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# Contents

## **Regular Papers**

SEVIER

Gloria Sánchez-Cabrera, Marco A. Leyva, Francisco J. Zuno-Cruz, María G. Hernández-Cruz, Maria I. Rosales-Hoz

J. Organomet. Chem. 694 (2009) 1949

The hydrogenation reaction of  $[Ru_3(CO)_{10}-(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2]$ : Migration of a  $C_6F_5$  group from a phosphorus to a ruthenium atom. X-ray crystal structures of  $[Ru_3(CO)_9(\mu-H)_{4\mu_2}-(C_6F_5)PCH_2CH_2P(C_6-F_5)_2]$ ,  $[Ru_3(CO)_7(\mu-H)_3(\eta^1-C_6F_5)_{4\mu_3}-PCH_2-(\mu_3-\mu_3)_3(\eta^1-\mu_3)_3(\eta^1-\mu_3)_3(\eta^2-$ 

## Antonio Antiñolo, Rafael Fernández-Galán, Noelia Molina, Antonio Otero, Iván Rivilla, Ana M. Rodríguez

J. Organomet. Chem. 694 (2009) 1959

New alkenyl-substituted group 4 *C-ansa*metallocene complexes. Reactivity of the substituent at the carbon *ansa* bridge CH\_2P(C\_6F\_5)\_2]] and [Ru\_3(CO)\_8(\mu-H)\_2{\mu\_3-PCH\_2-CH\_2P(C\_6F\_5)\_2}]

The reaction of  $[Ru_3(CO)_{10}\{(C_6F_5)_2P(CH_2)_2-P(C_6F_5)_2\}]$  with hydrogen leads to the formation of phosphide and phosphinidene trinuclear clusters by successive loss of  $C_6F_5$  groups from one of the phosphorus atoms of the diphosphine ligand, which then bond; through a  $\sigma$  bond; to one of the metal atoms. The ligand remains bonded through the two phosphorus atoms in all the products.



The reactivity of a new family of *ansa*metallocene group 4 complexes containing an alkene substituent in the carbon bridge atom in catalytic hydrogenation, hydrosilylation and hydroboration processes is described. These complexes, through the Si–Cl bond, open up the possibility of supporting such catalysts on different inorganic surfaces.



## Jiří Pinkas, Ivana Císařová, Ana Conde, Rosa Fandos, Michal Horáček, Jiří Kubišta, Karel Mach

J. Organomet. Chem. 694 (2009) 1971

Thermolysis of titanocene methyl compounds bearing *t*-butyl- and benzyl-tetramethylcyclopentadienyl ligands

Thermolytic elimination of methane from titanocene methyl compounds [TiMe( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>] and [TiMe<sub>2</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>] (R = *t*-Bu or CH<sub>2</sub>Ph) results in the formation of  $\sigma$ -Ti–C bonds to *t*-butyl or benzyl group to give compounds 6, 7, 11, and 12.



## Santiago Gómez-Ruiz, Goran N. Kaluđerović, Željko Žižak, Irina Besu, Zorica D. Juranić, Sanjiv Prashar, Mariano Fajardo

J. Organomet. Chem. 694 (2009) 1981

Anticancer drugs based on alkenyl and boryl substituted titanocene complexes

The cytotoxic activity of different alkenyl and boryl substituted titanocene derivatives has been studied against human tumour cell lines, observing that the substituent on the cyclopentadienyl ring has a remarkable influence on the final anticancer activity



## Yoshio Kabe, Houjin Hachiya, Tomohisa Saito, Daisuke Shimizu, Masakatsu Ishiwata, Kazuharu Suzuki, Yuko Yakushigawa, Wataru Ando

J. Organomet. Chem. 694 (2009) 1988

Diastereoselective syntheses and oxygenation of silyl fulleroids

The addition of silyl diazomethane with fullerene  $C_{60}$  afforded diastereoselectively silyl fulleroids with the silyl group located above five-membered ring through thermal N<sub>2</sub> extrusion of pyrazoline intermediate. The silyl fulleroids were found to react with  $^{1}O_{2}$  to give silyl enol ether via 1,3-silyl migration of a diketone.



