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Volume 692, issue 8, 15 March 2007

www.elsevier.com/locate/jorganchem

# Contents

# Communications

# Giorgio Della Sala, Antonietta Artillo, Susagna Ricart, Aldo Spinella

J. Organomet. Chem. 692 (2007) 1623

Synthesis of uracil derivatives by oxidation of Fischer tungsten-carbene uracil complexes

Oxidation of Fischer tungsten–carbene uracil complexes allows the preparation of 6-substituted uracils. In this investigation several commonly used oxidants have been considered and, finally, *t*-butyl hydroperoxide, employed for the first time in the oxidation of Fischertype carbene complexes, proved to be a good alternative to the other already available methods.



# Xiomara Yáñez Rueda, Sergio Castillón

J. Organomet. Chem. 692 (2007) 1628

Rhodium-catalyzed intermolecular hydroacylation of 1-alkynes: Effect of phosphines and MK-10 on the reaction selectivity The use of bulky ligands in the rhodiumcatalyzed reaction of aldehydes with 1-octyne increases the percentage of ketones 2 produced, in detriment of ketones 1.  $\begin{array}{c} \overset{O}{\underset{H_{+}}{H_{+}H_{-}}} H \overset{(Fh(m-C))(col)_{L^{2}}PR^{1}}{\underset{Montmoriloon)_{L^{2}}{PR^{1}}} R \overset{O}{\underset{H_{+}}{H_{+}}} H \overset{O}{\underset{H_{+}}{H_{+}}} C_{e}H_{13} + R \overset{O}{\underset{H_{+}}{H_{+}}} C_{e}H_{13} \\ \overset{O}{\underset{H_{+}}{H_{+}}} H \overset{O}{\underset{H_{+}}{H}} H \overset$ 

# **Regular papers**

# Sungjin Park, Youngkyu Do

J. Organomet. Chem. 692 (2007) 1633

Synthesis, characterization, and ethylene polymerizations of various N–O chelated mono  $Cp^*$  titanium complexes

Various mono Cp type titanium mononuclear complexes (1-5) and dinuclear complexes (6 and 7) containing 2-pyridinecarboxylate ligand were synthesized and structurally characterized. The 1 and 2/MMAO catalytic systems for ethylene polymerization exhibited a moderate activity and produced polyethylenes with multi-modal molecular weight distributions.



#### Alla B. Antonova, Zoya A. Starikova, Nina A. Deykhina, Dmitry A. Pogrebnyakov, Anatoly I. Rubaylo

J. Organomet. Chem. 692 (2007) 1641

Chemistry of vinylidene complexes. XVI. Crystal and molecular structure of the novel tetranuclear  $\mu_2$ - $\mu_3$ -bis-vinylidene complex ( $\eta^2$ dppe)PdMn(µ<sub>3</sub>-C=CHPh)PdMn(µ-C=CHPh)- $(CO)_4Cp_2$ 

The reaction between Cp(CO)<sub>2</sub>MnPd(µ-C=CHPh)(PPh<sub>3</sub>)<sub>2</sub> and dppe gave  $(\eta^2$ dppe)PdMn(µ<sub>3</sub>-C=CHPh)PdMn(µ-C=CHPh)- $(CO)_4Cp_2$ . It is the first crystallographically characterized complex containing the Pd-Mn-Pd-Mn chain and two bridging vinylidene ligands with different types of coordination: the symmetric µ2-coordination and µ3-coordination

#### William H. Watson, Srikanth Kandala, Michael G. Richmond

J. Organomet. Chem. 692 (2007) 1648

Ligand degradation and phosphorus scavenging in the reaction between 1,2bis(diphenylphosphino)benzene (dppbz) and Ru<sub>6</sub>(µ<sub>6</sub>-C)(CO)<sub>17</sub>: Synthesis and X-ray structure of the edge-bridged squarepyramidal cluster HRu<sub>6</sub>(µ<sub>5</sub>-C)(µ<sub>3</sub>-P)(CO)<sub>14</sub>-(dppbz)

The hexaruthenium cluster  $Ru_6(\mu_6-C)(CO)_{17}$ reacts with the diphosphine ligand 1,2-bis(diphenylphosphino)benzene (dppbz) to afford the novel cluster  $HRu_6(\mu_5-C)(\mu_3-P)(CO)_{14}$ -(dppbz). The edge-bridged square-pyramidal structure of the title cluster and the presence of a capping phosphido ligand have been confirmed by X-ray crystallography. The unprecedented reactivity between Ru<sub>6</sub>(µ<sub>6</sub>-C)-(CO)<sub>17</sub> and dppbz is discussed relative to other diphosphine ligands.

