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## Contents

### **Regular Papers**

### Régis M. Gauvin, C. Mazet, Jacky Kress

J. of Organomet. Chem. 658 (2002) 1

Solution structure and decomposition pathway of zwitterionic zirconium (IV) benzyl complexes

Two zwitterionic complexes of formula  $[Zr(ABA^n)(CH_2Ph)][(\eta^6-PhCH_2)B(C_6F_5)_3]$   $[ABA^n = N, N'$ -bis(trialkylsilyl)-2-amidobenzylamido] are described and their thermal decomposition into  $Zr(ABA^n)(C_6F_5)_2$  is analyzed.



### Sheng-Yong Yang, Xiang-Yuan Li, Yi-Zhi Huang

J. of Organomet. Chem. 658 (2002) 9

Electronic reason for the stabilization of osmabenzyne

Fragment orbital interaction analysis and density functional theory calculations have been employed to examine the effects of the chloride ligands *trans* and *cis* to the carbyne carbon and the silyl groups on the stabilization of osmabenzyne  $Os[=C-C(SiMe_3)=C(CH_3)-C(SiMe_3)=C$  H]Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.



# Aránzazu Carbayo, José V. Cuevas, Gabriel García-Herbosa

J. of Organomet. Chem. 658 (2002) 15

Intramolecular C–N bond formation in the reductive elimination of *ortho*-palladated arylhydrazones of acetophenone

Conversion of acetophenonephenylhydrazone into isoindolinone or N-phenylindazole can be achieved specifically in high yields and under mild conditions. The *ortho* palladated acetophenonephenylhydrazone dimeric complex shown in the scheme can be carbonylated to a mononuclear complex which undergoes reductive elimination giving C-N bond formation, spontaneously or under basic conditions.



# Rohan E.J. Beckwith, Nicola Heron, Nigel S. Simpkins

J. of Organomet. Chem. 658 (2002) 21

Chlorotrimethylsilane-mediated Michael addition reactions of chiral benzylic anions derived from  $\eta^6$ -chromiumtricarbonyl complexes

The Michael addition of chiral organolithiums, resulting from benzylic metallation of certain  $\eta^6$ -chromiumtricarbonyl complexes, to  $\alpha,\beta$ -unsaturated ketones and esters, is strongly influenced by the presence of chlorotrimethylsilane. In most cases yields of Michael adducts are greatly improved in the presence of Me<sub>3</sub>SiCl.



### Prakash C. Srivastava, Sangeeta Bajpai, Roli Lath, Chhabi Ram, Meena Srivastava, Smriti Bajpai, Ray J. Butcher, Michael Zimmer, Michael Veith

J. of Organomet. Chem. 658 (2002) 34

Synthesis, spectroscopic characterisation of 1,1,2,3,4,5,6-heptahydro-1,1-di(carboxyla-to)telluranes and 1,3-dihydro- $2\lambda^4$ -benzotellurole-2,2-diyl dicarboxylates Crystal structures of 1,1,2,3,4,5,6-heptahydro-1,1-di(benzoato)tellurane and 1,3-dihydro- $2\lambda^4$ -benzotellurole-2,2-diyl dibenzoate

# Manish Chandra, A.N. Sahay, Shaikh M. Mobin, Daya Shankar Pandey

J. of Organomet. Chem. 658 (2002) 43

Synthetic, spectral and structural aspects of some Rh(III) pentamethylcyclopentadiene complexes containing N,N'-donor bridging ligands

1,1,2,3,4,5,6-Heptahydro-1,1-di(carboxylato)telluranes and 1,3-dihydro- $2\lambda^4$ -benzotellurole-2,2-diyl dicarboxylates have been characterised by IR, (<sup>1</sup>H, <sup>13</sup>C, <sup>125</sup>Te)-NMR. UV, <sup>13</sup>C/<sup>125</sup>Te CP/MAS spectral data and thermogravimetric analysis. Te...O secondary bonds directed polymeric (*zig-zag chains*) associations are present in C<sub>5</sub>H<sub>10</sub>Te(OCOC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> whereas tetrameric (*stair like*) associations exist in C<sub>8</sub>H<sub>8</sub>Te(O-COC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.

