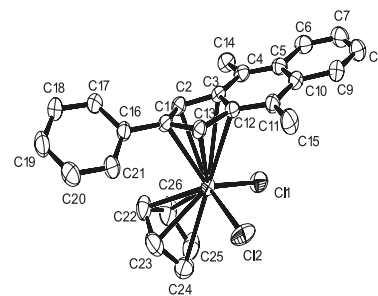


Do Han Kim, Jung A Lee, Bun Yeoul Lee, Young Keun Chung

*J. Organomet. Chem.* 690 (2005) 1822

Synthesis of zirconocenes bearing benz[*f*]indenyl ligand and their use as a catalyst in ethylene polymerization

Benz[*f*]indenyl zirconium complexes have been successfully synthesized and characterized. Their catalytic activities were evaluated for the polymerization of ethylene. The complexes combined with MAO can be highly active single site catalysts, which display activities comparable with that of the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO system and provide very high molecular weight polyethylenes. The melting point of the polymers indicates the formation of linear polyethylene.

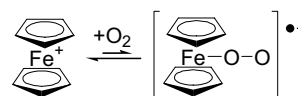


J.P. Hurvois, C. Moinet

*J. Organomet. Chem.* 690 (2005) 1829

Reactivity of ferrocenium cations with molecular oxygen in polar organic solvents: Decomposition, redox reactions and stabilization

Adducts between oxygen and ferrocenium species can differently evolve according to the polar organic solvent (oxidizable or not) and the absence or the presence of another reagents.

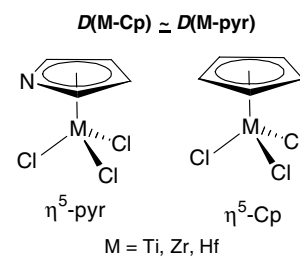


Alberto R. Dias, Luis F. Veiros

*J. Organomet. Chem.* 690 (2005) 1840

Are cyclopentadienyl complexes more stable than their pyrrolyl analogues?

The bond dissociation enthalpies of η<sup>5</sup>-coordinated pyrrolyl and cyclopentadienyl complexes with group 4 metals, [M(η<sup>5</sup>-X)Cl<sub>3</sub>], are calculated by means of a thermochemical cycle combining DFT/B3LYP results and experimental data. The values obtained for D(M-Cp) and D(M-pyr) are very similar, suggesting that the known instability of pyrrolyl complexes, when compared to cyclopentadienyl analogues, should be caused by kinetic reasons.

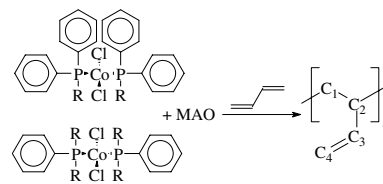


**Giovanni Ricci, Alessandra Forni,  
Aldo Boglia, Anna Sommazzi,  
Francesco Masi**

*J. Organomet. Chem.* 690 (2005) 1845

Synthesis, structure and butadiene polymerization behavior of  $\text{CoCl}_2(\text{PR}_x\text{Ph}_{3-x})_2$  ( $\text{R}$  = methyl, ethyl, propyl, allyl, isopropyl, cyclohexyl;  $x$  = 1, 2). Influence of the phosphorous ligand on polymerization stereoselectivity

The synthesis and characterization of cobalt(II) phosphine complexes of general formula  $\text{CoCl}_2(\text{PR}_x\text{Ph}_{3-x})_2$  ( $\text{R}$  = alkyl/allyl group;  $x$  = 1, 2) are described. The X-ray crystal structures of some of them are reported. Treatment of these complexes with methylaluminoxane leads to highly active catalysts giving 1,2 polybutadienes having different tacticity depending on the phosphorous ligand.



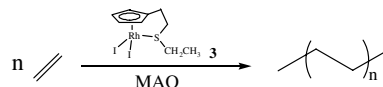
$\text{R}$  = methyl, ethyl, *normal*-propyl, *iso*-propyl, allyl, cyclohexyl

**Xiu-Feng Hou, Yin-Qiang Cheng,  
Xin Wang, Guo-Xin Jin**

*J. Organomet. Chem.* 690 (2005) 1855

Half-sandwich cyclopentadienyl rhodium complexes bearing pendant sulfur or oxygen ligands and their catalytic behaviors in ethylene polymerization

Two rhodium complexes with sulfur or oxygen functionalized cyclopentadienyl ligands  $[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{CH}_3]\text{RhI}_2$  (**3**),  $\{[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3]\text{RhI}_2\}_2$  (**4**) have been synthesized and characterized. **3** and **4** can be used as a catalyst for ethylene polymerization in the presence of methylaluminoxane (MAO) as co-catalyst.



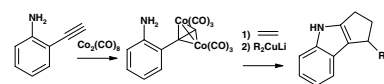
## Notes

**Michael P. Coogan, Li-ling Ooi,  
Derek S. Wilkins**

*J. Organomet. Chem.* 690 (2005) 1861

Pauson–Khand reaction of 2-ethynyl aniline: Synthesis of fused ring indoles by organocuprate conjugate addition followed by spontaneous dehydration

The Pauson–Khand reaction of 2-ethynyl aniline gives the expected cyclopentenone product, with the aniline alpha to the ketone. Treatment with organocuprates gives not the simple conjugate addition product, but the indole derived from an addition–cyclisation–nucleophilic attack sequence.

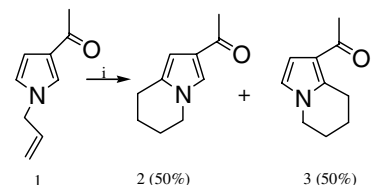


**Silvia Rocchiccioli, Roberta Settambolo,  
Raffaello Lazzaroni**

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Domino reaction sequences in the rhodium-catalyzed hydroformylation of 3-acetyl-1-allylpyrrole: a short route to 5,6,7,8-tetrahydroindolizines

The rhodium-catalyzed hydroformylation of 3-acetyl-1-allylpyrrole (**1**) gives an equimolar mixture of the tetrahydroindolizines **2** and **3** via two different domino processes. Interestingly, **3** forms via a stabilized 8-hydroxyindolizine which, although often postulated as an intermediate in the cyclization mechanism under *oxo* conditions, has been isolated and characterized here for the first time.



$i$  =  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{CO}/\text{H}_2$  (1:1), 30 atm, 140°C, toluene

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