# Jesse L. Kuiper, Patricia A. Shapley

J. Organomet. Chem. 692 (2007) 1653

Aerobic alcohol oxidation catalyzed by a new, oxygen-bridged heterometallic compound  $[PPh_4][Ru(N)Me_2(\mu_2-O)_2Pd((-)-sparteine)]$ 

The reaction between the new hydroxy compound [PPh4][Ru(N)(OH)2Me2] and Pd(O-SiMe<sub>3</sub>)<sub>2</sub>((-)-sparteine) produces a new heterobimetallic compound [PPh4][Ru(N)- $Me_2(\mu_2-O)_2Pd((-)-sparteine)]$ . The Ru/Pd bimetallic compound catalyzes the oxidation of aryl and allyl alcohols to the corresponding carbonyl compound in air and the rearrangement of allylic alcohols unsaturated aldehydes.

Padavattan Govindaswamy, Bruno Therrien, Georg Süss-Fink, Petr Štěpnička, Jiří Ludvík

J. Organomet. Chem. 692 (2007) 1661

Mono and dinuclear iridium, rhodium and ruthenium complexes containing chelating carboxylato pyrazine ligands: Synthesis, molecular structure and electrochemistry

The reaction of  $[{(\eta^5-C_5Me_5)MCl_2}_2]$  (M = Ir, Rh) and  $[{(\eta^6-arene)RuCl_2}_2]$  (arene = p-Pr<sup>i</sup>C<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) with various pyrazinecarboxylic acids in methanol yields neutral mononuclear and dinuclear complexes with chelating pyrazinecarboxylato ligands.









# Contents

# Manoja K. Samantaray, Vimal Katiyar, Keliang Pang, Hemant Nanavati, Prasenjit Ghosh

J. Organomet. Chem. 692 (2007) 1672

Silver *N*-heterocyclic carbene complexes as initiators for bulk ring-opening polymerization (ROP) of L-lactides

Silver complexes of amido-functionalized and nonfunctionalized *N*-heterocyclic carbenes have been synthesized and structurally characterized. These complexes efficiently catalyze the ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions.



#### Benudhar Punji, Maravanji S. Balakrishna

J. Organomet. Chem. 692 (2007) 1683

Large bite bisphosphite,  $2,6-C_5H_3N\{CH_2OP-(-OC_{10}H_6)(\mu-S)(C_{10}H_6O-)\}_2$ : Synthesis, derivatization, transition metal chemistry and application towards hydrogenation of olefins

A large bite bisphosphite ligand and its chelate neutral (Rh<sup>I</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>), cationic (Ru<sup>II</sup>, Pd<sup>II</sup>) and bridge binuclear (Au<sup>I</sup>) complexes is described. The ruthenium complex **5** shows good activity for the catalytic hydrogenation of styrene and  $\alpha$ -methyl styrene.



#### Paloma Ovejero, María José Mayoral, Mercedes Cano, María Cristina Lagunas

J. Organomet. Chem. 692 (2007) 1690

Luminescence of neutral and ionic gold(I) complexes containing pyrazole or pyrazolate-type ligands

Gold(I) complexes based on pyrazole (Hpz) and pyrazolate ( $pz^-$ ) type ligands have been shown to be luminescent in solid state independently of the presence or not of intermetallic Au–Au interactions. They exhibit different patterns of emission bands attributed to ligand-to-metal charge transfer (LMCT) transitions involving Hpz or pz<sup>-</sup> ligands.



## Lucila Márquez-Pallares, Jorge Pluma-Pluma, Marisol Reyes-Lezama, Marisol Güizado-Rodríguez, Herbert Höpfl, Noé Zúñiga-Villarreal

J. Organomet. Chem. 692 (2007) 1698

Synthetic studies for the preparation of phosphorus carbonyl rhenacycles with the selenoimidodiphosphinate ligand [N(SePPh<sub>2</sub>)<sub>2</sub>]

The synthesis of the rhenacycles [Re-(CO)<sub>3</sub>(PR<sub>3</sub>){Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>- $\kappa^2 Se$ }], PR<sub>3</sub> = PPh<sub>3</sub> (1), PMePh<sub>2</sub> (2), and PMe<sub>2</sub>Ph (3) by an easy high yield procedure is described. Attempts at the preparation of the spiro compound [Re(CO)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>- $\kappa^2$ P)-{Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>-2*Se*}] resulted in the formation of complexes, [Re<sub>2</sub>(CO)<sub>6</sub>{Ph<sub>2</sub>P(Se)-NP(Se)Ph<sub>2</sub>- $\kappa^2 Se$ }<sub>2</sub> ( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] (4), and [Re(CO)<sub>3</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>- $\kappa^2$ P){Ph<sub>2</sub>-P(Se)NP(Se)Ph<sub>2</sub>- $\kappa Se$ }] (5). All new inorganic rhenacycles 1–5 were characterized in solution and in solid state.



