

## Contents

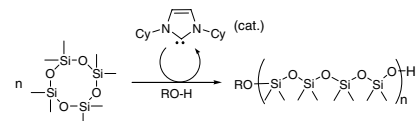
### Communication

**Marta Rodriguez, Sebastien Marrot,  
Tsuyoshi Kato, Sébastien Stérin,  
Etienne Fleury, Antoine Baccaredo**

*J. Organomet. Chem.* 692 (2007) 705

Catalytic activity of N-heterocyclic carbenes in ring opening polymerization of cyclic siloxanes

Taking advantage of the strong nucleophilic properties of NHC 1a, the efficient catalytic (anionic-like) ROP of cyclotetrasiloxane  $D_4$  was achieved in mild conditions. Of particular interest, with this NHC/ROH system the molecular weight of the silicone polymers can be regulated simply by varying the quantity of neutral alcohol initiator.



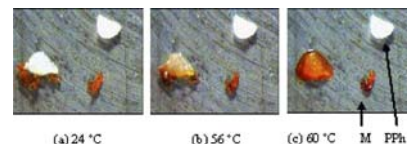
### Review

**Muhammad D. Bala, Neil J. Coville**

*J. Organomet. Chem.* 692 (2007) 709

Organometallic chemistry in the melt phase

In this review organometallic chemistry reactions in the *melt phase* are described. Examples from the literature highlight procedures used to generate melts and results that have been obtained in this area of synthesis are described.



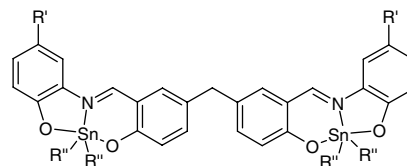
### Regular Papers

**Victor Barba, Edgar Vega, Rolando Luna,  
Herbert Höpfl, Hiram I. Beltrán,  
Luis S. Zamudio-Rivera**

*J. Organomet. Chem.* 692 (2007) 731

Structural and conformational analysis of neutral dinuclear diorganotin(IV) complexes derived from hexadentate Schiff base ligands

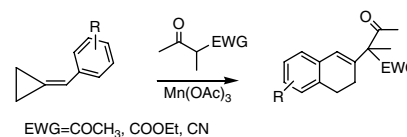
The structural and conformational analysis of seven dinuclear diorganotin(IV) compounds is reported, which have been prepared from hexadentate Schiff base ligands having a twofold ONO donor system. The spectroscopic analyses showed that in solution the compounds have a distorted trigonal bipyramidal coordination geometry for the tin atoms and are apparently involved in a fast equilibrium between two molecular conformations. In the solid state a distorted octahedral geometry can be favored through Sn...O intermolecular interactions and a molecular conformation that is intermediate between the *cis*- and *trans*-isomer, having mirror and  $C_2$ -symmetry, respectively.



**Wei-Jun Fu, Xian Huang***J. Organomet. Chem.* 692 (2007) 740

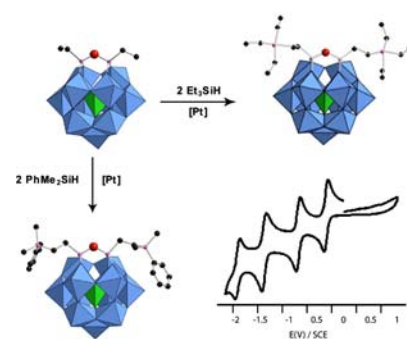
Mn(III)-based oxidative tandem free-radical cyclizations of methylenecyclopropanes with substituted dicarbonyl compounds

Manganese(III) acetate-mediated tandem radical cyclization reactions of methylenecyclopropanes with methyl substituted dicarbonyl compounds in acetic acid give dihydronaphthalene derivatives in moderate yields under mild conditions.

