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Regular Papers

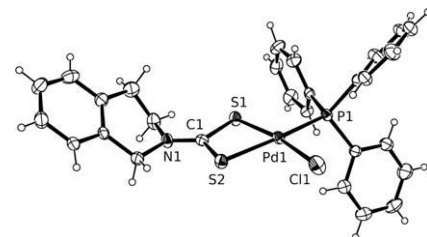
Farkhanda Shaheen, Amin Badshah, Marcel Gielen, Gianluca Croce, Ulrich Florke, Dick de Vos, Saqib Ali

J. Organomet. Chem. 695 (2010) 315

In vitro assessment of cytotoxicity, anti-inflammatory, antifungal properties and crystal structures of metallacyclic palladium(II) complexes

Metallacyclic palladium(II) complexes [Pd(L)-(R₃P)Cl], L = TIQDTC (1,2,3,4-tetrahydroisoquinolinedithiocarbamate), 4MpipDTC (4-methylpiperadinedithiocarbamate), MPizDTC (N-methylpiperazinedithiocarbamate), R₃P =

Ph₃P, (o-tolyl)₃P, Ph₂ClP, were synthesized in a 1:1 molar metal–ligand ratio. These complexes were characterized by elemental analyses, FT-IR, multinuclear (¹H, ¹³C and ³¹P) NMR. The X-ray crystal structures of [Pd(TIQDTC)(Ph₃P)Cl] and [Pd(TIQDTC)((o-tolyl)₃P)Cl] show a slightly distorted square planar environment around the Pd(II) ion with S–Pd–S and P–Pd–Cl average bond angles of 74.51 and 92.41, respectively. These complexes were screened for cytotoxic, antifungal, anti-inflammatory and antibacterial activity. Some complexes exhibit a significant activity against fungi.

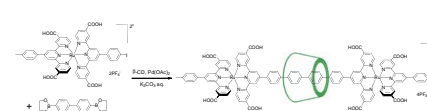


Gang Chen, Jianlong Xia, Ziyong Li, Guang-Ao Yu, Shan Jin, Sheng Hua Liu

J. Organomet. Chem. 695 (2010) 323

A novel conjugated [2]rotaxane with an Ru-containing axle constructed from a carboxy-functionalized bis-terpyridyl ruthenium complex and β-cyclodextrin: Synthesis, characterization, and properties

A novel Ru-containing conjugated [2]rotaxane, which utilizes a carboxy-functionalized bis-terpyridyl ruthenium complex as an end group, has been prepared by Suzuki coupling in the presence of β-CD, and its photophysical properties have shown that insulation by the cyclodextrin reduces the fluorescence intensity compared to the free dumbbell.

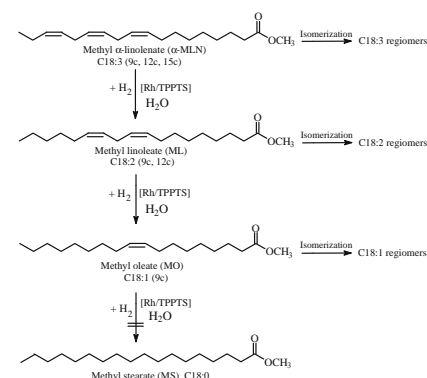


Achilleas Bouriazos, Sotiris Sotiriou, Constantinos Vangelis, Georgios Papadogianakis

J. Organomet. Chem. 695 (2010) 327

Catalytic conversions in green aqueous media: Part 4. Selective hydrogenation of polyunsaturated methyl esters of vegetable oils for upgrading biodiesel

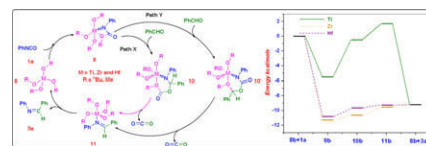
This study deals with the selective hydrogenation of polyunsaturated methyl esters of linseed, sunflower and soybean oils to monounsaturated (C18:1) counterparts which is 1st generation biodiesel of increased oxidative stability, energy and environmental performance at a low pour point employing industrially applied water-soluble Rh/TPPTS catalytic complexes [TPPTS = P(C₆H₄-*m*-SO₃Na)₃] in green aqueous/organic two-phase systems.