Reactions of the chloro-bridged dimeric rhodium complex [{ $(\eta^5-C_5Me_5)Rh(\mu-Cl)-Cl$ }] with the bridging ligands pyridine-2carbaldehyde azine (paa), *p*-phenylenebis(picoline)-aldamine (pbp) or *p*-biphenylene-bis(picoline)aldamine (bbp) gave binuclear complexes [ $(\eta^5-C_5Me_5)ClRh(-\mu-L)-RhCl(\eta^5-C_5Me_5)$ ]<sup>2+</sup> (L = paa, pbp or bbp) in high yield. Structure of the representative binuclear complex [ $(\eta^5-C_5Me_5)ClRh(\mu-paa)RhCl(\eta^5-C_5Me_5)$ ](BF<sub>4</sub>)<sub>2</sub> has been confirmed by single crystal X-ray analysis.



### Daniel L. Reger, Kenneth J. Brown, Mark D. Smith

J. of Organomet. Chem. 658 (2002) 50

Rhenium tricarbonyl complexes of tris(pyrazolyl)methane ligands: first structural characterization of an isomer pair of tris(pyrazolyl)methane derivatives and the supramolecular structure of the homobimetallic complex  $\{1,4-C_6H_4[CH_2OCH_2C-(pz)_3]_2]Re(CO)_3]_2\}$  (Br)<sub>2</sub>

{[tris(pyrazolyl)meth-А series of ane]Re(CO)<sub>3</sub>}<sup>+</sup> complexes have been prepared. The solid state structures of the isomeric pair {[HC(3-i-Prpz)<sub>3</sub>]Re(CO)<sub>3</sub>}Br and {[HC(3-i-Prpz)<sub>2</sub>(5-i-Prpz)]Re(CO)<sub>3</sub>}Br have similar coordination environments about the metal. The structure of the bimetallic complex {1,4-C<sub>6</sub>H<sub>4</sub> [CH<sub>2</sub>OCH<sub>2</sub>C(pz)<sub>3</sub>]<sub>2</sub>[Re- $(CO)_{3}_{2}(Br)_{2}$  (see figure), which has two  $[Re(CO)_3]^+$  units linked by a bitopic ligand, is organized by  $\pi - \pi$  and (C)H··· $\pi$  interactions into a two-dimensional supramolecular network of two interpenetrating 'zigzag' chains.



### Leyong Wang, Wen-Hua Sun, Lingqin Han, Haijian Yang, Youliang Hu, Xianglin Jin

J. of Organomet. Chem. 658 (2002) 62

Late transition metal complexes bearing 2,9bis(imino)-1,10-phenanthrolinyl ligands: synthesis, characterization and their ethylene activity

### A series of iron, cobalt and nickel halide complexes, $LMX_2$ (M = Fe, X = Cl; M = Co, X = Cl; M = Ni, X = Br) bearing 2,9-bis(imino)-1,10-phenanthrolinyl ligands [L= 2,9-(ArNCH)<sub>2</sub>C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>] are synthesized. The solid-state structures of **4** and **7** have been determined by single-crystal X-ray diffraction. Treatment of the complexes $LMX_2$ with MAO leads to activate ethylene as oligomerization catalysts.



### K.K. Bhasin, Jaspreet Singh

J. of Organomet. Chem. 658 (2002) 71

A novel and convenient synthesis towards 2pyridylselenium compounds: X-ray crystal structure of 4,4'-dimethyl-2,2'-dipyridyl diselenide and tris(2-pyridylseleno)methane Various 2,2'-dipyridyl diselenides are synthesised by the reaction of diselenide anion, formed by reducing elemental selenium with 100% hydrazine hydrate in NaOH, with 2-bromopyridines. Hydrazine hydrate readily cleaves the selenium-selenium bond in these diselenides to generate 2-pyridylselenolate anion, which on quenching with halomethanes affords 2-pyridylseleno methanes. X-ray crystal structure of 4,4'-dimethyl-2,2'-dipyridyl diselenide (4) and tris(2-pyridylseleno)methane (13) is described.