**Dominique Agustin, Jérôme Dallery, Cristina Coelho, Anna Proust, René Thouvenot***J. Organomet. Chem.* 692 (2007) 746

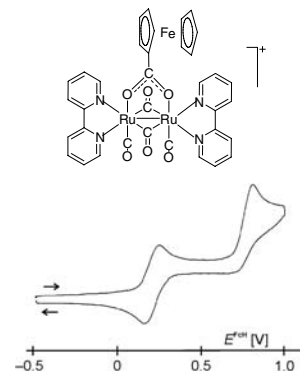
Synthesis, characterization and study of the chromogenic properties of the hybrid polyoxometalates [PW<sub>11</sub>O<sub>39</sub>(SiR)<sub>2</sub>O]<sup>3-</sup> (R = Et, (CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub> (n = 0, 1, 4), CH<sub>2</sub>CH<sub>2</sub>SiEt<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>Ph)

The hydrosilylation reactions of the terminal vinylic functions of [PW<sub>11</sub>O<sub>39</sub>(Si-CH=CH<sub>2</sub>)<sub>2</sub>O]<sup>3-</sup> towards Et<sub>3</sub>SiH and PhSiMe<sub>2</sub>H have been achieved. These compounds are the first examples of hydrosilylation on a hybrid tungstophosphate core. The chromogenic behaviour of these species has been demonstrated in solution.

**Mathieu Auzias, Bruno Therrien, Georg Süß-Fink, Petr Štěpnička, Jiří Ludvík***J. Organomet. Chem.* 692 (2007) 755

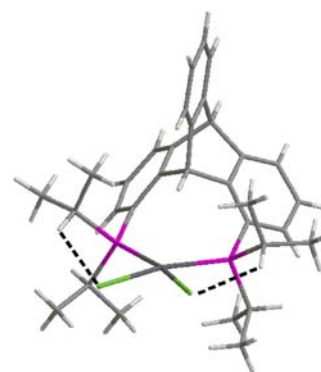
Synthesis, structure and electrochemistry of cationic diruthenium complexes of the type [(N∩N)<sub>2</sub>Ru<sub>2</sub>(CO)<sub>2</sub>(μ-CO)<sub>2</sub>(μ-OOCFc)]<sup>+</sup> containing a ferrocenecarboxylato bridge and two chelating aromatic diimine ligands

The cationic diruthenium complexes [(N∩N)<sub>2</sub>Ru<sub>2</sub>(CO)<sub>2</sub>(μ-CO)<sub>2</sub>(μ-OOCFc)]<sup>+</sup> containing a ferrocenecarboxylato bridge and diimine chelates have been synthesised from Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCFc)<sub>2</sub>(py)<sub>2</sub> and the corresponding aromatic diimine N∩N. Cyclic voltammetry of the hexafluorophosphate salts in dichloromethane shows a reversible oxidation of the ferrocenyl substituted followed by the irreversible oxidation of the diruthenium core.

**Clarite Azerraf, Olga Grossman, Dmitri Gelman***J. Organomet. Chem.* 692 (2007) 761

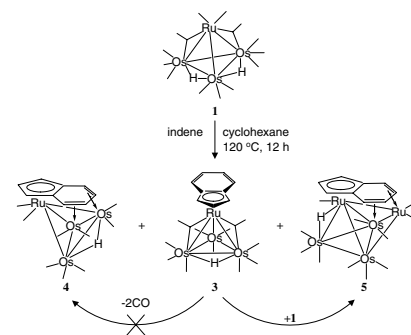
Rigid *trans*-spanning triptycene-based ligands: How flexible they can be?

A series of transition metal complexes bearing the strongly triptycene-based ligand have been prepared and fully characterized. Their structural features and coordination preferences were studied and compared to the previously reported structurally related compounds.



