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# Contents

# Communication

# Rhett T. Watson, Jillian Basinger, Endy Y. Min, Paul S. Wagenknecht

J. Organomet. Chem. 690 (2005) 2159

Synthesis of a Lewis acid bearing cyclopentadienyl ligand and its tricarbonylmanganese(I) complex Compounds containing both a Lewis acid and a transition metal in close proximity are of interest for bifunctional binding of small molecules. The synthesis of a complex comprising both a metal carbonyl and a Lewis acidic organotin moiety is reported.



# **Regular papers**

### Alexandre Martinez, Catherine Hemmert, Heinz Gornitzka, Bernard Meunier

J. Organomet. Chem. 690 (2005) 2163

Synthesis and activity of macrocyclized chiral Mn(III)–Schiff-base epoxidation catalysts

A series of chiral macrocyclic Mn(III)Salen has been prepared with two salicylidene moieties linked in their 3 and 3' positions by aliphatic polyethers bridges of variable lengths or by a more rigid aromatic junction arm, in order to study the flexibility of the linkers in asymmetric catalysis. These complexes have been tested in the asymmetric epoxidation of *cis*-disubstituted olefins with several oxygen atom donors.



## Moncef Bellassoued, Sinda Mouelhi, Pierre Fromentin, Aurélien Gonzalez

J. Organomet. Chem. 690 (2005) 2172

Two-carbon homologation of ketones via sily ketene acetals: Synthesis of  $\alpha$ , $\beta$ -unsaturated acids and  $\alpha$ -trimethylsilyl  $\delta$ -ketoacids

The trisilylated reagent 1 reacts with saturated ketones to give  $\alpha$ , $\beta$ -unsaturated acids and with  $\alpha$ , $\beta$ -unsaturated ketones to give  $\alpha$ -trimethylsilyl  $\delta$ -ketoacids.



### Contents

### Amal Shibli, Hijazi Abu Ali, Israel Goldberg, Morris Srebnik

J. Organomet. Chem. 690 (2005) 2180

Direct preparation and structure determination of tertiary and secondary amine boranes from primary or secondary amine boranes A series of novel secondary and tertiary amine boranes derivatives have been synthesized in a one-pot reaction and structurally characterized (solution  ${}^{1}$ H,  ${}^{13}$ C and  ${}^{11}$ B NMR spectroscopy; three crystal analyses). The synthesis was done according to the following reaction.



# Yizong Zhou, Tao Jiang, Sumei Ren, Jingsheng Yu, Zhicheng Xia

J. Organomet. Chem. 690 (2005) 2186

Synthesis, crystal structure and in vitro antitumor activity of di-*n*-butyltin 4'-(7-oxabicyclo [2,2,1]-5-heptane-2,3-dicarbox-imide) benzoates

The carboxylic acid reacts with the di-n-butyltin oxide yielding two different compounds depending on molar ratio acid/tin engaged in the reaction:bis[di-*n*-butyl-(carboxylato)tin]oxide (compound 1) for a 1:1 ratio and di-*n*-butyltindi(carboxylate) (compound 2) for a 2:1 ratio. in vitro test shows that compound 1 and 2 exhibit high cytotoxicity against P388 and HL-60.



# Axel Diefenbach, F. Matthias Bickelhaupt

J. Organomet. Chem. 690 (2005) 2191

Activation of C–H, C–C and C–I bonds by Pd and  $\mathit{cis-Pd}(CO)_2I_2$ . Catalyst–substrate adaptation

The main source of the rise in activation energies that we find for *cis*-Pd<sup>II</sup>(CO)<sub>2</sub>I<sub>2</sub>compared to Pd<sup>0</sup>-catalyzed C–X bond activation is the activation strain. The latter appears to correlate with the strength of the activated C–X bond: both decrease along C–H, C–C and C–I.