# Paul K. Baker, Michael G.B. Drew, Deborah S. Moore

J. of Organomet. Chem. 658 (2002) 77

Reaction of  $[WI_2(CO)_3(NCMe)_2]$  with 3,3dimethyl-1-butyne in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave the new bis(alkyne) complex,  $[WI_2(CO)(NCMe)(\eta^2-HC_2Bu')_2]$ , 1, (see structure). The reactions of **1** with nitriles and phosphite ligands are also described. Three of the reaction products, namely [WI<sub>2</sub>(CO)(NCPh)( $\eta^2$ -HC<sub>2</sub>Bu<sup>t</sup>)<sub>2</sub>] and [WI<sub>2</sub>-(CO){P(OR)<sub>3</sub>}<sub>2</sub>( $\eta^2$ -HC<sub>2</sub>Bu<sup>t</sup>)] (R = Me and Et), have been crystallographically characterised. The cationic complexes, [WI(CO)-(NCMe){P(OR)<sub>3</sub>}<sub>2</sub>( $\eta^2$ -HC<sub>2</sub>Bu<sup>t</sup>)][BF<sub>4</sub>] (R = Me, Et and Pr<sup>i</sup>) have also been prepared. Detailed <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>13</sup>C-<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}-NMR studies are described which gave comprehensive structural information on these complexes in solution.



### Damon A. Brown, David M. Kimari, Anna M. Duzs-Moore, Theodore A. Budzichowski, Douglas M. Ho, Santosh K. Mandal

J. of Organomet. Chem. 658 (2002) 88

Reactions of dirhenium heptoxide with manganese(I) and rhenium(I) hydrido, alkoxo, methylcarbonato, carbonato-bridged, and methoxymethyl complexes. The X-ray structures of fac-(CO)<sub>3</sub>(dppp)MnOReO<sub>3</sub> and fac-(CO)<sub>3</sub>(dppp)ReOReO<sub>3</sub>  $Re_2O_7$  reacts with manganese(I) and rhenium(I) hydrido, alkoxo, and related complexes to yield the corresponding M(I)– Re(VII) complexes. The first X-ray crystal structure of a Mn(I)–Re(VII) complex has been determined.



### Aman Akkari-El Ahdab, Ghassoub Rima, Heinz Gornitzka, Jacques Barrau

J. of Organomet. Chem. 658 (2002) 94

Some aspects of chemistry of the N $\rightarrow$ Si chelated aryloxydihydrosilanes R(ArO)SiH<sub>2</sub> (R=Ph, ArO) and of the 2,2-diaryloxytrisilane (Me<sub>3</sub>Si)<sub>2</sub>Si(OAr)<sub>2</sub>{ArO=2,4,6-[(CH<sub>3</sub>)<sub>2</sub>-NCH<sub>2</sub>]<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O}

The aryloxydihydrosilanes  $R(ArO)SiH_2$ (R = Ph, ArO) were found to behave as very effective reducing agents and to be also potential precursors of stable silicenium ions, silanethiones and transition metal-silylene complexes. Irradiation at 254 nm or thermolysis of the 2,2-diaryloxytrisilane (Me<sub>3</sub>Si)<sub>2</sub>Si(OAr)<sub>2</sub> lead both to the formations of the transient silylenes (ArO)<sub>2</sub>Si and (Me<sub>3</sub>Si)(ArO)Si through two decomposition modes.



### Hidetake Seino, Chirima Arita, Masanobu Hidai, Yasushi Mizobe

J. of Organomet. Chem. 658 (2002) 106

Reactions of tetraphosphine complex  $[Mo\{meso - o - C_6H_4(PPhCH_2CH_2PPh_2)_2\}$ -  $(Ph_2PCH_2CH_2PPh_2)]$  with nitrile, CO, and isocyanide

A Mo complex containing a linear tetraphosphine meso-o-C<sub>6</sub>H<sub>4</sub>(PPhCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> as well as a diphosphine Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> has been converted into a series of nitrile, CO, and isocyanide complexes, in which the tetraphosphine ligand displays not only the  $\eta^4$ - but also  $\eta^3$ -and  $\eta^2$ -coordination modes.