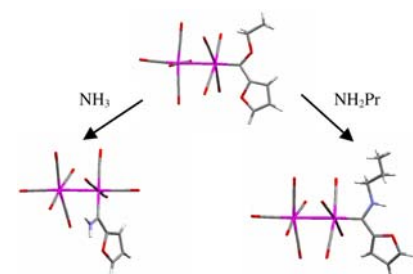
**Yong Leng Kelvin Tan, Weng Kee Leong***J. Organomet. Chem.* 692 (2007) 768Reactivity of the heteronuclear cluster  $\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_{13}$  with indene

The heteronuclear cluster  $\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_{13}$  (**1**) reacts with indene under thermal activation to afford the novel clusters  $\text{RuOs}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-CO})_2(\eta^5\text{-C}_9\text{H}_7)$  (**3**),  $\text{RuOs}_3(\mu\text{-H})(\text{CO})_9(\mu_3, \eta^5: \eta^2: \eta^2\text{-C}_9\text{H}_7)$  (**4**) and  $\text{Ru}_2\text{Os}_3(\mu\text{-H})(\text{CO})_{11}(\mu_3, \eta^5: \eta^2: \eta^2\text{-C}_9\text{H}_7)$  (**5**), the latter two possessing indenyl ligands in the  $\mu_3, \eta^5: \eta^2: \eta^2$  bonding mode. Cluster **5** exists as a mixture of two isomers.

**Daniela I. Bezuidenhout, David C. Liles, Petrus H. van Rooyen, Simon Lotz***J. Organomet. Chem.* 692 (2007) 774

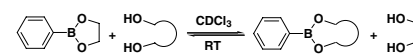
Axial and equatorial carbene ligands of dimanganese and dirhenium monocarbene complexes: Synthesis, characterisation and structural studies

The coordination site of the carbene ligands of dinuclear Group VII transition metal complexes can be converted from an axial to an equatorial configuration depending on the steric and electronic effects of both the  $\text{M}(\text{CO})_5$ -fragment and the carbene ligand substituent.

**Chandra D. Roy, Herbert C. Brown***J. Organomet. Chem.* 692 (2007) 784

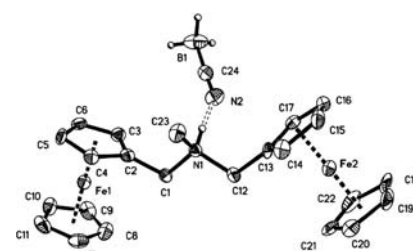
Stability of boronic esters – Structural effects on the relative rates of transesterification of 2-(phenyl)-1,3,2-dioxaborolane

Transesterification of a representative achiral cyclic phenylboronic ester, 2-(phenyl)-1,3,2-dioxaborolane with a wide variety of structurally modified diols, has been studied to understand the factors influencing the relative stabilities of boronic esters. Alkyl substituents on the  $\alpha$ -carbons of diols slow down the transesterification, but produce thermodynamically more stable boronic ester.

**Nathan C. Tice, Sean Parkin, John P. Selegue***J. Organomet. Chem.* 692 (2007) 791

Synthesis, characterization and crystal structures of boron-containing intermediates in the reductive amination of ferrocene-carboxaldehyde to a bis(ferrocenylmethyl) amine

Reductive amination of ferrocene-carboxaldehyde with *N*-(ferrocenylmethyl)-*N*-methylamine and  $\text{NaCNBH}_3$  gives the tertiary ammonium salt, di(*N*-(ferrocenylmethyl))-*N*-methylammonium cyanoborohydride. Hydrolysis of the reaction mixture produces the amine, di(*N*-(ferrocenylmethyl))-*N*-methylamine. Thermolysis of di(*N*-(ferrocenylmethyl))-*N*-methylammonium cyanoborohydride in refluxing tetrahydrofuran converts it to the cyanoborane adduct, di(*N*-(ferrocenylmethyl))-*N*-methylamine–cyanoborane, with elimination of  $\text{H}_2$ .

