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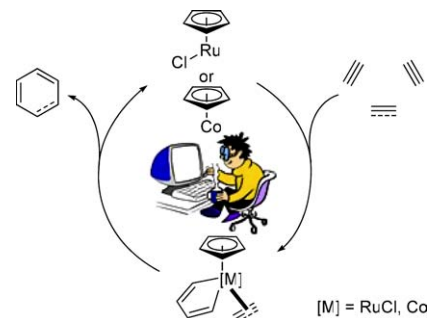
Review

Jesús A. Varela, Carlos Saá

J. Organomet. Chem. 694 (2009) 143

CpRuCl- and CpCo-catalyzed or mediated cyclotrimerizations of alkynes and [2+2+2] cycloadditions of alkynes to alkenes: A comparative DFT study

Recent progress in computational chemistry has allowed the possibility to better understand the mechanisms of metal-catalyzed and metal-mediated reactions. This ability is especially important in those cases where experimental results are difficult to obtain, such as the characterization of the catalytic intermediates. The mechanistic studies for CpRuCl- and CpCo-catalyzed and mediated cyclotrimerizations of alkynes and [2+2+2] cycloadditions of alkynes to alkenes are presented.



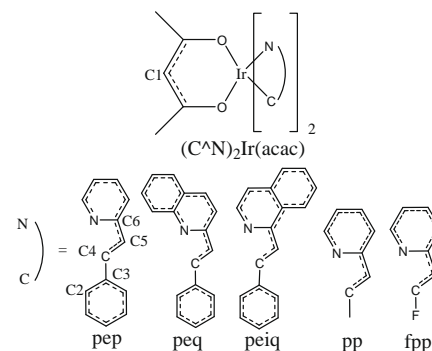
Regular Papers

Tao Liu, Xin Zhou, Qing-Jiang Pan, Bao-Hui Xia, Hong-Xing Zhang

J. Organomet. Chem. 694 (2009) 150

A novel series of iridium complexes with alkenylquinoline ligands: Theoretical study on electronic structure and spectroscopic property

The present theoretical calculations on 1–5 showed that the phosphorescent color and the quantum efficiencies of these Ir(III) complexes can be tuned by changing the π -conjugation effect strength of the C^N ligand.

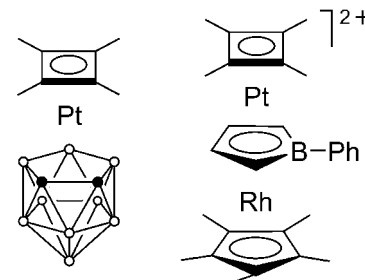


Dmitry A. Loginov, Zoya A. Starikova, Elena A. Petrovskaya, Alexander R. Kudinov

J. Organomet. Chem. 694 (2009) 157

Metallacarboranes and triple-decker complexes with the $(C_4Me_4)Pt$ fragment

(Cyclobutadiene)platinacarboranes were prepared by reaction of $(C_4Me_4)PtCl_2$ with carborane anions. Triple-decker complexes with bridging boratabenzene and borole ligands were synthesized by stacking of sandwich compounds with the $[(C_4Me_4)Pt]^{2+}$ fragment.

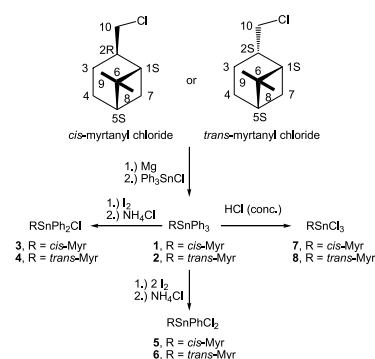


**Jens Beckmann, Andrew Duthie,
Marian Grassmann**

J. Organomet. Chem. 694 (2009) 161

Synthesis and structure of some *cis*- and *trans*-myranylstannanes

The syntheses of enantiomerically pure *cis*- and *trans*-myranylstannanes 1–8 starting from (–)- β -pinene is described. The full characterization of 1–8 was achieved by ^1H , ^{13}C , ^{119}Sn NMR spectroscopy and in selected cases by X-ray crystallography.