Akshai Kumar, Ashoka G. Samuelson*J. Organomet. Chem.* 695 (2010) 338

Room temperature metathesis of aryl isocyanates and aromatic aldehydes catalyzed by group(IV) metal alkoxides: An experimental and computational study

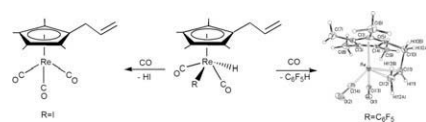
Aromatic aldehydes and aryl isocyanates do not react at room temperature. In the presence of catalytic amounts of group(IV) alkoxides, the two undergo metathesis to produce imines with the extrusion of carbon dioxide. Among the alkoxides of group(IV) metals, Ti was found to be more efficient than Zr and Hf. Computational studies on model metal alkoxides are helpful in understanding this reactivity pattern.

**Fernando Godoy, Alejandra Gómez, Gloria Cárdenas-Jirón, A. Hugo Klahn, Fernando J. Lahoz***J. Organomet. Chem.* 695 (2010) 346

Synthesis and reactivity of η^5 -tetramethylcyclopentadienyl-propenyl rhenium complexes: Molecular structure of $[(\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_2]$

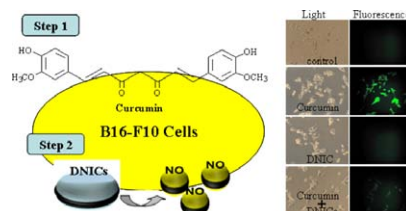
The fulvene complexes $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)\text{Re}(\text{CO})_2(\text{R})]$ (**1a**, R=I; **1b**, R=C₆F₅) react at the exocyclic methylene carbon with a vinylmagnesium bromide solution to produce the anionic species $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_2(\text{R})]^-$. Protonation with HCl at 0 °C produces the hydride complexes $[\text{trans-}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_2(\text{R})(\text{H})]$ (**2a**, R=I; **2b**, R=C₆F₅). Thermolysis

of a hexanes solution of the iodo-hydride (**2a**) under a CO atmosphere yields the complex $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_3]$ (**3**) and $[\text{Re}(\text{CO})_5\text{I}]$ as by-product. Thermolysis of **2b** produced three new products, mainly the chelated complex $[(\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_2]$ (**4**) and complex **3**, with a non-coordinated olefin group, in moderated yield, and traces of $[\text{Re}(\text{CO})_5(\text{C}_6\text{F}_5)]$. Thermolysis of an hexanes solution of **2** in presence of an excess of PMe₃, afforded the phosphine derivative $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Re}(\text{CO})_2(\text{PMe}_3)]$ (**5**). All the complexes were characterized by IR, ¹H, ¹³C and ³¹P NMR spectroscopies and mass spectrometry. The molecular structure of **4** has also been determined. The molecule exhibits a formal three-legged piano-stool structure, with two CO groups, and the third position corresponding to the η^2 -coordination of the propenyl side arm of the $\eta^5\text{-C}_5\text{Me}_4$ ring.

**Yu-Der Wen, Yun-Lung Ho, Rong-Jen Shiau, Jung-Kai Yeh, Jheng-Yu Wu, Wei-Lung Wang, Show-Jen Chiou***J. Organomet. Chem.* 695 (2010) 352

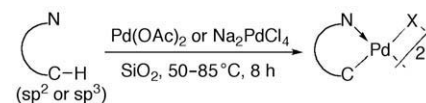
Synergistic antitumor effect of curcumin and dinitrosyl iron complexes for against melanoma cells

The pretreatment of curcumin followed by the treatment of $[\text{Na}][(\text{NO})_2\text{Fe}(\text{SCH}_2\text{-CON}(\text{CH}_3)_2)_2]$ (**NC03**) showed the synergistic antitumor effect against B16-F10 cells.

**Irina P. Smoliakova, Jessica L. Wood, Valeria A. Stepanova, Relindis Y. Mawo***J. Organomet. Chem.* 695 (2010) 360

Solvent-free cyclopalladation on silica gel

Solvent-free cyclopalladation of tertiary, secondary and primary benzylamines, as well as oxazolines on SiO₂ provides the corresponding palladacycles with a (sp²)C-Pd or (sp³)C-Pd bond in the yields comparable with or exceeding those reported for conventional solvent conditions.

