

Available online at www.sciencedirect.com



Volume 687, Issue 1, 1 December 2003



www.elsevier.com/locate/jorganchem

Contents

Regular Papers

Alan R. Bassindale, Zhihua Liu, David J. Parker, Peter G. Taylor, Peter N. Horton, Michael B. Hursthouse, Mark E. Light

J. Organomet. Chem. 687 (2003) 1

The reactions of dialkyl and diarylethoxysilanes with T_6 silsesquioxane cages X-ray crystallographic studies of the mono- T_6D_1 and bis- T_6D_2 insertion ring expansion products We have successfully performed ring-expanding insertion reactions of T₆ silsesquioxane cages using dialkyl and diarylethoxysilanes. The reaction of hexacyclohexylsilsesquioxane (T₆) with dialkyl and diaryldiethoxysilanes gives predominantly a T₆D₂ bis-insertion compound, while the reaction of T₆ with dimethylethoxysilane gives one mono-insertion T_6D_1 and various T_6D_2 bis-insertion compounds as isolable components whose structures we have characterised by X-ray crystallography.



Yanjun Li, Tatsuro Kijima, Taeko Izumi

J. Organomet. Chem. 687 (2003) 12

Ruthenium-catalyzed carbon-carbon formation to synthesize tetraarylethanes and tetraarylxylylene through dechlorinative dimeric reaction Dechlorinative coupling-dimerization reactions using tris-triphenylphosphine ruthenium (II) in the presence of hydrogen atmosphere were investigated. Dechlorinations of α -chlorodiarylmethanes and 1,3-dichlorobenzylbenzene were carried out to provide corresponding alkanes in high yields, which were observed to be an efficient novel route to synthesize 1,1,2,2-tetraarylethanes and 1,2,9,10-tetraphenyl-di-*m*-xylylene.



Yu-Fun Tzeng, Chih-Yu Wu, Wen-Shu Hwang, Chen-Hsiung Hung

J. Organomet. Chem. 687 (2003) 16

Reactions of *N*-(2-thienylmethylidene)-2thienylmethylamine derivatives with diiron nonacarbonyl: characterization and structures of cyclometallated diiron complexes $Fe_2(CO)_6(R-C_4HS-CH_2NCH_2-C_4H_3S)$ and linear tetrairon clusters $Fe_4(CO)_{10}(R-C_4HS-CH=NCH_2-C_4H_3S)_2$ The reaction of ligand **1** with Fe₂(CO)₉ yields products **2**, **3**, and **4**. **2** is a cyclometallated complex, in which the organic ligand is (μ - η^1 : η^2 -thienyl β -C, α , β -C=C; η^1 : η^1 -(N))-coordinated to the diiron center. **3** and **4** are novel linear tetrairon complex isomers, in which the two organic ligands are (μ - η^1 -thienyl β -C: η^1 -N; η^2 -thienyl α , β -C=C: η^2 -C=N)-coordinated to two diiron centers, respectively.



Lan-Young Hong, Feng Cao, Dong-Jin Kim, Hee-Gweon Woo, Bo-Hye Kim, Myong-Shik Cho, Xiao-Dong Li, Dong-Pyo Kim

J. Organomet. Chem. 687 (2003) 27

Effect of polyborazine additive on thermolysis of polyphenylsilane and polyvinylsilane To improve the ceramic residue yields and processabilities of polyphenylsilane (PPS) and polyvinylsilane (PVS), polyborazine (PBN) was employed as an additive. The enhanced properties were attributed to an increased molecular weight. Spectral analysis suggested that dehydrocoupling of SiH_3 in PVS and Si-H in PPS by PBN was responsible for the improved ceramic yields.



Yoshito Takeuchi, László Párkányi, Alajos Kálmán, Miki Nishikawa, Katsumi Tanaka, Wasuke Mori, Masashi Kinoshita

J. Organomet. Chem. 687 (2003) 33

X-ray crystallographic study of some pentacoordinated organogermanium compounds The pentacoordination in 2-substituted-5oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid is due to the presence of -S-C-C-Omoiety rather than that of $-SCH_2COOH$ since not only their pyridinium salts but also $-SCH_2CH_2OH$ derivative also exhibit pentacoordination.