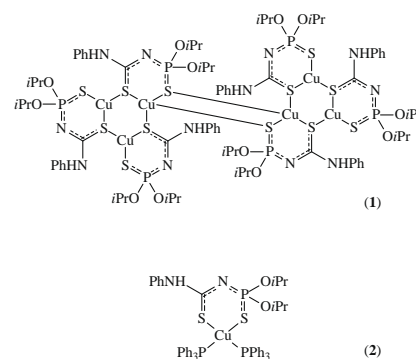


**Felix D. Sokolov, Maria G. Babashkina,
Franck Fayon, Aydar I. Rakhmatullin,
Damir A. Safin, Tania Pape,
F. Ekkehardt Hahn**

J. Organomet. Chem. 694 (2009) 167

Novel bicyclic hexanuclear copper(I) aggregate: Structure and solid state ^{31}P CPMAS NMR spectra of $[(\text{Cu}_3\text{L}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ complexes of *N*-(diisopropoxythiophosphinyl)-*N'*-phenylthiourea (HL)

New *N*-thiophosphorylthiourea $\text{PhNHC}(\text{S})\text{-NHP}(\text{S})(\text{O}i\text{Pr})_2$ (HL) chelates of the Cu^{I} cation of type $[(\text{Cu}_3\text{L}_3)_2]$ have been synthesized and characterized by single crystal X-ray diffraction, FT-IR, ^1H , ^{31}P NMR in solution and by CPMAS ^{31}P NMR spectroscopy in the solid state. In the solid state the aggregate $[(\text{Cu}_3\text{L}_3)_2]$ represents the first example of a spontaneous “side-by-side” association of two neutral cyclic $[\text{Cu}_3\text{L}_3]$ moieties using two Cu–S–Cu bridges formed by the sulfur atoms of the PS-groups. A comparison of the structure and the spectral parameters of $[(\text{Cu}_3\text{L}_3)_2]$ with those of the mononuclear analogue $[\text{Cu}(\text{PPh}_3)_2\text{L}]$ was performed. The values of the $^1J(^{31}\text{P}\text{-}^{63,65}\text{Cu})$ and $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ coupling constants of the $[\text{Cu}(\text{PPh}_3)_2]^+$ moiety in the solid state spectra are reported.

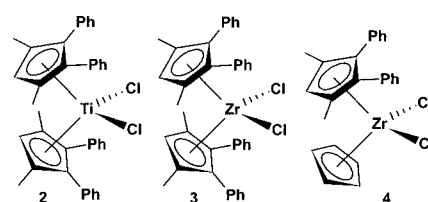


**Michal Horáček, Jiří Pinkas, Jan Merna,
Róbert Gyepes, Philippe Meunier**

J. Organomet. Chem. 694 (2009) 173

Preparation of titanocene and zirconocene dichlorides bearing bulky 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and their behavior in polymerization of ethylene

Synthesis of new titanocene dichloride 2 and zirconocene dichlorides 3, 4 bearing bulky 1,4-dimethyl-2,3-diphenylcyclopentadienyl ligand and their catalytic activity in polymerization of ethylene have been described. Whereas both zirconocene dichlorides 3 and 4 in combination with methylaluminoxane (MAO) exhibited only negligible activity at 30–50 °C, they were highly active at 80 °C. The 2/MAO system was found practically inactive at the same conditions.

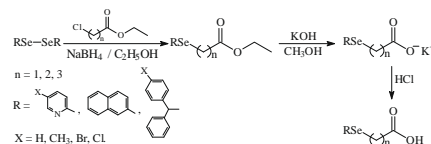


**Aman Bhalla, Yogesh Nagpal,
Rajeev Kumar, S.K. Mehta, K.K. Bhasin,
S.S. Bari**

J. Organomet. Chem. 694 (2009) 179

Synthesis and characterization of novel pyridyl/naphthyl/(diphenyl)methylseleno substituted alkanolic acids: X-ray structure of 2-pyridylselenoethanoic acid, 2-naphthylselenoethanoic acid and 2-(diphenyl)methylselenoethanoic acid

A number of novel and synthetically important pyridyl/naphthyl/(diphenyl)methylseleno substituted alkanolic acids have been synthesized by basic hydrolysis and subsequent acidification of ethyl pyridyl/naphthyl/(diphenyl)methylseleno substituted alkanooates, which were conveniently prepared from ethyl chloroalkanoates and dipyrldyl/dinaphthyl/bis-(diphenylmethyl) diselenide using sodium borohydride in ethanol. The molecular structures of 2-pyridyl/naphthyl/(diphenyl)methyl selenoethanoic acid have been established through X-ray crystallography.