### Kom-Bei Shiu, Jiun-Yu Chen, Gene-Hsiang Lee, Fen-Ling Liao, Bao-Tsan Ko, Yu Wang, Sue-Lein Wang, Chu-Chieh Lin

J. of Organomet. Chem. 658 (2002) 117

Syntheses and structures of some coordinatively saturated and unsaturated diruthenium carbonyl complexes Novel chemical transformation from  $[Ru_2(CO)_4(\mu$ -DPPM)\_2( $\mu$ -OAc)][PF<sub>6</sub>] (1) into coordinatively saturated  $[Ru_2(\mu$ -CO)\_2( $\mu$ -DPPM)\_2(MeCN)\_4][BF\_4]\_2 (2) is shown. Upon addition of a uni-negative anion X<sup>-</sup> to 2, a series of unsaturated adducts  $[Ru_2(\mu$ -CO)\_2( $\mu$ -DPPM)\_2X\_2] (X<sup>-</sup> = Cl<sup>-</sup>, 3a; Br<sup>-</sup>, 3b; I<sup>-</sup>, 3c; SH<sup>-</sup>, 3d; Stol<sup>-</sup>, 3e; S<sup>i</sup>Pr<sup>-</sup>, 3f) were readily formed. The rich chemistry of these adducts is described.



### Gabriela A. Grasa, Zakhia Moore, Kenneth L. Martin, Edwin D. Stevens, Steven P. Nolan, Valérie Paquet, Hélène Lebel

J. of Organomet. Chem. 658 (2002) 126

Structural characterization and catalytic activity of the rhodium–carbene complex  $Rh(PPh_3)_2(IMes)Cl$  (IMes = bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene)

The rhodium N-heterocyclic carbene complex  $Rh(PPh_3)_2(IMes)Cl(2)$  is an active catalyst for the hydroboration of simple olefins at room temperature. The catalytic activity of **2** was also tested in the methylenation of aldehydes. The crystal structure of **2** is also reported.



### Bradley M. Kraft, William D. Jones

J. of Organomet. Chem. 658 (2002) 132

Carbon-fluorine bond activation of perfluorinated arenes with  $Cp^*_2ZrH_2$  Reaction of  $Cp*_2ZrH_2$  with fluorinated aromatics leads to several products in which C-F bond cleavage has occurred. The nature of these products and the mechanism(s) of their formation are discussed.



### Kenneth K. Laali, Gerald F. Koser, Songping D. Huang, Mahinda Gangoda

J. of Organomet. Chem. 658 (2002) 141

1-Triflato-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane and 1,3-bis-triflato-5,7-dimethyl-1,3,5,7-tetrasilaadamantane; synthesis, complexation study and X-ray structure of 1hydroxy-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane The hitherto unknown mono- and bis-triflates have been synthesized chemoselectively and in high yields from 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane by reaction with ICl-AgOTf at room temperature Lewis acid complexation studies with the mono-triflate and the X-ray structure of 1hydroxy-1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane are reported.

### Victoria A. Ershova, Anatoly V. Golovin, Vladimir M. Pogrebnyak

J. of Organomet. Chem. 658 (2002) 147

Catalytic isomerization of N-allylic substrates with chiral Os<sub>3</sub> clusters as potentially enantioselective reaction The proposed reaction mechanism for the *N*-allylic substrates isomerization catalysed by chiral clusters  $(\mu$ -H)Os<sub>3</sub> $(\mu$ -OCNR<sup>1</sup>R<sup>2</sup>)-(CO)<sub>10</sub> at ambient temperature involves the alkene insertion into the Os-O bond and suggests that both bridging ligands of the cluster molecule maintain their certain positions through the whole catalytic cycle. This catalytic reaction is perspective for its development as an enantioselective process.