# Montserrat Ferrer, Mounia Mounir, Laura Rodríguez, Oriol Rossell, Silverio Coco, Pilar Gómez-Sal, Avelino Martín

J. Organomet. Chem. 690 (2005) 2200

Effect of the organic fragment on the mesogenic properties of a series of organogold(I) isocyanide complexes. X-ray crystal structure of  $[Au(C \equiv CC_5H_4N)-(CNC_6H_4O(O)CC_6H_4OC_{10}H_{21})]$ 

Rod-like organogold(I) complexes [AuR-(CNC<sub>6</sub>H<sub>4</sub>O(O)CC<sub>6</sub>H<sub>4</sub>OC<sub>10</sub>H<sub>21</sub>-*p*)] (R = Cl, C=C-C<sub>5</sub>H<sub>4</sub>N, C=C-C<sub>6</sub>H<sub>4</sub>C=N, C=C-C<sub>6</sub>H<sub>4</sub>-C=C-C<sub>5</sub>H<sub>4</sub>N, C<sub>5</sub>F<sub>4</sub>N, C<sub>6</sub>F<sub>4</sub>C<sub>5</sub>H<sub>4</sub>N, C<sub>6</sub>F<sub>5</sub>) were prepared and characterized. The X-ray crystal structure of the compound with R = C=C-C<sub>5</sub>H<sub>4</sub>N shows linear molecules in which the gold atoms are not involved in direct gold–gold interactions. Six of these compounds are liquid crystals and their optical, thermal and thermodynamic data were analyzed and compared in terms of molecular polarizability.



### Andrew J.M. Caffyn, Martin J. Mays

J. Organomet. Chem. 690 (2005) 2209

A comparison between the reaction of  $P_2Ph_4$ with [{Co<sub>2</sub>(CO)<sub>6</sub>}<sub>2</sub>( $\mu$ - $\eta^2$ : $\mu$ - $\eta^2$ -HOCH<sub>2</sub>C $\equiv$ C -C $\equiv$ CCH<sub>2</sub>OH)] and the reaction of [Co<sub>2</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>6</sub>] with HOCH<sub>2</sub>C $\equiv$ C-C  $\equiv$ CCH<sub>2</sub>OH

Reaction of  $P_2Ph_4$  with the diyne-diol complex [{ $Co_2(CO)_6$ }\_2(\mu-\eta^2:\mu-\eta^2-HOCH\_2-C\equivC-C\equivCCH\_2OH] gives [{ $Co_2(\mu-P_2Ph_4)-(CO)_4$ }{ $Co_2(CO)_6$ }( $\mu-\eta^2:\mu-\eta^2-HOCH_2C\equivC-$ 

### Naoshi Iwama, Satoshi Hayakawa, Taku Kato, Yasuko T. Osano, Toshihiko Sugano

J. Organomet. Chem. 690 (2005) 2220

Novel bridged bis-azulenyl and bistetrahydroazulenyl hafnocenes: Synthesis, structure, and propylene polymerization behavior

Novel bridged bis-azulenyl and bis-tetrahydroazulenyl hafnocenes were synthesized. The structure was confirmed by X-ray crystallographic analysis to fold  $C_2$  symmetry. These hafnocenes were found to be active catalysts for propylene polymerization in the presence of methylaluminoxane (MAO), and the preliminary polymerization behavior of those catalysts was evaluated.  $R^{1}$   $H^{1}$   $R^{1}$   $H^{2}$   $H^{1}$   $H^{2}$   $H^{1}$   $H^{2}$   $H^{2}$   $H^{1}$   $H^{2}$   $H^{2$ 

**b**:  $R^1$  = Et,  $R^2$  = 4-CIPh

## José G. López-Cortés, Luis F. Contreras de la Cruz, M. Carmen Ortega-Alfaro, Ruben A. Toscano, Cecilio Alvarez-Toledano, Henri Rudler

J. Organomet. Chem. 690 (2005) 2229

Improved approaches and structures of new ferrocenyl carbene complexes of chromium, tungsten, and molybdenum