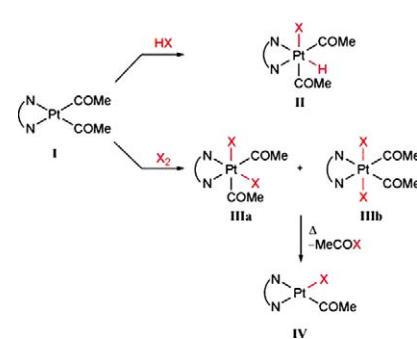


**Michael Werner, Christoph Wagner,
Dirk Steinborn**

J. Organomet. Chem. 694 (2009) 190

Reactivity of diacetylplatinum(II) complexes: Oxidative addition of halogens and hydrogen halides

Diacetylplatinum(II) complexes (**I**) having 2,2'-bipyridine type coligands (NN \curvearrowright NN) were found to react with halogens X₂ (Br₂, I₂) yielding diacetyldihaloplatinum(IV) complexes (**II**) in a strongly solvent dependent diastereometric ratio (*cis/trans*). Thermally induced reductive elimination reactions of complexes **II** led to the formation of acetylhaloplatinum(II) complexes (**IV**). Reactions of **I** with HX (HCl, HBr, HI) under anhydrous conditions resulted in the formation of diacetyl(hydro)platinum(IV) complexes (**III**). The reactivity of complexes **I** in these oxidative addition and reductive elimination reactions will be discussed with respect to that of the requisite dialkyl platinum complexes [PtR₂(NN \curvearrowright NN)].

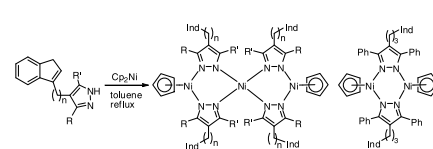


**Weiqiang Tan, Zhengkun Yu, Bing Liu,
Kaikai Wu, Zishuang Liu, Jinzhu Chen**

J. Organomet. Chem. 694 (2009) 199

Synthesis and structural characterization of (CH₂)_n-bridged indenyl-pyrazoles and their cyclopentadienyl nickel(II) complexes

A new class of (CH₂)_n-bridged indenyl-pyrazoles and their cyclopentadienyl nickel(II) complexes of types [CpNi{4-(Ind-(CH₂)_n-RR'Pz)}₂]₂Ni and [CpNi{4-(Ind-(CH₂)₃-3,5-Ph₂Pz)}₂] (Ind = 1*H*-inden-3-yl, *n* = 1–3, RR' = 3,5-disubstituents) were successfully synthesized and structurally characterized.

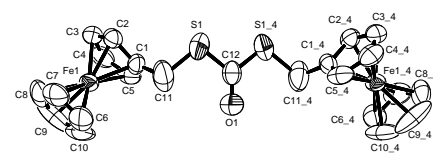


**Douglas Onyancha, Vincent Nyamori,
Cedric W. McClelland, Christopher Imrie,
Thomas I.A. Gerber**

J. Organomet. Chem. 694 (2009) 207

Solvent-free reactions of *N,N'*-thiocarbonyl-diimidazole with ferrocenylcarbinols

The reactions of ferrocenylcarbinols with *N,N'*-thiocarbonyl-diimidazole under both solvent-free conditions and in dichloromethane are described. The reaction of ferrocenylmethanol afforded *S,S*-bis(ferrocenylmethyl)dithiocarbonate, reaction of α -substituted ferrocenylcarbinols provided ferrocenylalkylimidazolides while ω -ferrocenylcarbinols yielded ferrocenylimidazolecarbothioates.

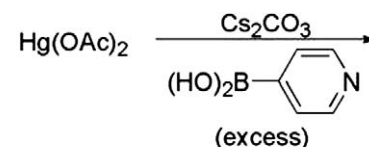


David V. Partyka, Thomas G. Gray

J. Organomet. Chem. 694 (2009) 213

Facile syntheses of homoleptic diaryl-mercurials via arylboronic acids

Mercury-carbon bond formation between mercury(II) acetate and arylboronic acids in the presence of cesium carbonate occurs in moderate to excellent yields. A variety of functional groups and steric bulk are tolerated on the arylboronic acid.