## Zia-ur-Rehman, Afzal Shah, Niaz Muhammad, Saqib Ali, Rumana Qureshi, Ian Sydney Butler

J. Organomet. Chem. 694 (2009) 1998

Synthesis, characterization and DNA binding studies of penta- and hexacoordinated diorganotin(IV) 4-(4nitrophenyl)piperazine-1-carbodithioates Two chlorodiorganotin(IV) and a diphenyltin(IV) derivative of 4-(4-nitro-phenyl)piperazine-1-carbodithioate ligand have been synthesized, and characterized by elemental analysis, Raman, IR, multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn) spectroscopy, and mass spectrometry. The interaction of these complexes with DNA was studied by cyclic voltammetry and UV–Vis spectroscopy.



## Sandra Taubmann, Christine E. Denner, Helmut G. Alt

J. Organomet. Chem. 694 (2009) 2005

Catalytic dehydrogenation of cyclooctane with titanium, zirconium and hafnium metallocene complexes

Metallocene complexes in combination with cocatalysts like methylalumoxane (MAO) are not only excellent catalysts for olefin polymerization but also appropriate catalysts for the activation of alkanes in homogeneous (autoclave) and heterogeneous (fixed bed reactor) reactions. The activities of the catalysts depend on the temperature, the cocatalysts, additives, the central metal and the ligand structure. Generally, complexes with low steric demands and MAO as cocatalyst gave the highest activities. None of the catalysts required a hydrogen acceptor like an external olefin.



#### Arthur Connell, Peter J. Holliman, Ian R. Butler, Louise Male, Simon J. Coles, Peter N. Horton, Michael B. Hursthouse, William Clegg, Luca Russo

J. Organomet. Chem. 694 (2009) 2020

The highly regiospecific synthesis and crystal structure determination of 1,1'-2,5' substituted ring-locked ferrocenes

1,1'-Ferrocene biscarboxaldehyde (1) has been prepared and the aldehyde groups were subsequently protected with acetal groups to produce 1,1'-bisacetalferrocene (2). Compound (2) has been used to prepare novel regiospecific ferrocenophane derivaties.



#### Beatriz González, Pablo Lorenzo-Luis, Pedro Gili, Antonio Romerosa, Manuel Serrano-Ruiz

J. Organomet. Chem. 694 (2009) 2029

Behaviour of  $[RuClCp(mPTA)_2](OSO_2CF_3)_2$ in water vs. the pH: Synthesis and characterisation of  $[RuCpX(mPTA)_2](OSO_2-CF_3)_m$ , X =  $(H_2O-\kappa O, DMSO-\kappa S, n = 3; OH^-\kappa O, n = 2)$  (mPTA = N-methyl-1,3,5-triaza-7-phosphaadamantane) The aquo-soluble ruthenium(II) complexes  $[RuCp(mPTA)_2(L)]\cdot X_n$  (L = H<sub>2</sub>O- $\kappa$ O, X =  $^{-}OSO_2CF_3$ , n = 3 (3); L = Cl, X=BF<sub>4</sub>, n = 2 (4); L = DMSO- $\kappa$ S, X =  $^{-}OSO_2CF_3$ , n = 3 (5); were synthesised. The thermal analysis of complexes 1–3 and the crystal structure of the complexes 1 and 5 are also presented.



## A.M. Ortiz, P. Sharma, D. Pérez, Noé Rosas, A. Cabrera, L. Velasco, A. Toscano, S. Hernández

J. Organomet. Chem. 694 (2009) 2037

New 1,2-disubstituted ferrocenyl stibines containing N-heterocyclic pendant arm: Sb–N hypervalent compounds

New 1,2-disubstituted ferrocenyl stibines viz. containing -CH<sub>2</sub>NR or -CH<sub>2</sub>NHR pendant arm at the *ortho*-position have been synthesized and characterized by various physicochemical methods.

#### Carolina Manzur, Lorena Millán, Mauricio Fuentealba, Alexander Trujillo, David Carrillo

J. Organomet. Chem. 694 (2009) 2043

Syntheses and crystal structures of two new cationic 3,5-dimethylpyrazole derivatives containing organoiron mixedsandwiches as substituent groups These new ferrocenylstibines were prepared by the nucleophilic substitution reaction of diphenyl[(*N*,*N*,*N*-trimethylaminomethylferrocenyl)iodide]stibine by different primary amines and secondary heterocyclic amines viz. furan-2-1-ylmethylamine, *p*-aminoacetophenone, 3-(1hydroxyethyl)-aniline, 4-hydroxypiperidine, 1ethylpiperazine and 4-(4-bromophenyl)-4-hydroxypiperidine. Molecular structure of stibine (2), (3), (5) and (7) have been determined by X-ray crystallography. Stibine (2), (5) and (7) show a weak hypervalent Sb–N interaction while stibine (3) does not show this interaction in solid state.



