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# Contents

# **Regular papers**

# Richard Frantz, Jean-Olivier Durand, Gerard F. Lanneau

J. Organomet. Chem. 689 (2004) 1867

Substituent effects of phosphonate groups electronic repartition of  $\pi$ -conjugated ferrocene analogues of stilbene

The synthesis of *para*-substituted ferrocene analogues of stilbene was performed by using the Heck reaction, starting from vinylferrocene. The variation of the electronic density of these compounds with the electronic withdrawing strength of the substituents was studied using <sup>13</sup>C NMR spectroscopy, absorption spectra and cyclic voltammetry.



### José Ruiz, Consuelo Vicente, Venancio Rodríguez, Natalia Cutillas, Gregorio López, Carmen Ramírez de Arellano

J. Organomet. Chem. 689 (2004) 1872

Mononuclear palladium-siloxo complexes of the type [Pd(N–N)( $C_6F_5$ )(OSiR<sub>3</sub>)] [(N–N) = 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me<sub>2</sub>bipy), or *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmeda)] have been prepared by reaction of the corresponding hydroxo complexes [Pd(N–N)( $C_6F_5$ )(OH)] with silanols HOSiR<sub>3</sub>.



# Reinout Meijboom, John R. Moss, Alan T. Hutton, Tracy-Ann Makaluza, Selwyn F. Mapolie, Fazlin Waggie, Mark R. Domingo

J. Organomet. Chem. 689 (2004) 1876

Hydrozirconation of first-generation allyl-functionalized dendrimers and dendrimer model compounds

Several allyl-functionalized dendrimers and mono-functional model compounds have been prepared. These have been hydro-zirconated using  $[Cp_2ZrHCI]_x$  to give zirconocene terminated dendrimers. These dendrimers have been characterized using spectroscopic techniques, particularly NMR.



# Michael J. Chetcuti, Steven R. McDonald

J. Organomet. Chem. 689 (2004) 1882

Some reactions of Ni–Mo and Ni–W propargylic cations with nucleophiles

Nucleophiles such as H<sup>-</sup> or MeO<sup>-</sup> add to Ni–Mo and Ni–W stabilized  $\mu$ -carbocations to generate neutral  $\mu$ -alkyne complexes. The larger nucleophile 'BuO does not react. A competitive decomposition reaction affords the addition product of C<sub>3</sub>H<sub>3</sub><sup>-</sup> to the cationic carbon center; this compound can also be made directly from the reaction of C<sub>3</sub>H<sub>3</sub><sup>-</sup> with the Ni–Mo carbocation.



#### Ignacio Fernández, Richard D. Price, Philip D. Bolton, Mary F. Mahon, Matthew G. Davidson, Fernando López-Ortiz

J. Organomet. Chem. 689 (2004) 1890

X-ray and multinuclear NMR study of the mixed aggregate [(Ph\_2P(O)N(CH\_2Ph)CH\_3)·LiOC\_6H\_2-2,6-{C(CH\_3)\_3}\_2-4-CH\_3)·C\_7H\_8]\_2: a model for the directed metalation of phosphinamides

Lithiation of 2,6-di-*tert*-butyl-4-methylphenol in toluene in the presence of  $Ph_2P$ -(O)N(CH<sub>2</sub>Ph)CH<sub>3</sub> leads to a lithium aryloxide dimer consisting of a Li<sub>2</sub>O<sub>2</sub> fourmembered ring with each lithium atom is coordinated to a phosphinamide. The structure found in the solid state by X-ray crystallography is retained in toluene solution as determined by multinuclear NMR spectroscopy. The new complex described gives insight into the mechanism of lithiation of phosphinamides.



#### Owen J. Curnow, Glen M. Fern, Michelle L. Hamilton, Elizabeth M. Jenkins

J. Organomet. Chem. 689 (2004) 1897

Synthesis, structures and *rac/meso* isomerization behaviour of bisplanar chiral bis(phosphino- $\eta^5$ -indenyl)iron(II) complexes Several phosphino-indenyl-ferrocene complexes with additional methyl or trimethylsilyl substituents were prepared and characterized. Some of these were observed to undergo *raclmeso* isomerization processes via an indenide ring-flipping mechanism.



# Ester Guiu, Carmen Claver, Sergio Castillón

J. Organomet. Chem. 689 (2004) 1911

Ir(I) complexes with oxazoline-thioether ligands: nucleophilic attack of pyridine on coordinated 1,5-cyclooctadiene and application as catalysts in imine hydrogenation

Iridium complexes A or B containing oxazoline-thioether ligands are obtained depending on the iridium precursor. Complex A results from the attack of pyridine to coordinated 1,5-cyclooctadiene and Ir–C formation.