### Jianhua Cheng, Dongmei Cui, Wenqi Chen, Tao Tang, Baotong Huang

J. of Organomet. Chem. 658 (2002) 153

Syntheses and crystal structures of bis(tetrahydrofurfurylindenyl) lanthanocene chlorides  $(C_4H_7OCH_2C_9H_6)_2LnCl$  (Ln = Nd, Sm, Dy, Ho, Er, Yb) A series of bis(tetrahydrofurfurylindenyl) lanthanocene chloride complexes  $(C_4H_7OCH_2C_9H_6)_2LnCl$  (Ln = Nd(1), Sm (2), Dy (3), Ho (4), Er (5), Yb (6)) were synthesized. The X-ray crystallographic structures of all the six complexes were determined with the same structure. These crystals can be exposure to air for long time before decomposition.



### Yew Chin Neo, Jeremy Shu Lip Yeo, Pauline Meng Neo Low, Sheau Wei Chien, Thomas C.W. Mak, Jagadese J. Vittal, T.S. Andy Hor

J. of Organomet. Chem. 658 (2002) 159

Isolation and structural characterization of some stable Pd(II) carboxylate complexes supported by 1,1'-bis(diphenylphosphino) ferrocene (dppf) A series of Pd(II) dppf carboxylates were isolated and crystallographically characterized. The complexes vary significantly in stability, those of less basic carboxylates being more resistive to reductive decomposition.



### Ashok K.S. Chauhan, Arun Kumar, Ramesh C. Srivastava, Ray J. Butcher

J. of Organomet. Chem. 658 (2002) 169

Synthesis and characterization of monomeric diorganotellurium dihalides: crystal and molecular structures of diphenacyltellurium dibromide and -diiodide Diphenacyltellurium dibromide is prepared by heating elemental tellurium with phenacyl bromide. Metathesis of the dibromide with KI affords the corresponding diiodide. The primary geometry about the Te atom in both the compounds is  $\varphi$ -trigonal-bipyramidal with axial halogens. Weak intramolecular coordination of both the carbonyl groups is indicated by IR spectra as well as X-ray crystal structures and the resulting 14–Te–6 system is devoid of any intermolecular Te···X secondary interactions.



### Nihal Zengin, Cemal Kaya

J. of Organomet. Chem. 658 (2002) 176

A new method for calculating the COfactored force constants of pentacarbonyliron

The paper presented an analytical approach to solving the CO-factored force fields of pentacarbonyliron. This approach led to the relations  $k_1 = (\lambda_1 + \lambda_2 + 4\lambda_3 - \beta)/(6\mu)$ ,  $k_2 = (\lambda_1 + \lambda_2 + 2\lambda_4 + \beta)/(4\mu)$ ,  $k_1 = (\lambda_1 + \lambda_2 - 2\lambda_4 + \beta)/(4\mu)$ ,  $k_c = (\lambda_1 + \lambda_2 - 2\lambda_3 - \beta)/(6\mu)$ 

# $[(\lambda_1 - \lambda_2)\sqrt{(\lambda_1\lambda_2)}]/[\sqrt{6\mu(\lambda_1 + \lambda_2)}]$ where $\beta = (\lambda_1 - \lambda_2)^2/(\lambda_1 + \lambda_2)$ ; $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ are the $\lambda$ parameters of $a'_1, e'$ and $a''_2$ modes, respectively. The force constants calculated from these relations were compared with those obtained by other methods and employed to predict C–O stretching frequencies of isotopically enriched species of pentacarbonyliron. The results obtained indicated that the analytical approach presented leads to a valid solution to the secular equations for pentacarbonyliron.