Ferrocenyllithium reacts with  $M(CO)_6$  (M = Cr, W, Mo) in *THF* to give, after alkylation at oxygen, the corresponding carbene complexes 3a-c in good yield. Complexes 3a, b were characterized by X-ray analysis. These complexes react with pentylamine to give the corresponding aminocarbene complexes 7a-c and with allylamine to give, in the case of chromium and tungsten, the corresponding and expected aminocarbene complexes 8a, b, and for molybdenum, complex 9c in which the double bond is already coordinated to the metal. 8a, b could be converted in 9a, b in excellent yield. The structure of 9a could be confirmed by an X-ray analysis. Alkylations at nitrogen could be carried on complex 9c as well as on complexes 9a, b.



# Hanns-Dieter Amberger, Hauke Reddmann, Frank T. Edelmann

J. Organomet. Chem. 690 (2005) 2238

Zur Elektronenstruktur metallorganischer Komplexe der f-Elemente LXI. Welche Oxidationszahl hat Cer im tiefvioletten 1,1',4,4'-Tetrakis(trimethylsilyl)cerocen? The low-temperature luminescence, absorption and magnetic circular dichroism spectra of deep purple  $Ce[C_8H_6(1,4-SiMe_3)_2]_2$  do not contradict results of earlier quantum chemical computations which predict a predominantly trivalent oxidation state of Ce in cerocene.



### Attila Szorcsik, László Nagy, Michelangelo Scopelliti, Andrea Deák, Lorenzo Pellerito, Kaspar Hegetschweiler

J. Organomet. Chem. 690 (2005) 2243

Doina Sirbu, Giambattista Consiglio,

Barbara Milani, P.G. Anil Kumar,

Paul S. Pregosin, Sebastian Gischig

merisation: Counterion effect

J. Organomet. Chem. 690 (2005) 2254

Palladium complexes with meso-bioxazoline

ligands for alternating styrene/CO copoly-

Two sets of mono- and dicationic palladium com-

Preparation and structural characterization of organotin(IV) complexes with ligands containing a hetero  $\{N\}$  atom and a hydroxy group or hydroxy and carboxyl groups

<sup>*n*</sup>Bu<sub>2</sub>Sn(IV)<sup>2+</sup> and <sup>*t*</sup>Bu<sub>2</sub>Sn(IV)<sup>2+</sup> complexes of -OH, or -OH and -COOH group(s) and aromatic {N} donor atom containing ligands were prepared by metathetical reactions. These complexes were characterized by FT-IR and Mössbauer spectroscopic methods. The single crystal X-ray diffraction analysis of di-*n*-butyl and di-*tert*-butyl-bis(quinolin-8-olato-*O*,*N*)-tin(IV) complexes showed that the tin centres are in *cis*octahedral environment. The experimental <sup>119</sup>Sn Mössbauer nuclear quadrupole splittings, (*A*) – according to the point charge model formalism – support the formation of trigonal bipyramidal (TBP) or octahedral (O<sub>h</sub>) molecular structures.

in solution, was investigated by pulsed-gradient spin-echo (PGSE) diffusion measurements and (<sup>1</sup>H, <sup>19</sup>F)-HOESY NMR spectroscopy. A high degree of ion-pairing was found in each complex. The HOESY spectra showed that the  $BF_4^-$  and  $PF_6^-$  anions take up selective positions, on the side of the complex remote from the benzyl groups, but close to the acetonitrile ligand, while the triflate is, partially, occupying a pseudo fifth coordination position on the side of the cation remote from the two benzyl-groups. The complexes 8 and 10 were used as catalyst precursors for the copolymerisation of styrene with carbon monoxide, producing syndiotactic copolymers, with the exception of complex 10a, that led to isotactic copolymers.