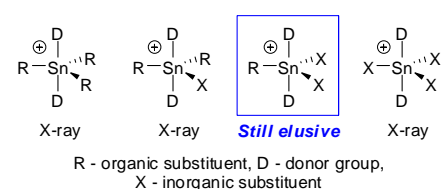


**Mikhail S. Nechaev, Oleg V. Chernov,
Ivan A. Portnyagin, Victor N. Khrustalev,
Rinat R. Aysin, Valery V. Lunin**

J. Organomet. Chem. 695 (2010) 365

In search for a pentacoordinated mono-
organo stannyl cation

Pentacoordinated monoorgano stannyl cation $\text{PhSn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2^+$ was generated by salt metathesis from $\text{PhSn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Cl}$ and $\text{Ag}[\text{WCA}]$ (WCA = weakly coordinating anion $\text{Al}(\text{OCH}(\text{CF}_3)_2)_4^-$ or $\text{B}(\text{C}_6\text{F}_5)_4^-$). It was not isolated due to its strong electrophilicity. Abstraction of anions $\text{OCH}(\text{CF}_3)_2^-$ and C_6F_5^- from aluminate and borate WCAs takes place.

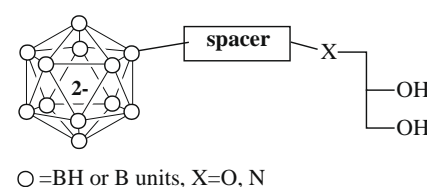


**Andrey Semioshkin, Julia Laskova,
Olga Zhidkova, Ivan Godovikov,
Zoya Starikova, Vladimir Bregadze,
Detlef Gabel**

J. Organomet. Chem. 695 (2010) 370

Synthesis and structure of novel *closo*-
dodecaborate-based glycerols

The reactions of oxonium derivatives of $[\text{B}_{12}\text{H}_{12}]^{2-}$ with different glycerol-based nucleophiles were studied. A series of novel *closo*-dodecaborate-based glycerols with different net charges of the molecules were prepared. A structure of {2-[2-(4-(2,3-dihydroxypropyl)-dipiperazinium-1-yl)-ethoxy]-ethoxy}-undecahydro-*closo*-dodecaborate was determined and the existence of different intermolecular H-bonds was shown.

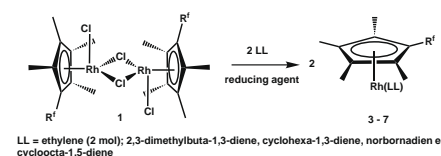


**Jan Čermák, Alena Krupková,
Kateřina Auerová, Milan Zamrzla,
Thu Huong Nguyen Thi, Pavel Vojtíšek,
Ivana Císařová**

J. Organomet. Chem. 695 (2010) 375

Tetramethyl(perfluoroalkyl)cyclopentadienyl rhodium(I) complexes with ethylene or diene ligands. Crystal structure of $[(\eta^5\text{-C}_5\text{Me}_4\text{C}_6\text{F}_{13})\text{Rh}(\text{CO})_2]$

Tetramethyl(perfluoroalkyl)cyclopentadienyl rhodium(I) complexes with ethylene or diene (norbornadiene, cycloocta-1,5-diene, 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene) ligands were obtained by reduction of $[(\text{C}_5\text{Me}_4\text{C}_n\text{F}_{2n+1})\text{RhCl}_2]_2$ dimers by zinc in THF or by propan-2-ol/sodium carbonate in the presence of the ligands. Crystal structure of $[(\eta^5\text{-C}_5\text{Me}_4\text{C}_6\text{F}_{13})\text{Rh}(\text{CO})_2]$ complex was determined by X-ray diffraction.