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

J. Organomet. Chem. 689 (2004) 1919

Irregular cyclization reactions in titanocenes bearing pendant double bonds

Methyl-substituted titanocene intermediates bearing pendant double bonds did not undergo intramolecular cycloaddition to cyclopentadienyl-ring-tethered titanacyclopentanes in case that the alkenyl chain was short and the double bond sterically hindered by Me group or the alkenyl chain was too long as in 2-methylallyl or (but-3-en-1-yl)dimethylsilyl derivatives, respectively. Instead, compounds **4** and **6** were formed in high and low yield, respectively.



# Elizaveta P. Shestakova, Yuri S. Varshavsky, Konstantin A. Lyssenko, Alexander A. Korlyukov,

Viktor N. Khrustalev, Marina V. Andreeva

J. Organomet. Chem. 689 (2004) 1930

Cationic methyl complexes of rhodium(III): synthesis, structure, and some reactions

Cationic methyl complexes of rhodium(III),  $[Rh(\beta-diket)(PPh_3)_2(CH_3)(CH_3CN)]^+$ , have been prepared and characterized as tetraphenylborates in isomeric forms *cis*-(PPh\_3)\_2 and *trans*-(PPh\_3)\_2. *Cis* isomers are kinetically labile in contrast to corresponding *trans* isomers.



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CO

2

#### Yu-Chiao Liu, Wen-Yann Yeh, Gene-Hsiang Lee, Shie-Ming Peng

J. Organomet. Chem. 689 (2004) 1944

Complexation and C-H bond activation of 1,5-cyclooctadiene on triosmium carbonyl clusters

The 1,5-cyclooctadiene cluster complex  $Os_3(CO)_{10}(\eta^4-C_8H_{12})$  (1) has been prepared, and thermolysis of which results in a vinylic C–H bond activation to form (µ-H)  $Os_3$  (CO)<sub>9</sub>(µ,  $\eta^4$ -C<sub>8</sub>H<sub>11</sub>) (2) in good isolated yield.

# Yong-Qiang Ma, Ning Yin, Jing Li, Qing-Lan Xie, Daniel Miguel

J. Organomet. Chem. 689 (2004) 1949

Alkylation and metalation of binuclear anions containing a novel tricyclohexylphosphonioethanetrithiolate ligand S(SR)C= $C(PCy_3)S$  Reactivity at the uncoordinated sulfur of anions **3** can be used to prepare neutral derivatives which incorporate a wide range of substituents from metal–ligand fragments to activated allyl or propargyl groups.



# Margarita Crespo, Emilia Evangelio

J. Organomet. Chem. 689 (2004) 1956

Five- and six-membered platinacycles derived from phenantryl and anthracenyl imines

# The reaction of $[Pt_2Me_4(\mu-SMe_2)_2]$ with ligands $Me_2NCH_2CH_2NCHAr$ in which Ar = 9-phenantryl or 9-anthracenyl produced compounds $[PtMe_2\{9-(Me_2NCH_2$ $CH_2NCH)- C_{14}H_9\}]$ . From these compounds, cyclometallated [C,N,N'] compounds [PtMe $\{9-(Me_2NCH_2CH_2NCH)C_{14}H_8\}]$ were obtained as a mixture of two isomers containing either a five- or a six-membered metallacycles for the phenantryl derivative and as a single isomer containing a six-membered metallacycle for the antracenyl analogue.



#### Helmut G. Alt, Robert W. Baker, Mahmoud Dakkak, Michael A. Foulkes, Marc O. Schilling, Peter Turner

J. Organomet. Chem. 689 (2004) 1965

Zirconocene dichloride complexes with a 1,2naphthylidene bridge as catalysts for the polymerisation of ethylene and propylene The 1,2-naphthylidene-bridged ansa-zirconocene dichloride complexes **12**, **13** and **14** were synthesised, and the molecular structures determined by single crystal X-ray diffraction studies. After activation with excess methylalumoxane (MAO), the complexes were used as homogeneous catalysts for the homopolymerisation of ethylene and propylene.



## Xiu Lian Lu, Jagadese J. Vittal, Edward R.T. Tiekink, G.K. Tan, Seah Ling Kuan, Lai Yoong Goh, T.S. Andy Hor

J. Organomet. Chem. 689 (2004) 1978

Comparative reactivity studies of dppfcontaining  $CpRu^{II}$  and  $(C_6Me_6)Ru^{II}$  complexes towards different donor ligands (dppf = 1,1'-bis(diphenylphosphino)ferrocene) Chloride ligand substitution in [CpRu (dppf)Cl] (1) or  $[(C_6Me_6)Ru(dppf)Cl]PF_6$  (3) is accompanied by nuclearity change in some cases.