### $\beta = (\lambda_1 - \lambda_2)^2 / (\lambda_1 + \lambda_2)$

### William Henderson, Steven R. Alley

J. of Organomet. Chem. 658 (2002) 181

Ferrocenyl hydroxymethylphosphines ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P(CH<sub>2</sub>OH)<sub>2</sub>] and 1,1'-[Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P(CH<sub>2</sub>OH)<sub>2</sub>}] and their chalcogenide derivatives

The ferrocenyl hydroxymethylphosphines FcP(CH<sub>2</sub>OH)<sub>2</sub> [Fc =  $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe $(\eta^5$ -C<sub>5</sub>H<sub>4</sub>)] and 1,1'-Fc'[P(CH<sub>2</sub>OH)<sub>2</sub>]<sub>2</sub> [Fc' = Fe $(\eta^5$ -C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] were synthesised by reactions of the primary phosphines FcPH<sub>2</sub> and 1,1'-Fc'(PH<sub>2</sub>)<sub>2</sub> with excess formaldehyde. Oxide, sulfide and selenide derivatives of these phosphines were also prepared. Crystal structure determinations on FcP(CH<sub>2</sub>OH)<sub>2</sub>, FcP(O)(CH<sub>2</sub>OH)<sub>2</sub> and FcP(S)(CH<sub>2</sub>OH)<sub>2</sub> were carried out in order to investigate hydrogen-bonding patterns in these substances.





### Kuang-Hway Yih, Gene-Hsiang Lee, Shou-Ling Huang, Yu Wang

J. of Organomet. Chem. 658 (2002) 191

Synthesis, reactivity and structures of diethyldithiophosphate molybdenum complexes: crystal structures of  $[Mo\{\eta^2-S_2P(OEt_2)\}_2(PhC\equiv CPh)_2]$  and  $[Mo(\eta^3-C_3H_5)\{\eta^1-S_2P(OEt_2)\}(Phen)(CO)_2]$ 

The reaction of  $[Mo(CH_3CN)(\eta^3-C_3H_5)-(CO)_2\{\eta^2-S_2P(OEt_2)\}]$  (1) with diphenylacetylene in refluxing dichloromethane afforded the bis(diphenylacetylene) complex  $[Mo\{\eta^2-S_2P(OEt_2)\}_2(PhC=CPh)_2]$  (2). Complex  $[Mo(\eta^3-C_3H_3)\{\eta^1-S_2P(OEt_2)\}(Phen)-(CO)_2]$  (4) was synthsized by the reaction of 1 and phenanthroline. The single crystal structures of 2 and 4 have been determined by X-ray diffraction analyses.



### Liang-Fu Tang, Wen-Li Jia, Xue-Mei Zhao, Pan Yang, Ji-Tao Wang

J. of Organomet. Chem. 658 (2002) 198

Synthesis of bis(pyrazol-1-yl)methanes with organogermyl and organosilyl groups on the methine carbon and their reaction with  $W(CO)_5(THF)$ . X-ray crystal structures of Ph<sub>3</sub>GeCHPz<sub>2</sub>W(CO)<sub>4</sub> and Me<sub>3</sub>SiCHPz<sub>2</sub>W-(CO)<sub>4</sub> (Pz = 3,5-dimethylpyrazole)

A series of new bis(pyrazol-1-yl)methane ligands with organogermyl and organosilyl groups on the methine carbon have been synthsized by reaction of bis(pyrazol-1yl)methyllithium with triphenylgermanium bromide and organosilyl chloride. Treatment of these ligands with W(CO)<sub>5</sub>(THF) resulted in new heterobimetallic complexes.



# Sergei N. Konchenko, Nikolai A. Pushkarevsky, Manfred Scheer

J. of Organomet. Chem. 658 (2002) 204

Synthesis and structure of the novel mixed Sb/Se and Sb/Te containing iron carbonyl clusters [Fe<sub>3</sub>( $\mu_3$ -Y)( $\mu_3$ -SbMes)(CO)<sub>9</sub>] (Y = Se, Te) and [Fe<sub>3</sub>( $\mu_3$ , $\eta^2$ : $\eta^1$ -SeSbMes)( $\mu_3$ -SbMes)(CO)<sub>10</sub>]

The reaction between the cluster dianion  $[Fe_3(\mu_3-Y)(CO)_9]^{2-}$  (1) (Y = Se (a), Te (b)) and MesSbBr<sub>2</sub> leads to the formation of *nido* clusters  $[Fe_3(\mu_3-Y)(\mu_3-SbMes)(CO)_9]$  (2a,b). The novel compound  $[Fe_3(\mu_3,\eta^2:\eta^1-SeSbMes)(\mu_3-SbMes)(CO)_{10}]$  (3) was obtained by a similar reaction by slightly modified reaction conditions. This molecule contains a so far unknown  $\mu_3, \eta^2: \eta^1-SeSbR$  ligand.