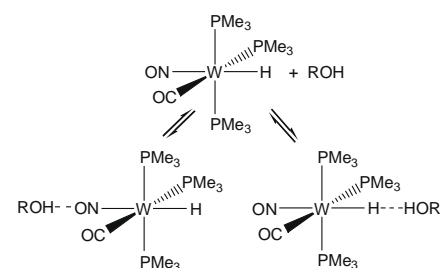


**Nataša Avramović, Jürgen Höck,
Olivier Blacque, Thomas Fox,
Helmut W. Schmalle, Heinz Berke**

J. Organomet. Chem. 695 (2010) 382

Hydridic reactivity of $\text{W}(\text{CO})(\text{H})(\text{NO})(\text{PMe}_3)_3$ – Dihydrogen bonding and H_2 formation with protic donors

Protonation of $\text{W}(\text{CO})(\text{H})(\text{NO})(\text{PMe}_3)_3$ (1) with various ROH protic donors produced organoxy complexes with evolution of H_2 . Dihydrogen bonding and hydrogen bonding equilibria to H_W and O_NO of 1 preceding this step were detected and analyzed in quantitative VT IR and NMR studies. The dihydrogen bonding enthalpy with 3,4,5- $\text{Me}_3\text{C}_6\text{H}_2\text{OH}$ amounts to -5.8 kcal/mol and the dihydrogen bonding $\text{H}\cdots\text{H}$ distance was determined to 1.9 Å.

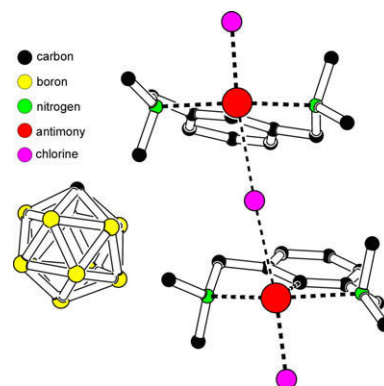


**Libor Dostál, Roman Jambor,
Robert Jirásko, Zdeňka Padělková,
Aleš Růžička, Jaroslav Holecěk**

J. Organomet. Chem. 695 (2010) 392

Structural study on the organoantimony(III) NCN – Chelated compounds [2,6-(Me₂NCH₂)₂C₆H₃]SbX₂ – Influence of the polar group X

It was demonstrated that the behaviour of polar group X in the compounds of the type [2,6-(Me₂NCH₂)₂C₆H₃]SbX₂ has a crucial effect on the geometry around the central antimony atom. The shapes of coordination polyhedron range from a bicapped – trigonal pyramid (X = CH₃COO), and a distorted tetragonal pyramid (X = CF₃COO) to a ψ -trigonal bipyramid (X = Cl, CB₁₁H₁₂). Even more, an unusual dinuclear ionic complex was prepared and characterized and in this case the structure of the organometallic cation can be described as one apex sharing distorted tetragonal pyramids.

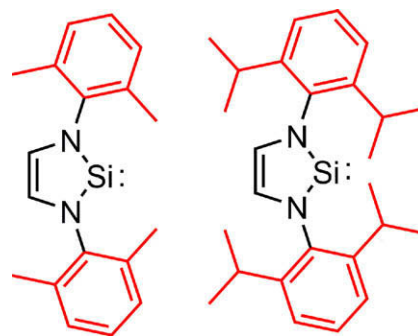


**P. Zark, A. Schäfer, A. Mitra, D. Haase,
W. Saak, R. West, T. Müller**

J. Organomet. Chem. 695 (2010) 398

Synthesis and reactivity of *N*-aryl substituted *N*-heterocyclic silylenes

N-aryl substituted silylenes of the 2-silamidazolidene type were synthesized by metal-reduction and their reactivity was studied.

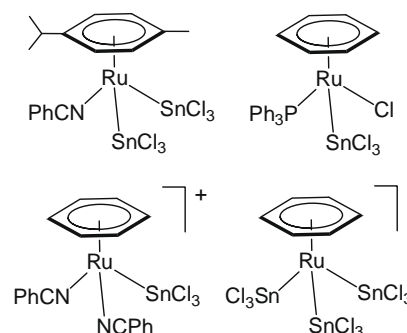


**Bruno Therrien, Trieu-Tien Thai,
Julien Freudenreich, Georg Süss-Fink,
Sergey S. Shapovalov,
Alexandr A. Pasynskii,
Laurent Plasseraud**

J. Organomet. Chem. 695 (2010) 409

Bimetallic ruthenium–tin chemistry: Synthesis and molecular structure of arene ruthenium complexes containing trichlorostannyl ligands