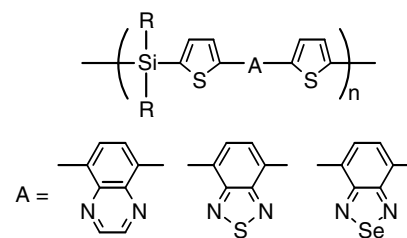


**Joji Ohshita, Sinji Kangai, Hiroto Yoshida, Atsutaka Kunai, Shotaro Kajiwara, Yousuke Ooyama, Yutaka Harima**

*J. Organomet. Chem.* 692 (2007) 801

Synthesis of organosilicon polymers containing donor–acceptor type  $\pi$ -conjugated units and their applications to dye-sensitized solar cells

Organosilicon polymers having donor–acceptor type  $\pi$ -conjugated units in the backbone were prepared and their applications to dye-sensitized solar cells (DSSCs) were examined. Of those, the polymer containing benzoselenadiazole units as the acceptor exhibited the best performance as the sensitizer.

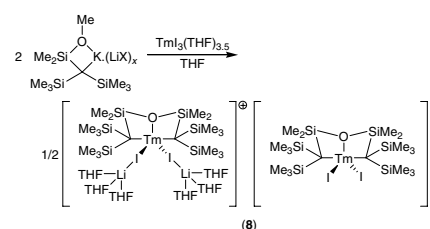


**Lyndsey J. Bowman, Keith Izod, William Clegg, Ross W. Harrington**

*J. Organomet. Chem.* 692 (2007) 806

$\sigma$ -Bonded organometallic derivatives of yttrium(III) and thulium(III): An unusual ligand coupling reaction mediated by thulium(III)

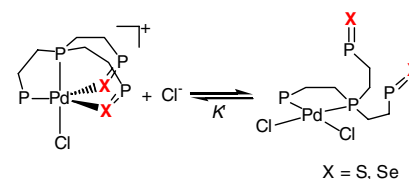
Reactions between  $\text{LnI}_3(\text{THF})_{3,5}$  and 2 equiv. of  $\{(\text{Me}_3\text{Si})_2(\text{Me}_2\text{MeOSi})\text{C}\}\text{K}$  (**1**) in THF yield the mono-substituted products  $\{(\text{Me}_3\text{Si})_2(\text{Me}_2\text{MeOSi})\}\text{LnI}_2(\text{THF})_2$  [ $\text{Ln} = \text{Y}$  (**5**),  $\text{Tm}$  (**6**)]; however, in the presence of lithium ions an unusual ate complex (**8**) is formed, via an unusual ligand coupling reaction.



**Sen-ichi Aizawa, Takashi Hase, Tsuyoshi Wada**  
*J. Organomet. Chem.* 692 (2007) 813

Rapid geometrical equilibrium of palladium(II) complexes with tris[2-(diphenylphosphino)ethyl]phosphine disulfide and diselenide and their catalytic activity for Suzuki coupling reaction

Palladium(II) complexes with tris[2-(diphenylphosphino)ethyl]phosphine disulfide and diselenide showed rapid equilibrium between the five- and four-coordinate structures in chloroform. Their retentive catalytic activity for Suzuki coupling is attributed to the  $\pi$ -accepting ability of the phosphine chalcogenide groups, which stabilize the catalytically active  $\text{Pd}(0)$  species.

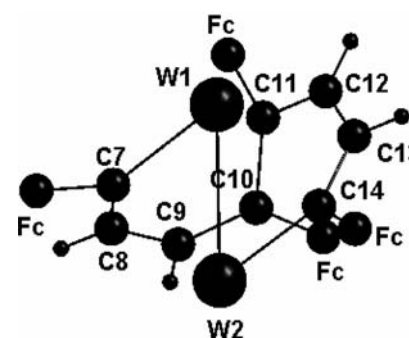


**Pradeep Mathur, Saurav Chatterjee, Atanu Das, Shaikh M. Mobin**

*J. Organomet. Chem.* 692 (2007) 819

Photochemical route to unusual tri-tungsten ferrocenylacetylene cluster  $[\text{W}_3\{\mu\text{-}\eta^2, \eta^2\text{-}(\text{H})\text{C}\equiv\text{CFc}\}_2(\text{CO})_{12}]$  (**1**) and a ditungsten ferrocenylacetylene cluster  $[\text{W}_2\{\mu\text{-}\eta^2, \eta^2, \eta^2, \eta^2\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\text{-C}(\text{Fc})=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\}_2(\text{CO})_6]$  (**2**). Both compounds were structurally characterised by single crystal X-ray diffraction methods. The W–W bonds in **1** are of donor–acceptor type and **2** displays an unusual cyclic structure.