plexes (8) and (10), having  $CF_3SO_3^-$ ,  $BF_4^-$  and  $PF_6^-$  as catalyst  $r_4$  as counterions, were synthesised. The interionic structure of the methyl-acetonitrile complexes  $[Pd((R,S)-Bn-Box)(CH_3)(NCCH_3)]-(X)$  (8) as catalyst  $r_4$  as catalyst  $r_6$  as cat

### Markus Schwarz, Marc Vollmann, Rudolf Wartchow, Holger Butenschön

J. Organomet. Chem. 690 (2005) 2363

Synthesis and cyclic voltammetry of some new metal carbene substituted cyclopentadienyliron half sandwich complexes Cyclopentadienylcarbene iron half sandwich complexes were prepared. In addition to an X-ray structure analysis cyclic voltammetry measurements are reported.

# Rajsapan Jain, Andrew P.J. Brunskill, John B. Sheridan, Roger A. Lalancette

J. Organomet. Chem. 690 (2005) 2272

A planar silacyclobutane, 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane and its unusual reaction with bis(1,5-cyclooctadiene)platinum(0) An unusual planar silacyclobutane, 1,1-(*rac*-1,1'-bi-2-naphthoxy)-1-silacyclobutane, is reported. Its reaction with bis(1,5-cyclooctadiene)platinum(0) Pt(cod)<sub>2</sub> gave 1,1'-bi-2naphthol rather than the expected insertion products or polymer. Anionic ring-opening polymerization gave the corresponding poly(carbosilane).









### Delia B. Soria, Joanna Grundy, Martyn P. Coles, Peter B. Hitchcock

J. Organomet. Chem. 690 (2005) 2278

Stabilisation of high oxidation-state niobium using 'electron-rich' bicyclic-guanidinates

The electron-rich guanidinate anion, [hpp]<sup>-</sup> (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine), stabilizes niobium in the +5 oxidation-state. Structural characterization of Nb(hpp)Cl<sub>4</sub> reveals an exposed metal, corroborated by isolation of the MeCN adduct. Comparison of bond lengths with the bis-ligand compound, Nb(hpp)<sub>2</sub>Cl<sub>3</sub> suggests electron density at the metal influences distribution of  $\pi$ -electron density in the ligand.



### Francis Labrue, Bénédicte Pons, Louis Ricard, Angela Marinetti

J. Organomet. Chem. 690 (2005) 2285

Synthesis and X-ray crystal structure of [2-(phosphinomethyl)ferrocenyl]diphenylphosphine

The air-stable primary phosphine, which bears a 1,2-disubstituted ferrocene framework, has been prepared by reduction of the corresponding phosphonate. Despite its relative inertness, the primary phosphine displays a normal coordinative behaviour toward  $[(p-cymene)RuCl_2]_2$ .



J. Organomet. Chem. 690 (2005) 2291

l'-Carbopalladated-4-ferrocenyl-1,3-oxazolines as catalysts for Heck reactions: Further evidence in support of the Pd(0)/Pd(II) mechanism 1'-Carbopalladated complexes derived from 4-ferrocenyl-1,3-oxazolines behave as precatalysts for the Heck coupling of iodo- and bromoarenes with alkenes. The reaction proceeds through a Pd(0)/Pd(II) catalytic cycle. The release of Pd(0) from the palladacycle takes place by coupling with the olefin in a non-catalytic Heck reaction.



## Elza Nelkenbaum, Moshe Kapon, Moris S. Eisen

J. Organomet. Chem. 690 (2005) 2297

Retro-Brook rearrangement induces the formation of an octahedral nickel-(benzamidinate) complex; synthesis, structure and catalytic activity The  $\beta$ -diketiminate lithium salt [{(SiMe<sub>3</sub>)-NC(Ph)}<sub>2</sub>CH][Li] reacts with Ni(acac)<sub>2</sub>(TME-DA) forming the isomerized neutral octahedral complex (PhC(NSiMe<sub>3</sub>)NC(Ph)=CHSiMe<sub>3</sub>)-Ni(acac)(TMEDA) (7). Complex 7 activated by MAO was found to be active in the polymerization of norbornene, producing high molecular weight (Mw 630,000) polymers. Complex 7 was also found an active catalyst ( $\eta = 29,300$ ), in the presence of MAO (methyl-alumoxane), in either toluene or di-chloromethane, for the oligomerization of ethylene producing only dimers (86%) and trimers (14%).