Janine Chantson, Helmar Görls, Simon Lotz

J. Organomet. Chem. 687 (2003) 39

Insertion of Pt into C–H and C–S bonds of thiophene derivatives. The X-ray crystal structure of a thiaplatinacycle of 3,6-dimethylthieno[3,2-*b*]thiophene

Both C–S and C–H activation have been observed upon treating 2,2'-bithiophene and 1-methyl-2-(2-thienyl)pyrrole with [Pt (PEt₃)₄]; the products being six-membered thiaplatinacycles and hydride complexes of the type *trans*-[PtH(PEt₃)₂(2-thienyl)]. The X-ray crystal structure of the thiaplatinacycle derived from 3,6-dimethylthieno[3,2-b]thiophene is presented.



R = 2-(1-methylpyrrolyl) or 2-thienyl

Et₂F

P.R. Deacon, N. Devylder, M.S. Hill, M.F. Mahon, K.C. Molloy, G.J. Price

J. Organomet. Chem. 687 (2003) 46

Organotin compounds bearing mesogenic sidechains: synthesis, X-ray structures and polymerisation chemistry

Light-sensitive poly-(diorganostannanes) containing mesogenic side-chains $\{R[C_6H_5C_6H_4O(CH_2)_5]Sn\}_m$ can be synthesised Wurtz coupling of by $RBr_2Sn(CH_2)_5OC_6H_4C_6H_5 \quad (R=Ph,$ Bu) but not from PhBr₂Sn(CH₂)₃OC₆H₄C₆H₅ which contains a chelating ether functionality.

 $\begin{array}{l} \mathsf{PhC}_{6}\mathsf{H}_{4}\mathsf{O}(\mathsf{CH}_{2})_{5}\mathsf{Sn}(\mathsf{R})\mathsf{X}_{2}\\ \mathsf{Na} \ / \ 15\text{-}\mathsf{crown}\text{-}5 \\ | \mathsf{toluene} \ / \ \mathsf{dark}\\ [\mathsf{PhC}_{6}\mathsf{H}_{4}\mathsf{O}(\mathsf{CH}_{2})_{5}\mathsf{Sn}(\mathsf{R})]_{\mathsf{n}}\\ \mathsf{R} = \mathsf{Ph}, \mathsf{Bu} \end{array}$

Pedro M.F.J. CostaMárcia MoraMaria José CalhordaVitor FélixPaula FerreiraMichael G.B. DrewHubert Wadepohl

J. Organomet. Chem. 687 (2003) 57

Mono- and binuclear bipyridyl derivatives of the $Mo(\eta^3-C_3H_5)(CO)_2$ fragment: structural studies and fluxionality in solution

Several mono- and binuclear bipyridyl complexes of the $Mo(\eta^3-C_3H_5)(CO)_2$ fragment were prepared and most of them structurally characterized. One of the two isomers shown here for 4,4'-Me₂-2,2'-bpy and NCMe or Br ligands is observed in the crystal structures. An arrangement with open channels is found for the binuclear derivative of 2,2'-bpy with a 4,4'-bpy bridge.



Fabrice LacroixChristine E. PlecnikShengming LiuFu-Chen LiuEdward A. MeyersSheldon G. Shore

J. Organomet. Chem. 687 (2003) 69

Cyclic organohydroborate complexes of metallocenes

 $VIII. Triphenylsiloxy derivatives of Group IV organometallic systems, Cp_2M(OSiPh_3)X (M = Ti, Zr, Hf; X = Cl, {(\mu-H)_2BC_8H_{14}})$

Model complexes of silica supported Group IV organometallic systems that are based on the triphenylsilanolate ligand, $[OSiPh_3]^-$, were prepared and structurally characterized. The zirconocene and hafnocene cyclic organohydroborates $Cp_2M(O-SiPh_3)\{(\mu-H)_2BC_8H_{14}\}$ are accessible through the chloride precursors $Cp_2MCl(O-SiPh_3)$. The analogous titanocene organohydroborate cannot be synthesized because reduction produces $[Cp_2Ti(\mu-Cl)_2TiCp_2]$.