## Run-Yu Tan, Juan Hong, Miao Du, Liang-Fu Tang

J. Organomet. Chem. 692 (2007) 1708

New multidentate heteroscorpionate ligands: *N*-Phenyl-2,2-bis(pyrazol-1-yl)thioacetamide and ethyl 2,2-bis(pyrazol-1-yl)dithioacetate as well as their derivatives *N*-phenyl-2,2-bis(pyrazol-1-yl)thioacetamide can coordinate by three different ways, as monodentate ligand by the sulfur atom, as neutral  $\kappa^2$ -( $\pi$ ,N) bidentate ligand, and as tridentate monoanionic  $\kappa^3$ -(N,N,S) chelating ligand to different metals.



#### Matthew Daniels, Rein U. Kirss

J. Organomet. Chem. 692 (2007) 1716

Dimerization of terminal alkynes catalyzed by chloro( $\eta^5$ -pentadienyl) bis(triphenylphosphine)-ruthenium(II) and kinetics of phosphine substitution

Exchange of PMe<sub>2</sub>Ph for PPh<sub>3</sub> in (η<sup>5</sup>-pentadienyl)ruthenium {bis(triphenylphosphine)}-chloride, (η<sup>5</sup>-C<sub>5</sub>H<sub>7</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl (1) under first order conditions in THF proceeds smoothly with a pseudo-first order rate constant of 17 ± 2 × 10<sup>-4</sup> s<sup>-1</sup> at 21 °C and activation parameters,  $\Delta H^{\dagger}$ = 16.1 ± 0.4 kcal mol<sup>-1</sup> and  $\Delta S^{\dagger}$  = -16 ± 1 cal K<sup>-1</sup> mol<sup>-1</sup>.

Reaction of 1 with NaPF<sub>6</sub> in acetonitrile yields  $[(\eta^5-C_5H_7)Ru(PPh_3)_2(CH_3CN)][PF_6]$  (7). Compound 1 is more active than other ruthenium(II) complexes CpRu(PPh\_3)\_2Cl, ( $\eta^5$ indenyl)Ru(PPh\_3)\_2Cl and TpRu(PPh\_3)\_2Cl in the dimerization of phenylacetylene, ethynylferrocene, trimethylsilylacetylene and 'butylacetylene.



# C.W. Liu, Ching-Shiang Fang, Chin-Wei Chuang, Tarlok S. Lobana, Ben-Jie Liaw, Ju-Chun Wang

J. Organomet. Chem. 692 (2007) 1726

Oxidative decarbonylation of Mo(CO)<sub>6</sub> with  $[-Se(Se)P(Oi-Pr)_2]_2$  generates the mixed-valent tetranuclear cluster Mo<sub>4</sub>( $\mu_3$ -Se)<sub>4</sub>[Se<sub>2</sub>P(Oi-Pr)<sub>2</sub>]<sub>6</sub> and a cationic trinuclear cluster [Mo<sub>3</sub>( $\mu_3$ -Se)-( $\mu_2$ -Se<sub>2</sub>)<sub>3</sub>{Se<sub>2</sub>P(Oi-Pr)<sub>2</sub>}<sub>3</sub>]<sup>+</sup>

## Mahmoud M.A. Mohamed, Elham M. Abd-Alla, Ahmed El-Sayed El-Badawy

J. Organomet. Chem. 692 (2007) 1735

Dimethyltin(IV) complexes with zwitterionic buffers (Mes and Mops)

Equilibrium studies in aqueous solution are reported for dimethyltin(IV) complexes of the zwitterionic buffers "Good's buffer". The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ calculated from the temperature dependence of the formation constant of the dimethyltin(IV)– Both tetranuclear cluster  $Mo_4(\mu_3-Se)_4[Se_2P(Oi-Pr)_2]_6$  (1) and cationic, trinuclear cluster  $[Mo_3(\mu_3-Se)(\mu-Se_2)_3\{Se_2P(Oi-Pr)_2\}_3]^+$  (2) were obtained in an one-pot reaction via Se transfer in the oxidative decarbonylation of  $Mo(CO)_6$  with  $[-Se(Se)P(Oi-Pr)_2]_2$ . While cluster 1 is the first  $[Mo_4(\mu_3-Se)_4]$  cubane core with outer selenium-donor ligands, the cluster 2 displays unusual, intermolecular Se $\cdots$ Se contacts to produce infinite chains. In addition, the "sandwiched" halide anion is attached to three, electrophilic Se<sub>ax</sub> atoms of one Mo<sub>3</sub> unit and one Se<sub>eq</sub> atom of the neighboring unit and these distances are far shorter than the sum of the van der Waals radii.