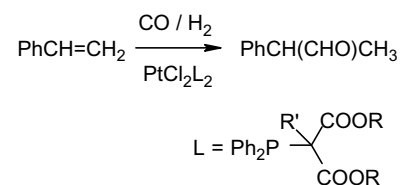


György Petőcz, Gábor Rangits, Megan Shaw, Henriette de Bod, D. Bradley G. Williams, László Kollár

J. Organomet. Chem. 694 (2009) 219

Platinum complexes of malonate-derived monodentate phosphines and their application in the highly chemo- and regioselective hydroformylation of styrene

Novel PtCl_2L_2 type complexes (where $\text{L} = 2$ -diphenylphosphino-malonate derivatives) were prepared and used as catalytic precursors for the hydroformylation of styrene. High regioselectivities towards branched aldehyde were obtained with all platinum-phosphine-tin(II) chloride catalytic systems. It has been revealed by ^{31}P NMR spectroscopy that the ratio of the *cis/trans* complexes is strongly dependent on the structure of the ligand.

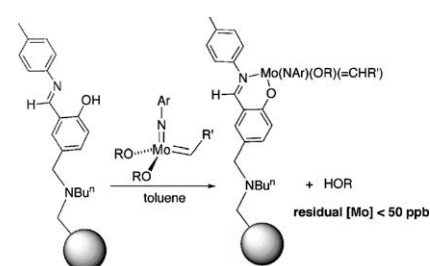


Kapil S. Lokare, Aaron L. Odom

J. Organomet. Chem. 694 (2009) 223

A readily-prepared and efficient solid-supported scavenger for molybdenum alkoxides and a structurally characterized model complex

The sequential addition of H_2NBU , 2-hydroxy-5-(chloromethyl)benzaldehyde, and *p*-toluidine to Merrifield's resin provides a scavenger for molybdenum metathesis catalysts that result in very low residual Mo concentrations. The site of reaction on the catalyst seems to be exclusively alkoxide replacement.

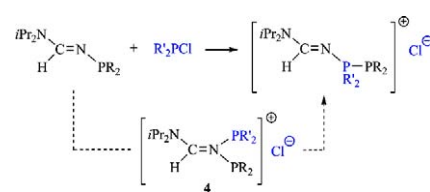


Thanh D. Le, Damien Arquier, Karinne Miqueu, Jean-Marc Sotiropoulos, Yannick Coppel, Stéphanie Bastin, Alain Igau

J. Organomet. Chem. 694 (2009) 229

Unprecedented rearrangement during the formation of P-P homoatomic *N*-phosphino formamidine complexes

Formation of the homoatomic P-P heteroleptic ($R \neq R'$) *N*-phosphino formamidine (phosfam) complexes $[\text{iPr}_2\text{N}-\text{C}(\text{H})=\text{NPR}'_2]\text{Cl}$ results in the formal insertion of the phosphino group of the corresponding alkyl chlorophosphanes $\text{R}'_2\text{P}\text{Cl}$ into the N-P bond of the starting phosfam ligand $\text{iPr}_2\text{N}-\text{C}(\text{H})=\text{N}-\text{PR}_2$. Computed data are in agreement with the transient formation of a heteroatomic N-P intermediate $[\text{iPr}_2\text{NC}(\text{H})=\text{N}(\text{PR}_2)\text{PR}'_2]\text{Cl}$ illustrated by 4.