Moonhyun Oh, Jeffrey A. Reingold, Gene B. Carpenter, Dwight A. Sweigart

J. Organomet. Chem. 687 (2003) 78

Hydrogen-bonded networks from $\eta^5\mbox{-semi-}$ quinone complexes of manganese tricarbonyl

Cationic $(\eta^6 - hydroquinone)Mn(CO)_3^+$ complexes are readily deprotonated to semiquinone and quinone analogues. The neutral $(\eta^5$ -semiquinone)Mn(CO)₃ complexes form supramolecular hydrogen bonded networks with geometries dictated by substituents on the semiquinone ring.



Manda Ćurić, Darko Babić, Željko Marinić, Ljiljana Paša-Tolić, Vjera Butković, Janez Plavec, Ljerka Tušek-Božić

J. Organomet. Chem. 687 (2003) 85

Synthesis and characterisation of Pd(II) complexes with a derivative of aminoazobenzene

Dynamic ¹H-NMR study of cyclopalladation reactions in DMF

Three new complexes of aminoazobenzene ligand **L** with Pd(II), labelled as **A**, **B**, and **C**, were synthesized and characterized. In DMF adducts **A** and **B** undergo spontaneous rearrangement into the cyclopalladated complex **C**. Dynamic ¹H-NMR studies of complexes **A** and **B** as well as the reactions of **L** with PdCl₂ and Na₂PdCl₄ in DMF explained the formation mechanism of all involved species, including cyclopalladated complex **C**.



Heiko Hartmann, Biprajit Sarkar, Wolfgang Kaim, Jan Fiedler

J. Organomet. Chem. 687 (2003) 100

Electron transfer reactions of $(C_5R_5)_2(CO)_2Ti$ (R = H or Me) with TCNE or TCNO

TCNE and TCNO react with $(C_5R_5)_2(CO)_2Ti$ to yield (C₅R₅)₂(CO)Ti(TCNX) of which the soluble species (R = Me) were characterized also in the oxidized and reduced forms through cyclic voltammetry, EPR, IR and UV-vis spectroelectrochemistry. For the neutral $(C_5R_5)_2(CO)Ti^{2+q}(TCNX^{-q})$ complexes the results support a rather large amount of charge transfer 1 < q < 2 from the metal to the acceptors TCNX.



Bernd Wrackmeyer, Elena V. Klimkina, Wolfgang Milius, Yuri N. Bubnov

J. Organomet. Chem. 687 (2003) 108

Reactivity of 1-boraadamantanes towards bis(trialkylstannyl)ethynes. First examples of 3-boratricyclo[5.3.1.1^{3,9}]dodecanes, and the molecular structure of a tetraalkyldiboroxane

1-Boraadamantane reacts with bis(trialkylstannyl)ethynes, $R_3Sn-C=C-SnR_3$ with R = Me, Et, in a 1:1 molar ratio by 1,1-organoboration under very mild conditions to give the 4-methylene-3-borahomoadamantane derivatives, respectively, which are dynamic at room temperature with respect to deorganoboration. These compounds react further by 1,1-organoboration to tricyclic butadiene derivatives. Hydrolysis gave a new diboroxane which was characterised by X-ray structural analysis.



Oana Bumbu, Anca Silvestru, Cristian Silvestru, John E. Drake, Michael B. Hursthouse, Mark E. Light

J. Organomet. Chem. 687 (2003) 118

Phenylmercury(II) derivatives of tetraorganodichalcogenoimidodiphosphorus acids. Crystal and molecular structure of [PhHg{(OPR₂)(SPPh₂)N}]₂ (R = Me, Ph)

New PhHg[(XPR₂)(YPR₂)N] derivatives were prepared and were characterized by IR and multinuclear NMR spectroscopy and mass spectrometry. The molecular

Markus Enders, Pablo Fernández, Shahram Mihan, Hans Pritzkow

J. Organomet. Chem. 687 (2003) 125

Quinolyl-functionalised Cp-chromium polymerisation catalysts: synthesis and crystal structures of alkylation products structure of PhHg[(OPR₂)(SPPh₂)N] [R = Me (1), Ph (2)] was investigated by X-ray diffraction. Both compounds exhibit dimer associations in the crystal through *S*,*O*-bridging organophosphorus ligands, resulting in 12-membered inorganic rings of different conformation which brings different additional chalcogen atoms in the proximity of the metal atom. Weak transannular Hg···O (2.754 Å) are established in 1, leading to a tricyclic ladder structure with a planar central Hg₂O₂ ring. The CHgSO coordination core has a distorted T-shaped arrangement, with the sulfur atom *trans* to the aromatic carbon.