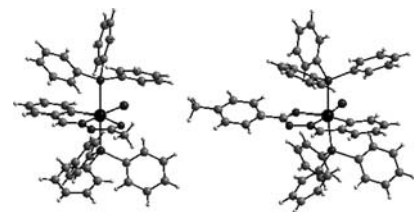
Photolysis of hexane solution containing tungsten hexacarbonyl and ferrocenylacetylene yielded the tritungsten cluster,  $[\text{W}_3\{\mu\text{-}\eta^2, \eta^2\text{-}(\text{H})\text{C}\equiv\text{CFc}\}_2(\text{CO})_{12}]$  (**1**), and the ditungsten,  $[\text{W}_2\{\mu\text{-}\eta^2, \eta^2, \eta^2, \eta^2\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\text{-C}(\text{Fc})=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})\}_2(\text{CO})_6]$  (**2**). Both compounds were structurally characterised by single crystal X-ray diffraction methods. The W–W bonds in **1** are of donor–acceptor type and **2** displays an unusual cyclic structure.



**Raji Raveendran, Samudranil Pal***J. Organomet. Chem.* 692 (2007) 824

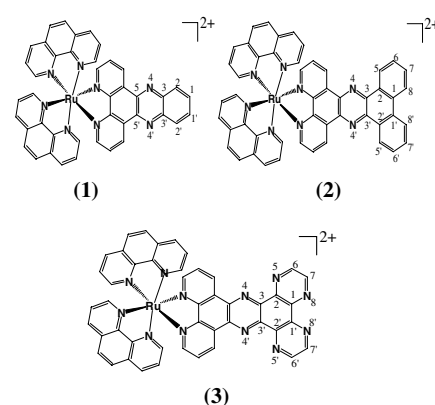
Ortho-metallated ruthenium(III) complexes with some acid hydrazide based Schiff bases

Synthesis, structure and properties of a series of cyclometallated ruthenium(III) complexes with acetic acid benzylidene-hydrazide and 4-R-benzoic acid benzylidene-hydrazides are described. The one-electron paramagnetic complexes show rhombic EPR spectra. All the complexes are electroactive and display ruthenium(III) → ruthenium(IV) oxidation.

**Jun Li, Jin-Can Chen, Lian-Cai Xu, Kang-Cheng Zheng, Liang-Nian Ji***J. Organomet. Chem.* 692 (2007) 831

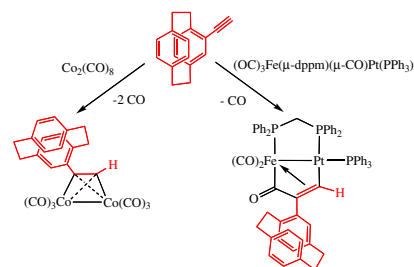
A DFT/TDDFT study on the structures, trend in DNA-binding and spectral properties of molecular “light switch” complexes  $[\text{Ru}(\text{phen})_2(\text{L})]^{2+}$  (L = dppz, taptp, phehat)

A DFT/TDDFT study on a series of molecular “light switch” complexes  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  (L = dppz, taptp, phehat) 1–3 has been carried out. The trend in the DNA-binding affinities and  $^1\text{MLCT}$  spectral properties of the complexes were theoretically explained.