# Tania R. van den Ancker, Lutz M. Engelhardt, Mark J. Henderson, Geraldine E. Jacobsen, Colin L. Raston, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 689 (2004) 1991

Syntheses and structures of highly hindered N-functionalised alkyl and amido group 12 complexes  $MR_2$  (M = Zn, Cd, and Hg), [MRCl]<sub>2</sub> (M = Zn and Hg)

Treatment MCl<sub>2</sub> (M = Zn, Cd and Hg) with two equivalents of Li(2-(C(SiMe<sub>3</sub>)<sub>2</sub>)(6-Me– C<sub>5</sub>H<sub>3</sub>N)), affords mononuclear metal(II) alkyls. These, in the solid state, show intramolecular M–N interactions in their four-membered chelate rings, which progressively weaken down the series. Similar treatment of HgCl<sub>2</sub> with one equivalent of Li(2-(C(SiMe<sub>3</sub>)<sub>2</sub>)(6-Me–C<sub>5</sub>H<sub>3</sub>N)), Li(2-(C-(SiMe<sub>3</sub>)<sub>2</sub>)(C<sub>5</sub>H<sub>4</sub>N)), or Li(2-(NSiMe<sub>3</sub>)(6-Me– C<sub>5</sub>H<sub>3</sub>N)), afford the corresponding alkyl- or amido mercury chloride. These, in the solid state are dimeric or polymeric in nature with near-linear 2-coordination.



#### Véronique Plantevin, Andrew Wojcicki

# J. Organomet. Chem. 689 (2004) 2000

Chemistry of Fischer-type rhenacyclobutadiene complexes. I. Deprotonation, addition/substitution of nucleophilic reagents at  $\alpha$ -carbon, and insertion of heteroatoms into rhenium–carbon bonds The rhenacyclobutadienes  $(CO)_4 Re(\eta^2-C(R)C(CO_2Me)C(OR'))$  undergo a number of reactions that parallel those of Fischer carbene complexes. They include deprotonation of R and alkylation of the conjugate base, aminolysis, addition of tertiary phosphine/CO substitution, and insertion of oxygen atom and NH into the Re=C bonds.



# Véronique Plantevin, Andrew Wojcicki

J. Organomet. Chem. 689 (2004) 2013

Chemistry of Fischer-type rhenacyclobutadiene complexes II. Reactions with alkynes and sulfonium ylides, and rearrangements induced by nitriles and pyridine The rhenacyclobutadienes  $(CO)_4 Re(\eta^2 - C(R)C(CO_2Me)C(X))$  (1: R = Me, Ph; X = alkoxy, amido group) react with a variety of alkynes to give ring-substituted  $\eta^5$ -cyclopentadienylrhenium tricarbonyl complexes. Complexes 1 also undergo rearrangement in nitriles and pyridine to yield rhenafuran-like products, and react with sulfonium ylides to afford similar 5-membered ring compounds.



#### Ysaura De Sanctis, Alejandro J. Arce, Farrah Cañavera, Ruben Machado, Antony J. Deeming, Teresa González, Esperanza Galarza

J. Organomet. Chem. 689 (2004) 2025

A zwitterionic triosmium cluster bearing a metallated azulene ligand coordinated perpendicularly as an alkylidene bridge The reaction of  $[Os_3(CO)_{10}(MeCN)_2]$  with azulene gives the oxidative addition product  $[Os_3(\mu-H)(\mu_2-\eta^1-C_{10}H_7)(CO)_{10}]$  **1**, where the 5-membered ring is coordinated as a  $\mu$ -al-kylidene to the metal cluster, and the 7-membered ring forms a tropylium cation.

# Kanahara A.N.S. Ariyaratne, Roger E. Cramer, Geoffrey B. Jameson, John W. Gilje

J. Organomet. Chem. 689 (2004) 2029

Uranium-sulfilimine chemistry. Hydrolysis of  $Cp*_2UCl_2$  with HNSPh<sub>2</sub>·H<sub>2</sub>O and the crystal structure of  $Cp*_2UCl(OH)$ (HNSPh<sub>2</sub>), a metallocene terminal hydroxy complex of tetravalent uranium

The reaction of  $Cp^*_2UCl_2(HNSPh_2)$  with HNSPh<sub>2</sub>·H<sub>2</sub>O in 1:1 stoichiometry, produces in good yield,  $Cp^*_2UCl(OH)(HNSPh_2)$ , the first structurally characterized metallocene f-element complex containing a terminal hydroxy ligand. By <sup>1</sup>H NMR spectroscopy and single crystal X-ray diffraction,  $Cp^*_2U-Cl(OH)(HNSPh_2)$  has been shown to be an intermediate in the formation of a tetra uranium-oxo-cluster  $[Cp^*(Cl)(HNSPh_2)U(\mu_3-O)(\mu_2-O)_2U(Cl)(HNSPh_2)]_2$ , which forms by hydrolysis of  $Cp^*_2UCl_2$  with excess HNSPh\_2·H<sub>2</sub>O.



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