A series of neutral, anionic and cationic arene ruthenium complexes containing the trichlorostannyl ligand have been synthesized from SnCl₂ and the corresponding arene ruthenium dichloride dimers [(η^6 -arene)Ru(μ_2 -Cl)Cl]₂: neutral complexes [(η^6 -C₆H₆)Ru(PPh₃)(SnCl₃)Cl], [(η^6 -Pr^cC₆H₄-Me)Ru(PPh₃)(SnCl₃)Cl] and [(η^6 -Pr^cC₆H₄-Me)Ru(NCPh)(SnCl₃)₂], a cationic complex [(η^6 -C₆H₆)Ru(NCPh)₂(SnCl₃)⁺] as well as anionic complexes [(η^6 -C₆H₆)Ru(SnCl₃)₃]⁻ and [(η^6 -Pr^cC₆H₄Me)Ru(SnCl₃)₂Cl]⁻.



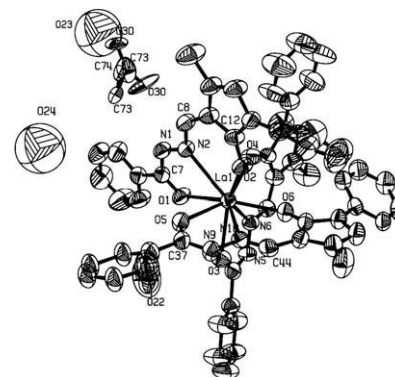
**Hong-Ge Li, Zheng-Yin Yang,
Bao-Dui Wang, Jin-Cai Wu**

J. Organomet. Chem. 695 (2010) 415

Synthesis, crystal structure, antioxidation and DNA-binding properties of the Ln complexes with 1-phenyl-3-methyl-5-hydroxypyrazole-4-carbaldehyde-(benzoyl)hydrazone

Two lanthanide complexes (Ln = La, Pr) with a PMFP Schiff-base, 1-phenyl-3-methyl-5-hydroxypyrazole-4-carbaldehyde-(benzoyl)hydrazone (H₂L) were synthesized

and characterized. The crystal structure of the La complex was determined by single-crystal X-ray diffraction, the coordination polyhedron is a tricapped trigonal prism configuration. Furthermore, the DNA-binding properties and abilities of antioxidation for hydroxyl radicals of the ligand and its Ln complex were investigated. The results showed that lanthanide complexes with PMFP Schiff-base have many potential practical applications.

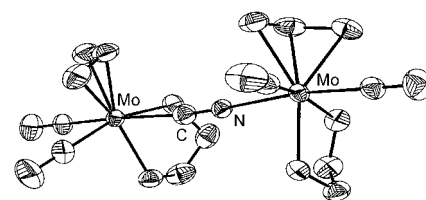


**Fu-Chen Liu, Tu-Chieh Tsai, Yu-Liang Lin,
Chen-Shiang Lee, Pei-Shan Yang,
Ju-Chun Wang**

J. Organomet. Chem. 695 (2010) 423

Syntheses, structures, and dynamic properties of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}; \text{X} = \text{Br}, \text{N}_3, \text{CN}$) and $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}, \text{W}$) possess asymmetric *endo*-forms, however, $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ ($M = \text{Mo}, \text{W}$) possess symmetric *endo*-form.

Compounds $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}; \text{X} = \text{Br}, \text{N}_3, \text{CN}$) and $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}, \text{W}$) were synthesized. In the solid state, $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}; \text{X} = \text{Br}, \text{N}_3$) and $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}, \text{W}$) possess asymmetric *endo*-forms, however, $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ ($M = \text{Mo}, \text{W}$) possess symmetric *endo*-form.

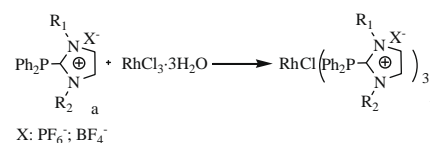


**Jiayun Li, Jiajian Peng, Ying Bai,
Guodong Zhang, Guoqiao Lai, Xiaonian Li**

J. Organomet. Chem. 695 (2010) 431

Phosphines with 2-imidazolium ligands enhance the catalytic activity and selectivity of rhodium complexes for hydrosilylation reactions

Phosphines with 2-imidazolium can specifically vary their physical and chemical properties by altering the attached substituents. Rhodium complexes employing 2-imidazolium phosphines as ligands exhibit excellent catalytic activity and selectivity. It is possible that close proximity of the positive charge to the phosphorus atom greatly enhances the catalytic activity and can afford highly efficient catalytic activity.