**Sébastien Clément, Laurent Guyard, Michael Knorr, Stefan Dilsky, Carsten Strohmann, Marta Arroyo***J. Organomet. Chem.* 692 (2007) 839

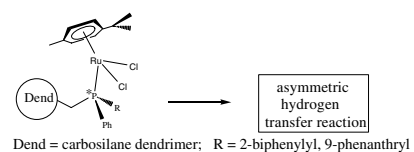
Ethynyl[2.2]paracyclophanes and 4-isocyano[2.2]paracyclophane as ligands in organometallic chemistry

4-Ethynyl[2.2]paracyclophane (PCP–C≡CH) was employed as starting material for assembling of a luminescent  $\pi$ -conjugated system containing a thiophene unit and for a bisilylation reaction. PCP–C≡CH has also been used for the preparation of various mono- and dinuclear organometallic complexes. The synthesis and reactivity of 4-isocyano[2.2]paracyclophane towards heterobimetallic iron–platinum and palladium–platinum complexes is also presented.

**Lara-Isabel Rodríguez, Oriol Rossell, Miquel Seco, Guillermo Muller***J. Organomet. Chem.* 692 (2007) 851

Rhodium or ruthenium units peripherally coordinated to carbosilane dendrimers functionalized with P-stereogenic phosphines

$\text{RuCl}_2(p\text{-cymene})$  and  $\text{RhCl}(\text{COD})$  units have been grafted on the periphery of P-stereogenic phosphine-containing carbosilane dendrimers. The catalytic properties of the corresponding metalodendrimers have been examined in the asymmetric hydrogen transfer reaction of acetophenone and the hydrogenation of dimethylitaconate, respectively.

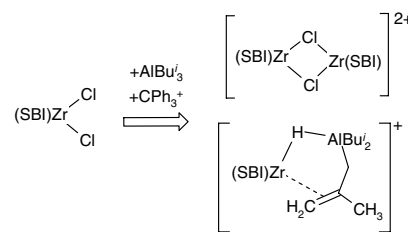


**Konstantin P. Bryliakov, Evgenii P. Talsi, Nina V. Semikolenova, Vladimir A. Zakharov, Jörg Brand, Carlos Alonso-Moreno, Manfred Bochmann**

*J. Organomet. Chem.* 692 (2007) 859

Formation and structures of cationic zirconium complexes in ternary systems *rac*-(SBI)ZrX<sub>2</sub>/AlBu<sub>3</sub><sup>t</sup>/[CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (X = Cl, Me)

Using multinuclear NMR spectroscopy, formation of cationic species was studied in ternary systems (SBI)ZrX<sub>2</sub>/AlBu<sub>3</sub><sup>t</sup>/[CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], where X = Cl, Me. In the first system (X = Cl), the crystallographically characterized ion pair [(SBI)Zr(μ-Cl)<sub>2</sub>Zr(SBI)]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub><sup>-</sup> predominates at low Al/Zr ratios (Al/Zr < 10), whereas at higher Al/Zr ratios (≥ 20) mainly [(SBI)Zr(μ-H)(μ-C<sub>4</sub>H<sub>7</sub>)-AlBu<sub>2</sub><sup>t</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is formed.

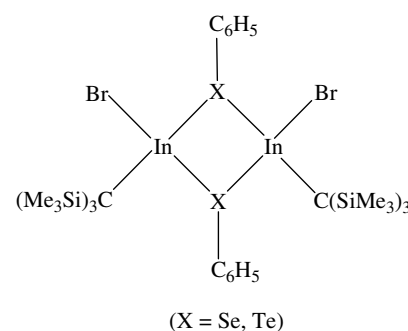


**Werner Uhl, Fabiano Molinos de Andrade, Cloviseppe, Jutta Kösters, Friedhelm Rogel**

*J. Organomet. Chem.* 692 (2007) 869

On the reactions of the tetraindiumcluster In<sub>4</sub>[C(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> with phenylselenium and phenyltellurium bromides

Reactions of the tetrahedral tetraindium(I) cluster In<sub>4</sub>[C(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> with phenylselenium bromide or phenyltellurium bromide yielded the dimeric indium-chalcogen compounds [RIn(μ-X-C<sub>6</sub>H<sub>5</sub>)Br]<sub>2</sub> containing bridging chalcogen and terminal bromine atoms.