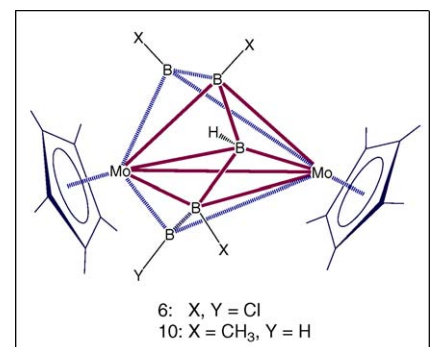


Rajendra Singh Dhayal, Satyanarayan Sahoo, V. Ramkumar, Sundargopal Ghosh

J. Organomet. Chem. 694 (2009) 237

Substitution at boron in molybdaborane frameworks: Synthesis and characterization of isomeric $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{X}_m$ (when $\text{X} = \text{Cl}$: $n = 5, 7, 8$; $m = 4, 2, 1$ and $\text{X} = \text{Me}$: $n = 6, 7$; $m = 3, 2$)

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{MoCl}_4$ with excess of $\text{LiBH}_4\cdot\text{thf}$ followed by pyrolysis with $\text{BHCl}_2\text{SMe}_2$ yielded B-Cl inserted $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Cl}_m$, 2-6 ($n = 5, 7, 8$; $m = 4, 2, 1$). In addition, *exo*-cluster substitution at B-H in $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_9$ was achieved using BuLi/MeI reagents which afforded $(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_5\text{H}_n\text{Me}_m$ (7-10) ($n = 6, 7$; $m = 3, 2$).

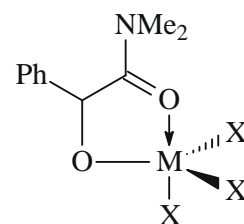


**S.Yu. Bylikin, A.G. Shipov,
E.P. Kramarova, Vad.V. Negrebetsky,
A.A. Korlyukov, Yu.I. Baukov,
M.B. Hursthouse, L. Male, A.R. Bassindale,
P.G. Taylor**

J. Organomet. Chem. 694 (2009) 244

O,O-Monochelate complexes of silicon and germanium halides: The derivatives of *l*-mandelic *N,N*-dimethylamide

Reactions of *O*-TMS-*l*-mandelic *N,N*-dimethylamide with SiCl_4 and GeCl_4 yield *O,O*-monochelates of pentacoordinate Si and Ge trichlorides. X-ray study shows that central atoms have distorted TBP environment with axial amide oxygen and equatorial ether oxygen. All compounds were studied by multinuclear NMR and their structures were analysed by quantum-chemical calculations.



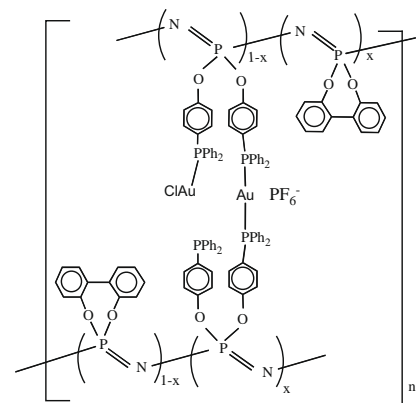
$M = \text{Si, Ge}; X = \text{Cl, Me}$

**Gabino A. Carriedo, Alejandro Presa,
M.L. Valenzuela, Marc Ventalon**

J. Organomet. Chem. 694 (2009) 249

Designed synthesis of metal-organic frameworks containing gold(I) cations supported in phosphazene-phosphine polymeric matrices

The reaction of phosphine-polyphosphazenes with $[\text{Au}(\text{THT})\text{Cl}]$ gave the polymers $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuCl})_x]\}_n$. The reaction of these with $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ in THF led to the metal-organic frameworks of idealized formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}x]\}_m$, $x = 0.15, 0.25$, containing cationic $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$ cross-linking sites. This insoluble polymeric matrices reacted with $[\text{Au}(\text{THT})\text{Cl}]$ to give materials of formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}(\text{AuCl})_{0.5}]\}_n$.

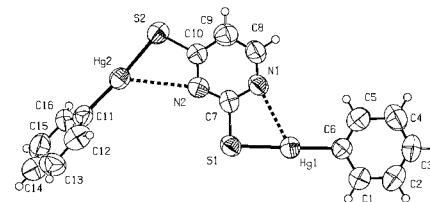


**Sebastião S. Lemos, Danilo U. Martins,
Victor M. Deflon, Javier Elena**

J. Organomet. Chem. 694 (2009) 253

Cationic and neutral phenylmercury(II) complexes with heterocyclic thione ligands. X-ray structures of $[\text{HgPh}(\text{dmpymtH})][\text{BF}_4] \cdot \text{H}_2\text{O}$ and $[\{\text{HgPh}\}_2(\mu\text{-dtu})]$

The phenylmercury(II) complexes with heterocyclic thione ligands $[\text{HgPh}(\text{dmpymtH})][\text{BF}_4]$ and $[\{\text{HgPh}\}_2(\mu\text{-dtu})]$ are mono- and dinuclear, respectively. In the solid state, the Hg(II) atoms adopt a [2+1] coordination sphere in both complexes due to intramolecular $\text{Hg} \cdots \text{N}$ secondary bonds.