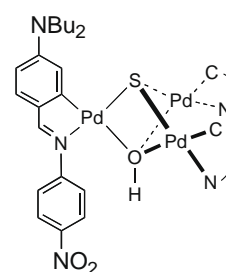


**Pablo Espinet, Jesús A. Miguel,
Jose M. Martín-Alvarez, Belén Villacampa**

J. Organomet. Chem. 695 (2010) 437

Synthesis, crystal structure and second-order nonlinear optical properties of the trinuclear palladium orthometalated complex $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^{\wedge}\text{N})_3]$ ($\text{HC}^{\wedge}\text{N} = p\text{-}(\text{Bu}_2^{\text{n}}\text{N})\text{-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-NO}_2\text{-}p$)

The binuclear cyclopalladated compound $[(\mu_2\text{-OH})_2\text{Pd}_2(\text{C}^{\wedge}\text{N})_2]$ ($\text{HC}^{\wedge}\text{N} = p\text{-}(\text{Bu}_2^{\text{n}}\text{N})\text{-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-NO}_2\text{-}p$) reacts with CS_2 to give $[(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3(\text{C}^{\wedge}\text{N})_3]$, which contains a $(\mu_3\text{-S})(\mu_3\text{-OH})\text{Pd}_3$ core that forces an all-cis arrangement of the three orthometalated ligands. The complexation of the imine produces a reduction of $\beta(0)$ contribution per imine moiety ($\sim 17\%$ variation) compared to the free imine.

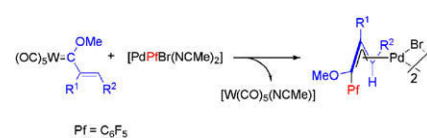


**Ana C. Albéniz, Pablo Espinet,
Alberto Pérez-Mateo**

J. Organomet. Chem. 695 (2010) 441

Palladium(II) allylic complexes by carbene transmetalation and migratory insertion reactions: Synthesis and side reactions

Asymmetrically substituted palladium η^3 -allyls can be synthesized from tungsten alkoxyvinylcarbenes and a palladium perfluoroaryl complex. The allyls are formed by transmetalation of the carbene fragment followed by migratory insertion of C_6F_5 to the new and highly reactive Pd carbene complex.

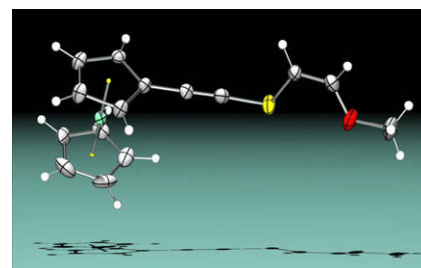


**Esther Delgado, Elisa Hernández,
Ángel Nievas, Avelino Martín,
María José Recio**

J. Organomet. Chem. 695 (2010) 446

Formation of multifunctional ligands by nucleophilic addition of alcohols and thiols to the alkyne groups in compound $C_5H_5FeC_5H_4C\equiv CSC\equiv CH$: Reactivity studies

Addition of HXR to the carbon–carbon triple bonds in the derivative $FcC\equiv CSC\equiv CH$ **1** generates the multifunctional ligands [(Z)- $FcC\equiv CSC(H)=C(H)XR$] [X = O, R = Me (**2a**); X = O, R = Et (**2b**); X = S, R = Ph (**3**); X = S, R = C_6F_5 (**5**)] and [(Z,Z)- $Fc(SR)CC(H)SC(H)=C(H)SR$] [R = Ph (**4**), C_6F_5 (**6**)]. Preliminary studies on the reactivity of compound **3** with metal carbonyls have been carried out.