### Contents

# Laurent Keller, Monica Vargas Sanchez, Damien Prim, François Couty, Gwilherm Evano, Jérome Marrot

J. Organomet. Chem. 690 (2005) 2306

Azetidines as ligands in the Pd(II) complexes series

Palladium (II) complexes bearing sterically congested azetidines as ligands have been prepared and characterized. Catalytic systems based on diamine, amino-imine and amino-imidate ligands have been tested in the Suzuki cross-coupling reaction.



### Murray V. Baker, Simon K. Brayshaw, Brian W. Skelton, Allan H. White, Charlotte C. Williams

J. Organomet. Chem. 690 (2005) 2312

Synthesis and structure of N-heterocyclic carbene complexes of rhodium and iridium derived from an imidazolium-linked cyclophane

In Rh and Ir complexes  $LM(diene)^+$  (L = a chelating bis(carbene) derived from an imidazolium-linked cyclophane), the M–L bonding is quite robust, but the diene may be displaced by CO to give  $LM(CO)_2^+$ . One or both CO groups in  $LM(CO)_2^+$  may be displaced by monodentate or bidentate phosphines, respectively.

Victor Wee Lin Ng, Seah Ling Kuan, Zhiqiang Weng, Weng Kee Leong, Jagadese J. Vittal, Lip Lin Koh, Geok Kheng Tan, Lai Yoong Goh

J. Organomet. Chem. 690 (2005) 2323

Reactivity of [CpCr(CO)<sub>3</sub>]<sub>2</sub> towards thione (C=S) moieties in some sulfur-containing substrates

 $[CpCr(CO)_3]_2$  reacts with (i) 2,5-dimercapto-1,3,4-thiadiazole, (ii) vinylene trithiocarbonate and (iii) isopropylxanthic disulfide to give the respective major products: (i) **2** and **5**, (ii) **4**, **6** and **7**, and (iii) **8**.

## Viatcheslav I. Sokolov, Rashid G. Gasanov, Lai Yoong Goh, Zhiqiang Weng, Anatoliy L. Chistyakov, Ivan V. Stankevich

J. Organomet. Chem. 690 (2005) 2333

(Cyclopentadienyl)chromiumtricarbonyl dimers as a source of metal-centered free-radicals to form stable  $\eta^2$ -bonded spin-adducts with fullerenes

Spin-adducts of C<sub>60</sub> and C<sub>70</sub> with metalcentered free radicals CpCr(CO)<sub>3</sub> have been generated in toluene via interaction between fullerenes and the metal-metal bonded dimeric complexes [CpCr(CO)<sub>3</sub>]<sub>2</sub> (Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>; Cp =  $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>). Their structures have been investigated using ESR spectroscopy and DFT-PBE calculations.







### Giuliano Alagona, Caterina Ghio

J. Organomet. Chem. 690 (2005) 2339

Alkyl-rhodium transition state stabilities as a tool to predict regio- and stereoselectivity in the hydroformylation of chiral substrates The hydroformylation reaction with H– Rh(CO)<sub>3</sub> was studied for three chiral olefins, employing different DFT methods/basis sets/ effective core potentials. Structural features of TS do not remarkably change with the computational description for each substrate. Relative stabilities of the lowest energy TS significantly differ for the ethereal substrate; conversely very small energy gaps are computed for both chiral alkenes. Use of B3P86/  $6-31G^*$ -LANL2DZ is recommended.