The quinolyl-functionalised Cp-chromium(III) complexes 1 and 2, which serve as precursors for highly active olefin polymerisation catalysts, were alkylated with benzylmagnesium chloride





Matthias Seibert, Kurt Merzweiler, Christoph Wagner, Horst Weichmann

J. Organomet. Chem. 687 (2003) 131

Ligand behaviour of P-functionally substituted organotin halides: palladium(II) and platinum(II) complexes with $Ph_2PCH_2CH_2$ SnCl₃

The P-functional organotin chloride $Ph_2PCH_2CH_2SnCl_3$ reacts with [(COD) MCl_2] and *trans*-[(Et_2S)_2MCl_2] (M = Pd, Pt) in molar ratio 1:1 to the zwitterionic complexes [(COD)M⁺(Cl)(PPh_2CH_2CH_2Sn⁻Cl_4)] (1: M = Pd; 2: M = Pt) and *trans*-[(Et_2S)_2M⁺(Cl)(PPh_2CH_2CH_2Sn⁻Cl_4)] (3: M = Pd; 4: M = Pt).



21

Andrea I. Licht, Helmut G. Alt

J. Organomet. Chem. 687 (2003) 142

Umsetzungen von ω -alkenylsubstituierten Zirconocendichloridkomplexen mit n-Alkyllithiumverbindungen in Gegenwart von Alkenen bzw. Alkinen

Die Umsetzung von ω -alkenylsubstituierten Zirconocendichloridkomplexen mit zwei Äquivalenten *n*-Butyllithium erfährt einen entscheidenden Einfluss in Gegenwart von Alkenen bzw. Alkinen. Es werden metallacyclische Zirconocenkomplexe mit neuarti-

Michael Stollenz, Manfred Rudolph, Helmar Görls, Dirk Walther

J. Organomet. Chem. 687 (2003) 153

Nickel(II) complexes of the type [RM(ox-am)MR] (oxam: oxalamidinate, R = n-butyl, n-hexyl): the first binuclear n-alkyl nickel complexes

gen Strukturen erhalten, wobei die zugesetzten Alkene bzw. Alkine mit den ω-Alkenylsubstituenten und dem intermediär entstehenden 1-Buten um den Einbau in die entstehende, metallacyclische Struktur konkurrieren. Die Umsetzung von ω-alkenylsubstituierten Zirconocendichloridkomplexen mit zwei Äquivalenten Ethyl- bzw. *n*-Hexyllithium ergibt analoge Reaktionsverläufe und analoge Metallacyclen wie die Reaktion mit *n*-Butyllithium.

The reaction between one equivalent of [(acac)Ni(A)Ni(acac)] (A: N^1,N^2 -bis(2-pyridylmethyl)- N^3,N^4 -bis-(2,4,6-trimethylphenyl)oxalamidinate) and two equivalents of R-Li (R = *n*-butyl; *n*-hexyl) results in the formation of the binuclear complexes [(R-Ni)(A)(Ni-R)].

Gino Paolucci, Manuela Vignola, Luca Coletto, Bruno Pitteri, Franco Benetollo

J. Organomet. Chem. 687 (2003) 161

Synthesis and characterization of Zr(IV) and Y(III) complexes with monocyclopentadienyl ligands containing an additional site tethered by a coordinating 2,6-pyridine bridge. X-ray crystal structures of the zirconium complexes

The reaction of the dilithium salt of monocyclopentadienyl ligand $rac \cdot 2$ with ZrCl₄ in a molar ratio of 1:1 in THF afforded the complex $rac \cdot 5$ which forms an insoluble oligomeric species after the loss of THF upon purification. From the mater liquor, two crystalline species, $rac \cdot 6$ and $rac \cdot 7$, were isolated, whose X-ray crystal structures are reported. The reaction of the same dilithium salt of the ligand with Y(OTf)₃ afforded the probably dimeric species $rac \cdot 8$ from which the derivative $rac \cdot 9$ was obtained after reaction with LiCH₂SiMe₃.