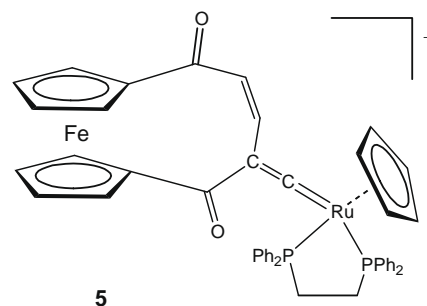
**Michael I. Bruce, Martyn Jevric,
Brian W. Skelton**

J. Organomet. Chem. 695 (2010) 453

Preparation and some chemistry of ferrocenylethynyl ketones

Reactions of $Fc'(CHO)_2$ **1** ($Fc' = 1,1'$ -ferrocenediyl) with $Li\equiv CR$ gave $Fc'\{CH(OH)C\equiv CR\}_2$ (R = $SiMe_3$, **2**, Fc **9**), oxidation (MnO_2) of which afforded $Fc'\{C(O)C\equiv CR\}_2$ (R = $SiMe_3$, **3**, Fc **10**), together with $Fc'\{C(O)C\equiv CH\}-1-[C(O)C\equiv CSiMe_3]-1'$ **4**. Reaction

between **4** and $RuCl(dppe)Cp$ in the presence of $Na[BPh_4]$ gave cyclic vinylidene $[Ru(=C=C(O)Fc'C(O)CH=CH)](dppe)Cp-BPh_4$ **5**. Separation of diastereomers of **2** and **9** and cyclisation gave corresponding ferrocenophanes $Fc'\{[CH(C\equiv CR)]_2O\}$ (R = $SiMe_3$ **6a**, **6b**; Fc **11a**, **11b**); **6a**, **6b** were converted to $Fc'\{[CH(C\equiv CH)]_2O\}$ **7a**, **7b**, and $Fc'\{[CH(\eta^2-C_2H[Co_2(\mu-dppm)(CO)_4])_2O]\}$ **8a**, **8b**.



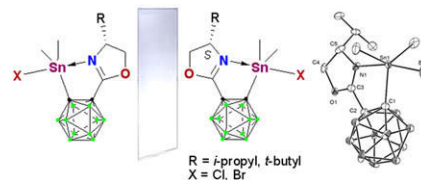
Notes

**Jong-Dae Lee, Hyo-Suk Kim,
Won-Sik Han, Sang Ook Kang**

J. Organomet. Chem. 695 (2010) 463

Chiral organotin complexes stabilized by C,N-chelating oxazolanyl-*o*-carboranes

A series of chiral organotin halides containing oxazolanyl-*o*-carboranes was prepared from *o*-carborane with a chiral oxazoline auxiliary. X-ray structural analysis of the representative chiral organotin compound (**4**) revealed the formation of a stable penta-coordinated tin center due to a $N \rightarrow Sn$ interaction.

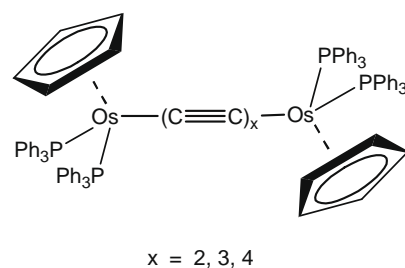


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Syntheses, structures and redox properties of $\{Os(PPh_3)_2Cp\}_2[\mu-(C\equiv C)_x]$ ($x = 2, 3, 4$): Comparisons with the Ru analogues

The syntheses of $\{Os(PPh_3)_2Cp\}_2[\mu-(C\equiv C)_x]$ ($x = 2, 3, 4$) from reactions between $OsBr(PPh_3)_2Cp^*$ and $Me_3Si(C\equiv C)_xSiMe_3$ in the presence of $KF/NaBPh_4$ are described. The molecular structure of $x = 3$ has been determined by a single-crystal XRD study. The oxidation potentials of these complexes are invariably lower (by between 0.16 and 0.64 V) than those of the Ru analogues.



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The first structurally characterized *N*-heterocyclic carbene complex with a ligand derived from pyrimidine

Oxidative addition of *N*-alkyl-2-halopyrimidinium cations to $[\text{Pd}(\text{PPh}_3)_4]$ gives straightforward access to the cationic complexes $[(\text{PPh}_3)_2(\text{NHC})\text{PdX}]\text{BF}_4$ (**3a,b**) with pyrimidine-derived NHC-ligands.