### Rolfe H. Herber, Israel Nowik, Masahiko Iyoda

J. of Organomet. Chem. 658 (2002) 210

Cofacial interaction of ferrocenyl groups and metal atom motional anisotropy in [10]annulene organometallics Two structurally related diferrocenyl-methano[10]annulenes have been examined by temperature-dependent <sup>57</sup>Fe Mössbauer effect spectroscopy. The anisotropy of the Tdependent metal atom motion is taken to be diagnostic of the cofacial interaction of two of the cyclopentadienyl rings in the 2,10-diferrocenyl complex.



### Ruitao Wang, Jie Sun, Jiabi Chen, Qiang Xu, Yoshie Souma

J. of Organomet. Chem. 658 (2002) 214

Unusual reactions of cationic bridging carbyne complexes of dimethylsilane-bridged bis( $\eta^5$ -cyclopentadienyl)diiron tricarbonyl with carbonylmetal anions

The reactions of the dimethylsilane-bridged cationic carbyne complexes of diiron,  $[Fe_2(\mu-CO)(\mu-CAr)(CO)_2\{\eta^5-C_5H_4\}_2Si (CH_3)_2$ ]BBr<sub>4</sub> with Na[M(CO)<sub>n</sub>CN] (M = Cr, Mo, W) give diiron bridging carbene complexes (9-14) or novel cationic bridging carbyne complexes (15-17). The latter reacts with NaSR to give bridging mercaptocarbene complexes. The novel benzonitrilecoordinated diiron complex and bridging arylcarbene complexes were also obtained from respective reactions of cationic carbyne complexes with NaN(SiMe<sub>3</sub>)<sub>2</sub> and Na[Fe(CO)<sub>4</sub>CN] [(Ph<sub>3</sub>P)<sub>2</sub>N][Cror (CO)<sub>4</sub>NO].

Two instances of the influence of organoelement substituent on the reactivity of radicals generated from  $R_3MCH_2CH=CH_2$ (M = Si or Sn) in photoinduced interaction with (Me\_3Si)\_2NBr have been considered. Depending on the element atom, the reaction proceeds either via hydrogen atom abstraction or recombination.





### Marc B. Taraban, Alexander I. Kruppa, Nikolai E. Polyakov, Mikhail G. Voronkov, Vladimir I. Rakhlin, Stanislav V. Grigor'ev, Olga S. Volkova, Rudolph G. Mirskov, Tatyana V. Leshina

J. of Organomet. Chem. 658 (2002) 228

Spin chemistry of organometallic compounds 2. Interaction of *N*-bromohexamethyldisilazane with allyltriorganolsilanes

### Michal Horáček, Petr Štěpnička, Jiří Kubišta, Róbert Gyepes, Ivana Císařová, Lidmila Petrusová, Karel Mach

J. of Organomet. Chem. 658 (2002) 235

Synthesis and crystal structures of  $\mu$ -1,3bis( $\eta^{5}$ -tetramethylcyclopentadienyl)-1,1,3,3tetramethyldisiloxane)[ $\eta^{2}$ -bis(trimethylsilyl)ethyne]titanium(II) and a doubly tucked-in product of its thermolysis Reduction of  $[\text{TiCl}_2\{\eta^5:\eta^5-(C_5\text{Me}_4\text{Si-Me}_2)_2\text{O}\}]$  (1) with magnesium in the presence of Me\_3SiC=CSiMe\_3 affords the *ansa*-[Ti $\{\eta^5:\eta^5-(C_5\text{Me}_4\text{SiMe}_2)_2\text{O}\}(\eta^2-\text{Me}_3\text{SiC}=C\text{SiMe}_3)]$  (2) complex in high yield. Compound 2 decomposes at 170 °C in high vacuum with liberation of 1,2-bis(trimethylsi-lyl)ethene to give predominantly asymmetric, allydiene complex *ansa*-[Ti $\{(\eta^5-C_5\text{Me}_4)\text{SiMe}_2\text{OSiMe}_2\{\eta^3:\eta^4-C_5\text{Me}_2(\text{CH}_2)_2\}]$  (3).