### Victor Barba, Julián Vázquez, Fernando López, Rosa Santillan, Norberto Farfán

J. Organomet. Chem. 690 (2005) 2351

Mono- and diboronates derived from tridentate ONO ligands and arylboronic acids The synthesis and characterization of eight monomeric boron complexes is described (A). In these compounds, the presence of donor or acceptor groups in the *para*-position of the B-phenyl group has an electronic effect on the CN moiety, which was determined by the linear correlation observed in a graph of <sup>1</sup>H NMR chemical shifts for the C(H)N group versus  $\sigma$  Hammett values. Furthermore, in the diboronates complexes like **B**, polarization on the CN moiety is increased.



### Simon A. Llewellyn, Malcolm L.H. Green, Andrew R. Cowley

J. Organomet. Chem. 690 (2005) 2358

Preparation and characterisation of cobalt (l) acyl compounds

The new cobalt (l) acyl compounds,  $[Co(PMe_3)(CO)_3(COMe)]$  1,  $[Co(PPhMe_2)-(CO)_3(COMe)]$  2,  $[Co(P(4-Me-C_6H_4)_3)(CO)_3-(COMe)]$  3 and  $[Co(P(4-F-C_6H_4)_3)(CO)_3-(COMe)]$  4, have been prepared from  $[Na(Co(CO)_4)]$ . The compound  $[Co(PCy_3)-(CO)_3(COMe)]$  5 has been prepared from  $[Co(PCy_3)(CO)_3(Me)]$  6. The crystal structures of 5 and 6 are reported.



## Frédéric Chérioux, Bruno Therrien, Saïd Sadki, Clément Comminges, Georg Süss-Fink

J. Organomet. Chem. 690 (2005) 2365

The dinuclear cations  $[Ru_2(\eta^6-p-Me-C_6H_4-i^Pr)_2(\mu_2-S-p-C_6H_4-Br)_3]^+$  and  $[Rh(\eta^5-C_5Me_5)-(\mu_2-S-p-C_6H_4-Br)_3]^+$  are found to undergo triple Suzuki coupling with 2- or 3-thiophene boronic acid to give  $[Ru_2(\eta^6-p-Me-C_6H_4-i^Pr)_2(\mu_2-S-p-C_6H_4-C_4H_3S)_3]^+$  and  $[Rh_2(\eta^5-C_5Me_3)_2(\mu_2-S-p-C_6H_4-C_4H_3S)_3]^+$ , respectively. The star-like complexes are potential precursors for the insertion of dinuclear organometallic entities in the main chain of conjugated molecules. The electrochemical and optical properties of these new complexes have been investigated.



## Maryam Mirza-Aghayan, Rabah Boukherroub, Mohammad Bolourtchian

J. Organomet. Chem. 690 (2005) 2372

Palladium-catalyzed protection of alcohols and cleavage of triethylsilyl ethers

Silvlethers are prepared in high yields by reaction of alcohols and different silanes in the presence of palladium (II) chloride catalyst at room temperature. Moreover, PdCl<sub>2</sub>/ Et<sub>3</sub>SiH system was found very efficient for the deprotection of triethylsilyl ethers in ethanol.

ROH cat. PdCl<sub>2</sub> Et<sub>3</sub>SiH RCH2-OSiEt3 cat. PdCl, Et,SiH, EtOH ROH

# Note

### Mauro Ravera, Rosaria D'Amato, Annalisa Guerri

J. Organomet. Chem. 690 (2005) 2376

Probing delocalisation across highly ethynylated mono and dinuclear Pt(II) tethers containing nitrogroups and organic models as redox active probes: X-ray crystal structure of trans-[Pt(C=C-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>- $(PPh_3)_2$ ]

Pt(II) organometallic and organic ethynylated compounds bearing nitro groups were synthesized and their electrochemical behaviour were investigated by cyclic voltammetry, revealing a chemical irreversibility for all the selected molecules.



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