Mes complex was investigated. The effect of dioxane as a solvent on the formation constants of dimethyltin(IV)–Mes complex was discussed. The bonding sites of the dimethyltin(IV) complexes in solid state with Mes and Mops were characterized by means of elemental analyses and FTIR. The NMR (<sup>1</sup>H, <sup>13</sup>C) spectra of the DMT–Mes complex exhibits the strongly distorted octahedron geometry around tin atom. Also, thermal analyses (TGA and DTA) were discussed. Thermodynamic parameters such as activation energy ( $E_a$ ), pre-exponential factor (A), entropy of activation ( $\Delta S^*$ ) and free energy of activation ( $\Delta G^*$ ) have been calculated for each step, employing integral method Coats and Redfern.



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# Michael I. Bruce, Paul A. Humphrey, Martyn Jevric, Gary J. Perkins, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 692 (2007) 1748

Heterometallic complexes containing 1,1'-(C $\equiv$ C)<sub>2</sub>Fc' units linking two different metal centres

Proto-desilylation of  $1-(Me_3SiC\equiv C)-1'-\{Cp^*-(dppe)RuC\equiv C\}Fc'$  (1) afforded the corresponding ethnyl derivative **2**, from which

the green  $Co_2(\mu$ -dppm)<sub>n</sub>(CO)<sub>8-2n</sub> (n = 0, 1) adducts **3** and **4** were obtained. Replacement of the ethynyl proton in reactions between **2** and AuCl(PPh<sub>3</sub>), Hg(OAc)<sub>2</sub> or FeCl(dppe)Cp<sup>\*</sup> gave complexes 1-(RC=C)-1'-{Cp<sup>\*</sup>(dppe)-RuC=C}Fc' [R = Au(PPh<sub>3</sub>) **5**, 1/2Hg **6**, Fe(dppe)Cp<sup>\*</sup> **8**]; the latter gave bis-vinylidene **9** with MeI, characterised (as was **2**) by a single crystal X-ray study. Oxidative coupling of **2** (CuCl/tmeda/acetone, air) gave diyne **10**, while coupling of **5** with Co<sub>3</sub>( $\mu_3$ -CBr)( $\mu$ -dppm)(CO)<sub>7</sub> afforded 1-{Cp<sup>\*</sup>(dppe)RuC=C}-1'-{(OC)<sub>7</sub>( $\mu$ dppm)Co<sub>3</sub>( $\mu_3$ -CC=C)} Fc' (**11**).  $Ph_{2}P \rightarrow Ph_{2} \qquad Ph_{2}P \rightarrow Ph_{2} \qquad Ph_{2}P \rightarrow Ph_{2}$ 

#### Michael I. Bruce, Martyn Jevric, Gary J. Perkins, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 692 (2007) 1757

Reactions between  $1,1'-(Me_3SiC\equiv C)_2Rc'$ [Rc' = ruthenocen-1,1'-diyl,  $Ru(\eta-C_3H_4-)_2$ ] and RuCl(PP)Cp' in the presence of KF gave  $1,1'-\{Cp(PP)RuC\equiv C\}_2Rc'$  [Cp' = Cp, PP = PPh<sub>3</sub> 1, P(*m*-tol)<sub>3</sub> 2, dppe 3, dppf 4; Cp' = Cp<sup>\*</sup>, PP = dppe 5]. Compounds 1 and 2 react with tcne to give two diastereomers **a/b** of the allylic (vinylcarbene) complexes 6 and 7, while methylation of 5 gave the bis-vinylidene [1,1'-{Cp<sup>\*</sup>(dppe)Ru=C=CMe}\_2Rc'](BPh\_4)\_2 (8). The X-ray structures of 4, 6b and 8 have been determined.



#### Note

# Xiu-Feng Hou, Shu Liu, Peng-Cheng Zhang, Guo-Xin Jin

J. Organomet. Chem. 692 (2007) 1766

Synthesis and molecular structure of hexanuclear organotitanium ion complex:  $[Cp'_{6}Ti_{6}(\mu_{3}\text{-}O)_{8}][C_{2}B_{10}H_{10}(\mu\text{-}S_{2})_{2}C_{2}B_{9}H_{10}]_{2}$ 

The synthesis and crystal structure of novel hexanuclear organotitanium ion complex  $[Cp_6'-Ti_6(\mu_3-O)_8][C_2B_{10}H_{10}(\mu-S_2)_2C_2B_9H_{10}]_2$ , which contains both a divalent cationic organotitanium oxide and the derivative 7,8-dicarbaundecaborate anions, are reported.



 $Cp' = \eta^5 - C_5 H_4 CH_2 CH_2 OCH_3$ 



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