Alexander Snell, Gerald Kehr, Olga Kataeva, Roland Fröhlich, Gerhard Erker

J. Organomet. Chem. 687 (2003) 171

Preparation and characterization of some structural variants of Cp*Ti(1,2-propandiolato) complexes Cp*Ti(CH₃)₃ reacts with *rac*-1,2-propandiol to yield the unsymmetrical oxygen-bridged complex [(Cp*Ti)₂(1,2-propandiolato)₃] (**6**). Cp*TiCl₃ reacts with 1,2-propandiol in a 1:1 stoichiometry in the presence of pyridine to yield [Cp*TiCl(1,2-propandiolato)]₂ (**8**). Complex **8** gives an active polymerization catalyst for the formation of syndiotactic polystyrene when treated with excess methylalumoxane.



Richard S. Herrick, Christopher J. Ziegler, Heather Bohan, Michael Corey, Mark Eskander, Joshua Giguere, Naomi McMicken, Iwona E. Wrona

J. Organomet. Chem. 687 (2003) 178

Preparation and characterization of molybdenum and tungsten compounds with diazabutadiene ligands constructed from amino esters and glyoxal

Crystal structures of meso and C_2 -symmetric isomers of Mo(CO)₄(dab-asp(OMe)-OMe)

The title compounds were prepared by heating solutions of ester protected amino acids (H-L-Ala-OEt, H- β -Ala-OEt, H-L-Val-OMe, GABA-OMe, H-L-Asp(OMe)-OMe) and glyoxal in the presence of M(CO)₄(pip)₂ (M = Mo, W).



Michael R. Eberhard, Shiro Matsukawa, Yohsuke Yamamoto, Craig M. Jensen

J. Organomet. Chem. 687 (2003) 185

Novel unsymmetrical PCP' pincer ligands and their palladium(II) complexes



Pooja Kumar, Ravi Shankar

J. Organomet. Chem. 687 (2003) 190

Novel pentacoordinate silicon compounds bearing [Si-N-C-N-C-N] chelate ring derived from biguanide ligands The SiH/NH dehydrocoupling reactions between the carbosilanes $R^1R_2^2SiCH_2CH_2Si-MeH_2$ and 1-propylbiguanide/1-phenylbiguanide afford novel pentacoordinate silicon compounds bearing [Si-N-C-N-C-N] chelate ring.



Zhen-Hong Wei, Qing-Feng XuHong-Xi Li, Jin-Xiang Chen, Jian-Ping Lang

J. Organomet. Chem. 687 (2003) 197

Stepwise addition of CuBr at $[(dtc)_2Mo_2(S)_2(\mu-S)_2]$ (dtc = diethyldithiocarbamate): syntheses and crystal structures of two Mo/Cu/S clusters $[(dtc)_2Mo_2(\mu_3-S)(\mu-S)_3(CuBr)]$ and $[(dtc)_2Mo_2(\mu_3-S)_4(CuBr)_2]$

Two novel heterobimetallic sulfide clusters $[(dtc)_2Mo_2(\mu_3-S)(\mu-S)_3(CuBr)]$ (1) and $[(dtc)_2Mo_2(\mu_3-S)_4(CuBr)_2]$ (2) have been prepared by stepwise reactions of $[(dtc)_2Mo_2S_2(\mu-S)_2]$ with CuBr in CH₂Cl₂. The molecular structures of 1 and 2 have been characterized by X-ray crystallography.



Mien Wei Lum, Weng Kee Leong

J. Organomet. Chem. 687 (2003) 203

Reactions of the triosmium cluster $Os_3(\mu-H)(\mu-OH)(CO)_{10}$ with naphthols

Reactions of the cluster $Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}$ with 1- and 2-naphthol have been investigated. The products have been structurally characterised to confirm the mode of anchoring of the naphthols.



The Publisher encourages the submission of articles in electronic form thus saving time and avoiding rekeying errors. Please refer to the online version of the Guide for Authors at http://www.elsevier.com/locate/jorganchem

Full text of this journal is available, on-line from ScienceDirect. Visit www.sciencedirect.com for more information.



This journal is part of **ContentsDirect**, the *free* alerting service which sends tables of contents by e-mail for Elsevier Science books and journals. You can register for **ContentsDirect** online at: www.elsevier.com/locate/contentsdirect



http://chemweb.com/gateways/elsevier.html