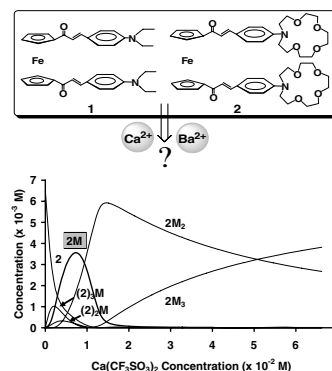


**Béatrice Delavaux-Nicot, Jérôme Maynadié, Dominique Lavabre, Suzanne Fery-Forgues**

*J. Organomet. Chem.* 692 (2007) 874

Ca<sup>2+</sup> vs. Ba<sup>2+</sup> electrochemical detection by two disubstituted ferrocenyl chalcone chemosensors. Study of the ligand-metal interactions in CH<sub>3</sub>CN

An original electrochemical barium detection with regard to calcium detection is performed by two disubstituted ferrocenyl ligands. The NMR behaviour of these ligands towards both salts is thoroughly examined. Different investigations allow us to better understand the nature of the unprecedented Ba<sup>2+</sup> electrochemical sensing by these two chalcone-like derivatives.

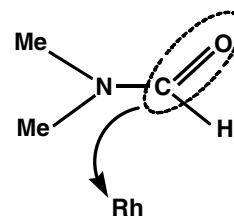


**Yuri S. Varshavsky, Tatiana G. Cherkasova**

*J. Organomet. Chem.* 692 (2007) 887

Remarks on the process of homogeneous carbonylation of rhodium compounds by *N,N*-dimethylformamide

The mechanistic scheme of rhodium carbonylation based on the direct carbonyl group transfer from DMF molecule to the Rh metal center is discussed with regard of new experimental results.

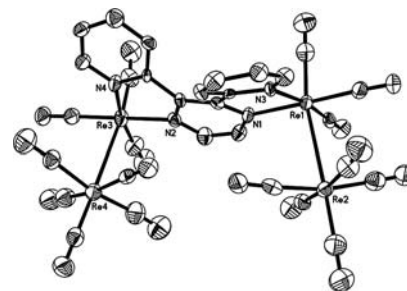


**Rubén A. Machado, María Cristina Goite, David Rivillo, Ysaura De Sanctis, Alejandro J. Arce, Antony J. Deeming, Lindora D'Ornelas, Anibal Sierralta, Reinaldo Atencio, Teresa González, Esperanza Galarza**

*J. Organomet. Chem.* 692 (2007) 894

Reactivity of 2,3-bis(2-pyridyl)pyrazine with  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ : Molecular structures of  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  and  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$

A new tetranuclear rhenium derivative  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$  was obtained from the reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  and 2,3-bis(2-pyridyl)pyrazine. The ligand behaves as an 8e-donor bridge between two  $\text{Re}(\text{CO})_3$  moieties through two  $\sigma, \sigma'-N, N'$  interactions.



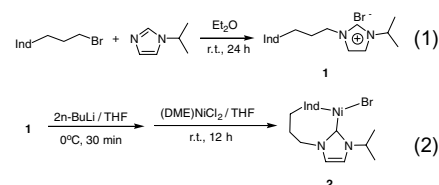
## Notes

**Hong-Mei Sun, Dong-Mei Hu, Yong-Sheng Wang, Qi Shen, Yong Zhang**

*J. Organomet. Chem.* 692 (2007) 903

Synthesis and characterization of indenyl-functionalized N-heterocyclic carbene complex of Ni(II)

A novel half-sandwich Ni(II) complex derived from anionic indenyl-functionalized NHC ligand,  $[\text{C}_9\text{H}_6(\text{CH}_2)_3\text{-C}\{\text{NCHCHN}^t\text{Pr}\}]^-\text{NiBr}$  (**2**), has been synthesized, structural characterized and used as initiator for styrene polymerization in the presence of  $\text{NaBPh}_4$ .