Two novel 3,5-Me<sub>2</sub>-pyrazole derivatives containing the organoiron mixed-sandwich moieties have been synthesized by reaction of the corresponding organometallic hydrazines with 2,4-pentanedione in MeCN. The cationic complexes have been fully characterized by elemental analysis and IR, UV-vis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and authenticated by single crystal X-ray diffraction analysis.



#### Contents

## José Ramon Garabatos-Perera, Holger Butenschön

J. Organomet. Chem. 694 (2009) 2047

New chiral ferrocenyloxazolines: The first planar chiral triferrocenylmethane derivative and its use in asymmetric catalysis New planar chiral enantiopure ferrocenyloxazolines have been prepared including ferrocenyldiphenylmethanol, diferrocenylphenylmethanol and triferrocenylmethanol derivatives, the latter being the first chiral triferrocenylmethanol derivative. The ferrocenyldiphenylmethanol derivative has been crystallographically characterized. Asymmetric ethylation of some arylaldehydes using diethylzinc in the presence of the planar chiral triferrocenylmethanol derivative afforded good yields and *ees*.



#### Ludmila Vigo, Merja J. Poropudas, Pekka Salin, Raija Oilunkaniemi, Risto S. Laitinen

J. Organomet. Chem. 694 (2009) 2053

Versatile coordination chemistry of rhodium complexes containing the bis(trimethylsilylmethyl)tellane ligand The treatment of  $RhCl_3 \cdot 3H_2O$  with  $Te(CH_2SiMe_3)_2$  afforded a mononuclear *mer*-[RhCl\_3{Te(CH\_2SiMe\_3)\_2}] (1), dinuclear [Rh<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Cl<sub>4</sub>{Te(CH\_2SiMe\_3)\_2}] (2), and [Rh<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Cl<sub>4</sub>(OHCH<sub>2</sub>CH<sub>3</sub>){Te(CH<sub>2</sub>SiMe\_3)\_2}] (3) depending on the molar ratio of the reactants.



## M. Fernanda N.N. Carvalho, Adelino M. Galvão, Ana S.D. Ferreira

J. Organomet. Chem. 694 (2009) 2061

Pentynol to furan conversion – Search for the best *trans*- $[MX_2(YNC_{10}H_{14}O)_2]$  catalyst

Rate constants  $(k_1, k_2)$ , catalytic activities, TON and TOF values concerning formation of 2-methyl-2-pent-4-ynyloxy-tetrahydrofuran (**B**) and 5-(2-methyl-tetrahydrofuran-2-yloxy)-pentan-2-one (**C**) from 4pentyn-1-ol (**A**) catalysed by *trans*-[MX<sub>2</sub>(YNC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>] show that the catalysts efficiency is highly dependent of Y.



## Jia-Sheng Zhang, Yue-Jian Lin, Guo-Xin Jin

J. Organomet. Chem. 694 (2009) 2069

Synthesis and characterization of heterometallic Rh/Ru complexes supported by 1,2-dichalcogenolato-ocarborane ligands The 16-electron half-sandwich complexes  $Cp^*Rh[E_2C_2(B_{10}H_{10})]$  (E = S, 1a; Se, 1b) react with  $[Ru(COD)Cl_2]_x$  under different conditions can give different types of heterobinuclear Rh/Ru complexes.



#### Alireza Ariafard, Brian F. Yates

J. Organomet. Chem. 694 (2009) 2075

In-depth insight into the electronic and steric effects of phosphine ligands on the mechanism of the R-R reductive elimination from  $(PR_3)_2PdR_2$ 

The aim of this study was to investigate both the electronic and steric effects of the ancillary phosphine ligand L on the reductive elimination of R-R from a series of  $L_2PdR_2$  and LPdR<sub>2</sub> complexes.

Concerted mechanism (direct reductive elimination)



#### Kuan-Yi Wu, Chang-Chih Hsieh, Yih-Chern Horng

J. Organomet. Chem. 694 (2009) 2085

Mononuclear zinc(II) and mercury(II) complexes of Schiff bases derived from pyrrolealdehyde and cysteamine containing intramolecular NH···S hydrogen bonds

The extensive intermolecular N–H···S hydrogen bonds in the structure of bis(2aminoethanethiolate)zinc(II) were substituted by new intramolecular N–H···S hydrogen bonds by using the pyrrole moiety as an extension of cysteamine. Similarly, a new Hg(N<sub>2</sub>S<sub>2</sub>) complex was successfully prepared. The (pyrrole)NH···S interactions of both new complexes were evidenced by IR, <sup>1</sup>H NMR spectra and X-ray analysis.