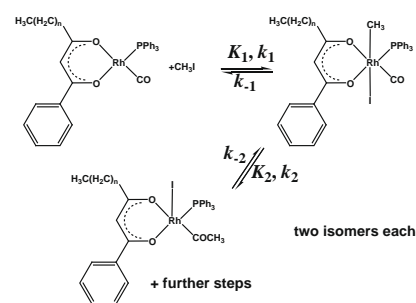


**Nomampondomise F. Stuurman,
Jeanet Conradie**

J. Organomet. Chem. 694 (2009) 259

Iodomethane oxidative addition and CO migratory insertion in monocarbonylphosphine complexes of the type $[\text{Rh}((\text{C}_6\text{H}_5)\text{COCHCO}((\text{CH}_2)_n\text{CH}_3))(\text{CO})(\text{PPh}_3)]$: Steric and electronic effects

Kinetic studies on the first oxidative addition step of $[\text{Rh}((\text{C}_6\text{H}_5)\text{COCHCOR})(\text{CO})(\text{PPh}_3)] + \text{CH}_3\text{I}$ to form $[\text{Rh}((\text{C}_6\text{H}_5)\text{COCHCOR})(\text{CH}_3)(\text{CO})(\text{PPh}_3)(\text{I})]$, $R = (\text{CH}_2)_n\text{CH}_3$, $n = 1-3$, revealed a second order oxidative addition rate constant approximately 500–600 times faster than that observed for the Monsanto catalyst $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

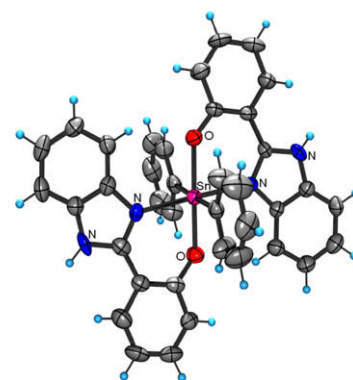


**Adriana Esparza-Ruiz,
Adrián Peña-Hueso, Iris Ramos-García,
Aurora Vásquez-Badillo,
Angelina Flores-Parra,
Rosalinda Contreras**

J. Organomet. Chem. 694 (2009) 269

Hypervalent triphenyl and diphenyl tin coordination compounds derived from 2-(1H-benzimidazol-2-yl)phenol

Reactions of 2-(1H-benzimidazol-2-yl)phenol (**1**) and SnPh_3Cl , SnPh_2Cl_2 and SnCl_4 afford one tetra coordinated OSnPh_3 compound and its pentacoordinated DMSO, H_2O , ethanol and pyridine adducts, where **1** acts as a monodentate ligand O-bound. Two hexacoordinated tin compounds bearing two coplanar ligands are reported. The ligands form six membered rings by O and N coordination. The tin geometry is *all-trans* octahedral. Compounds were identified by ^1H , ^{13}C and ^{119}Sn NMR and X-ray diffraction analyses.

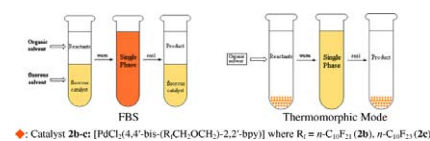


**Norman Lu, Yi-Chuan Chen,
Wei-Shung Chen, Ter-Lin Chen,
Sy-Juen Wu**

J. Organomet. Chem. 694 (2009) 278

Efficient, recoverable, copper-free Sonogashira reaction under FBS and thermomorph mode

Being soluble in polar organic solvents at $>120\text{ }^\circ\text{C}$ but insoluble at room temperature, **2b-c** were demonstrated to be recoverable in Pd-catalyzed Sonogashira reactions under FBS and thermomorph mode.