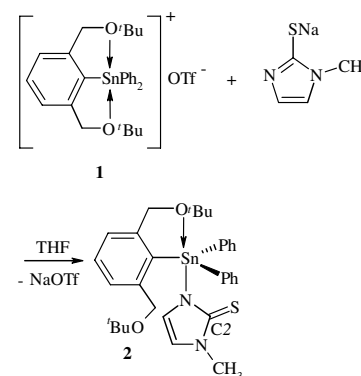


**Jana Martincová, Libor Dostál, Jan Taraba, Roman Jambor**

*J. Organomet. Chem.* 692 (2007) 908

Role of O,C,O-ligand in a new coordination mode of organotin compounds to 2-mercapto-1-methylimidazol. Stabilization of its thione form

The reaction of the organotin compound  $\text{Ph}_2\text{LSn}^+[\text{OTf}]^-$  (**1**), ( $\text{L}(\text{O}, \text{C}, \text{O}) = 2,6\text{-}(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3$ ), with the sodium salt Na(mimt), mimt = 1-methylimidazole-2-thiolate, resulted in the isolation of  $\text{Ph}_2\text{LSn}(\text{mimt})$  (**2**), where the polar group (mimt) has been stabilized as the thione-tautomeric form by the triorganotin fragment  $\text{Ph}_2\text{LSn}$ . Product **2** was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR and IR spectroscopy, ESI/MS, elemental analyses and X-ray diffraction.

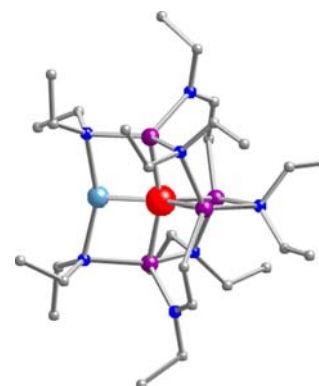


**Charlotte K. Williams, Andrew J.P. White**

*J. Organomet. Chem.* 692 (2007) 912

An amido lithium tetra-zinc oxo complex: Synthesis and X-ray crystal structure of  $(\mu_4\text{-oxo})\text{-pentakis}(\mu_2\text{-diethylamido})\text{-bis}(\text{N}(\text{ethyl})\text{-CHCH}_2)\text{-lithium-tetrazinc}$

The synthesis, characterisation and X-ray structure of an unusual amido lithium tetra-zinc oxo complex is reported. The complex illustrates the unexpected reactivity of bis-(di(alkyl)amido)zinc complexes.

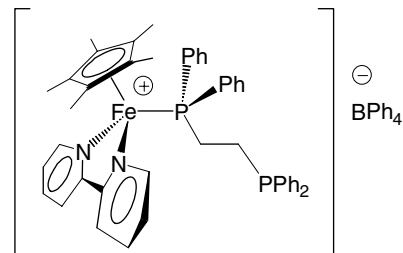


**Safaa Ibn Ghazala, Frédéric Paul, Loic Toupet, Claude Lapinte**

*J. Organomet. Chem.* 692 (2007) 917

Unexpected isolation and structural characterization of a redox-active Fe(II) piano-stool complex with an  $\eta^1$ -dppe ligand

A cationic complex featuring a pendant free diphenylphosphine arm has been isolated in good yield by reacting 2,2'-bipyridine with the known  $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}$  complex. This new compound has been structurally characterized.



**Nail M. Shavaleev, Harry Adams, Jonathan Best, Julia A. Weinstein**

*J. Organomet. Chem.* 692 (2007) 921

Platinum (II) phosphine complexes with acetylene ligands containing 1,4,5,8-naphthalenediimide: Synthesis, crystal structure and electrochemistry

A new acetylene ligand modified with the electron-accepting 1,4,5,8-naphthalenediimide group, its Pt(II) phosphine complexes and their optical and electrochemical properties are reported.