## Lu Yin, Wenjun Shan, Xian Jia, Xingshu Li, Albert S.C. Chan

J. Organomet. Chem. 694 (2009) 2092

Ru-catalyzed enantioselective preparation of methyl (*R*)-o-chloromandelate and its application in the synthesis of (*S*)-Clopidogrel The preparation of methyl (*R*)-o-chloromandelate via Ru-catalyzed asymmetric hydrogenation and transfer hydrogenation was investigated. With Ru-(*R*,*R*)-2,4,6-*i*-Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>SO<sub>2</sub>DPEN as the catalyst and HCOOH–Et<sub>3</sub>N azeotrope as the hydrogen donor, up to 92% ee was obtained in an optional condition.

## Jia-Feng Sun, Fei Chen, Brenda A. Dougan, Hui-Jun Xu, Yong Cheng, Yi-Zhi Li, Xue-Tai Chen, Zi-Ling Xue

J. Organomet. Chem. 694 (2009) 2096

Quinoline-functionalized N-heterocyclic carbene complexes of iridium: Synthesis, structures and catalytic activities in transfer hydrogenation Iridium quinoline-functionalized N-heterocyclic carbene (NHC) complexes [(NHC)Ir-(COD)Cl] (**2a–2d**) were synthesized and characterized. The COD was replaced by CO to yield [(NHC)Ir(CO)<sub>2</sub>Cl] (**3**). Two analogous Ir(I) complexes **5** and **6** with naphthalene-containing NHC have also been synthesized and characterized. These Ir(I) complexes have been proved to be active catalysts in the transfer hydrogenation.



## Ivan P. Klimenko, Andrey F. Medvedev, Victor A. Korolev, G.D. Kolomnikova, Yury V. Tomilov, Yuri N. Bubnov

J. Organomet. Chem. 694 (2009) 2106

First allylboration of organic compounds with the N=N double bond. Synthesis of *N*-allylpyrazolidines and allyl-1,2-diphenylhydrazine

The first example of addition of organoboron compound to N=N double bound was found. It turned out that triallylborane easily adds to the N=N bond of substituted pyrazolines and azobenzene gives rise to N-allylpyrazolidines and 1-allyl-1,2-diphenylhydrazine respectively. Reaction protocol is very easy and the yields are high.



#### Magdalena Zyder, Teresa Szymańska-Buzar

J. Organomet. Chem. 694 (2009) 2110

Activation of the Ge–H bond of Et<sub>3</sub>GeH in photochemical reaction with molybdenum(0) carbonyl complexes and hydrogermylation of norbornadiene The germane intermediate  $\sigma$ -complexes, characterized by high-field resonances, have been detected during the <sup>1</sup>H NMR spectroscopy monitoring of the photochemical reaction of Et<sub>3</sub>GeH with Mo(CO)<sub>6</sub>, [Mo(CO)<sub>4</sub>( $\eta^4$ -cod)], and [Mo(CO)<sub>4</sub>( $\eta^4$ -nbd)] in the NMR tube. The activation of the Ge–H bond of germane has been applied in the hydrogermylation of norbornadiene.



## Sasmita Mohanty, D. Suresh, Maravanji S. Balakrishna, Joel T. Mague

J. Organomet. Chem. 694 (2009) 2114

Phosphine free diamino-diol based palladium catalysts and their application in Suzuki-Miyaura cross-coupling reactions The inexpensive, phosphorus free, air and moisture stable palladium complexes of tetradentate ligands are found to be very efficient catalysts for Suzuki–Miyaura cross-coupling reactions.





## Note

## Adam C. Tomasik, Nicholas J. Hill, Robert West

J. Organomet. Chem. 694 (2009) 2122

Synthesis and characterization of three new thermally stable N-heterocyclic germylenes

Three new stable germylenes, *rac*-1,3-di*tert*-butyl-4,5-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide (1), 1,3-di-*tert*-butyl-4,4-dimethyl-1,3-diaza-2-germacyclopentane-2-ylide (2), and *rac*-1,3,4-tri-*tert*-butyl-1,3-diaza-2-germacyclopentane-2-ylide (3) have been synthesized by the reaction of their corresponding dichlorides with elemental lithium. Full synthetic procedures and characterizations are described.





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