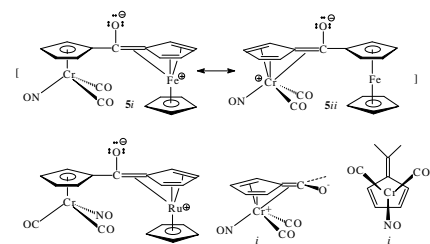


**Yu-Pin Wang, Pauling Wu,
Hsiu-Yao Cheng, Tso-Shen Lin,
Sue-Lein Wang**

J. Organomet. Chem. 694 (2009) 285

Unequivocal assignments of C(2,5) and C(3,4) on the Cp ring of cynichrodene derivatives bearing an electron-donating substituent in ^{13}C NMR spectra and X-ray structures of $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}(\eta^5\text{-C}_5\text{H}_5)$ and $(\text{CO})_2(\text{NO})\text{-Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{-M}(\eta^5\text{-C}_5\text{H}_5)$ (M = Fe, Ru) have been prepared. The qualitative relationship of the NO group orientation and the nonplanarity of Cp-cycloxy carbon has been addressed. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data and compared with calculations via density functional B3LYP correlation-exchange method.

Compounds $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{M}(\eta^5\text{-C}_5\text{H}_5)$ and $(\text{CO})_2(\text{NO})\text{-Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{-M}(\eta^5\text{-C}_5\text{H}_5)$ (M = Fe, Ru) have been prepared. The qualitative relationship of the NO group orientation and the nonplanarity of Cp-cycloxy carbon has been addressed. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data and compared with calculations via density functional B3LYP correlation-exchange method.

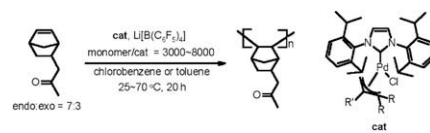


**Il Gu Jung, Young Tak Lee,
Soo Young Choi, Dae Seung Choi,
Youn K. Kang, Young Keun Chung**

J. Organomet. Chem. 694 (2009) 297

Polymerization of 5-norbornene-2-methyl acetate catalyzed by air-stable cationic (η^3 -substituted allyl) palladium complexes of N-heterocyclic carbene

In situ generated air-stable cationic allyl palladium N-heterocyclic carbene (NHC) complexes were used as catalysts for vinyl-addition polymerization of 5-norbornene-2-methyl acetate. As the steric bulkiness of the substituent(s) on the allyl group increases, the catalyst became more stable and the catalytic activity of the catalyst increased.



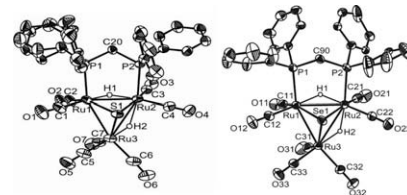
Notes

**Md. Iqbal Hyder, Noorjahan Begum,
Md. Delwar H. Sikder,
G.M. Golzar Hossain, Graeme Hogarth,
Shariff E. Kabir, Christian J. Richard**

J. Organomet. Chem. 694 (2009) 304

Synthesis and structure of sulfur and selenium capped dihydride triruthenium clusters $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-E})]$ (E = S, Se)

The synthesis, molecular structures and dynamic behavior of the dihydride triruthenium clusters $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-S})]$ (**2**) and $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-dppm})(\mu_3\text{-Se})]$ (**5**) are described. Both **2** and **5** are fluxional at room temperature being attributed to hydride migration between the non-bridged edges. Protonation of **2** with HBF_4 affords the cationic trihydride $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_3(\mu\text{-dppm})(\mu_3\text{-S})][\text{BF}_4]$ (**6**) in which the hydrides are non-fluxional due to the blocking of the free ruthenium-ruthenium edge.



**Sophie R. Beeren, Serin L. Dabb,
Barbara A. Messerle**

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Intramolecular hydroamination catalysed by Ag complexes stabilised *in situ* by bidentate ligands

Silver complexes generated *in situ* from AgOTf and a series of bidentate P- and N-donor ligands, including the novel pyrazole-phosphine ligand 1-(2-(diphenylphosphino)phenyl)pyrazole, were investigated as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine. The best catalyst (turnover rate = 129 h^{-1}) was formed from equimolar amounts of 1-(2-(diphenylphosphino)ethyl)pyrazole and AgOTf.