### Bernhard J. Rausch, Rolf Gleiter, Frank Rominger

J. of Organomet. Chem. 658 (2002) 242

Synthesis and cyclic voltammetry of 1,2,3trisubstituted bis(cyclopentadienyl)zirconium dichlorides The synthesis of the 1,2,3-trisubstituted cyclopentadienes 3-10 and their corresponding zirconocene dichlorides 11-18 from commercially available internal alkynes is presented. Cyclic voltammetry was used to measure the effect of various substituents at the five-membered ligand on the Lewis acidity of the zirconium central atom.



### Christophe M. Thomas, Bruno Therrien, Antonia Neels, Helen Stæckli-Evans, Georg Süss-Fink

J. of Organomet. Chem. 658 (2002) 251

New benzotriazole derivatives as multifunctional ligands Condensation of hydroximethylbenzotriazole with carboxylic acid derivatives of pyridine, triphenylphosphine, ferrocene and thiophene provides an easy access to multifunctional ligands containing the benzotriazol unit. Mono and dinuclear complexes of these ligands have been synthesized and characterized by X-ray crystallography.



### Helmut G. Alt, Rainer Ernst, Ingrid K. Böhmer

J. of Organomet. Chem. 658 (2002) 259

Dinuclear ansa zirconocene complexes containing a sandwich and a half-sandwich moiety as catalysts for the polymerization of ethylene Dinuclear zirconium complexes containing an ansa metallocene and a half-sandwich moiety can be activated with methylalumoxane (MAO) and then be applied as homogeneous and heterogeneous catalysts for ethylene polymerization to give bimodal molecular weight distributions. Such resins cannot be produced by mixing the corresponding mononuclear species.



### Martin Herker, Frank H. Köhler, Markus Schwaiger, Bernd Weber

J. of Organomet. Chem. 658 (2002) 266

Two nickelocenes and ferrocene in a rigid *cis/trans* chain

The trimetallic bridged metallocene **6** was synthesized by first assembling the nickelocene and then the ferrocene moieties. Crystal structure analysis and paramagnetic <sup>1</sup>H-, <sup>13</sup>C-, and <sup>29</sup>Si-NMR spectroscopy establish a *cis/trans* chain. The two unpaired electrons per nickelocene are delocalized partly into the ferrocene moiety. Delocalization on the *cis* side of **6** is less efficient than on the *trans* side.



### Ferda Kozanoglu, Saltuk Saldamli, Saim Özkar

J. of Organomet. Chem. 658 (2002) 274

Substitution kinetics of  $Cr(CO)_5(\eta^2-Z-cy-clooctene)$  with tetracyanoethylene

The Z-cyclooctene (zco) ligand in  $Cr(CO)_5(\eta^2$ -zco) is replaced by tetracyanoethylene (tcne) at an observable rate in the temperature range between -5 and  $+10^{\circ}C$  yielding the complex  $Cr(CO)_5(\eta^2$ -tcne) as the final product. The kinetics of this substitution reaction were studied in toluene

solution containing 5% by volume zco by quantitative FT-IR spectroscopy. The substitution reation obeys a pseudo-first order kinetics with respect to the concentration of the starting complex and the rate-determining step is the cleavage of metal-olefin bond in the complex  $Cr(CO)_5(\eta^2$ -zco). The large positive value of the activation entropy is consistent with the dissociative nature of reation. The large value of the activation enthalpy, close to the chromium-olefin bond dissociative rate-determining step of the substitution reation.

 $Cr(CO)_{5}(\eta^{2}-zco)$   $k_{-1} / +zco / k_{1} / -zco$   $Cr(CO)_{5}(solvent)$   $k_{2} / +tcne$   $Cr(CO)_{5}(\eta^{2}-tcne)$ 

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