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Contents

Regular papers

Sjoerd Harder, Reinout Meijboom, John R. Moss

J. Organomet. Chem. 689 (2004) 1095

Selective lithiation and crystal structures of G1-carbosilane dendrimers with dimethoxybenzene functionalities Lithiated dendrimers are extremely useful precursors for the syntheses of a variety of functionalized dendrimers. The crystal structures and lithiation of two dimethoxy-aryl substituted dendrimers are described and the three-dimensional networks of C–H···O bonds are discussed.



J. Organomet. Chem. 689 (2004) 1102

Reactions of organocobaloximes with aryldisulfonyl chlorides

Photochemical reactions of benzyl, heteroaromaticmethyl and allylcobaloximes with aryldisulfonyl chlorides yield symmetrical disulfones. Allyl cobaloximes yield allyldisulfones as the major product whereas bibenzyl is the major product in benzylcobaloximes. A time dependent ¹H NMR studies show that bibenzyl is formed from *O*-benzyldimethylglyoxime – a predominant product in the initial stage of the reaction.





Graham R. Lief, Daniel F. Moser, Lothar Stahl, Richard J. Staples

J. Organomet. Chem. 689 (2004) 1110

Syntheses and crystal structures of monoand bi-metallic zinc compounds of symmetrically- and asymmetricallysubstituted bis(amino)cyclodiphosph(V) azanes The degree of deprotonation and the metallation sites in the reactions of bis(alkyl/ arylamino)cyclodiphosph(V)azanes with diethylzinc are governed by the Brønsted acidities of the bis(amino)cyclodiphosph(V)azanes and the steric bulk of the ligands substituents.



Joshua R. Farrell, Clinton Becker, David P. Lavoie, Janet L. Shaw, Christopher J. Ziegler

J. Organomet. Chem. 689 (2004) 1122

New emissive *fac*-tricarbonylchlorobis (ligand)rhenium(I) complexes prepared from pyridine/thiophene hybrid ligands

A series of *fac*-tricarbonylchlorobis (ligand)rhenium(I) complexes where the ligands are various pyridine/thiophene hybrids including the new ligand 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-pyridine [4-py-EDOT] were prepared and found to be emissive in solution.

Carbene complexes Ph₃E–CH=WCl₂(OBu^t)₂

were synthesized and their structures were

determined by X-ray analysis.



H(9)

CI(1)

C(10)

C(16)

A.V. Safronova, L.N. Bochkarev, N.E. Stolyarova, I.K. Grigorieva, I.P. Malysheva, G.V. Basova, G.K. Fukin, Yu.A. Kurskii, S.Ya. Khorshev, G.A. Abakumov

J. Organomet. Chem. 689 (2004) 1127

Reactions of silicon-, germanium- and tincontaining carbene complexes of tungsten $Ph_3E-C=W(OBu')_3$ (E = Si, Ge, Sn) with hydrogen chloride: crystal structures of carbene complexes $Ph_3E-CH=WCl_2(OBu')_2$ (E = Si, Ge)

Ambroz Almássy, Branislav Horváth, Andrej Boháč, Marta Sališová, Gabriela Addová, Myron Rosenblum

J. Organomet. Chem. 689 (2004) 1131

Thermodynamic and kinetic parameters associated with the fluxional behavior of 2methyl- and 2,6-dimethyltroponeiron tricarbonyl complexes The fluxional behavior of 2-methyl- (1,4) and 2,6-dimethyl-derivatives of tricarbonyl[η^4 -tropone]iron (5,8) were studied in CDCl₃. The thermodynamic and kinetic parameters (rate constants, half lifes, activation energies) associated with haptotropic exchange were obtained. While the methyl group at C(2) appears to be responsible for the lower stability of 4 and 8 compared with 1 and 5, the Me group at C(6) influences more the rate of isomer exchange by raising the activation energy. Thus, the regioisomerisation of 4 to 1

 $\frac{1}{4(R:H), 8(R:M)} \xrightarrow{k}_{k_{-1}} \underbrace{R_{k_{-1}}}_{(CC)} \underbrace{R_{k_{-1}}}_$

Glen M. Fern, Sami Klaib, Owen J. Curnow, Heinrich Lang

J. Organomet. Chem. 689 (2004) 1139

 $\label{eq:constraint} \begin{array}{ll} Trimethylsilyl-functionalised & bis(indenyl)-iron(II) \ complexes: \ solid-state \ structure \ of \ [\eta^5-1,3-(SiMe_3)_2C_9H_5]_2Fe \end{array}$

The synthesis and characterisation of bis(indenyl)iron sandwich complexes featuring one or two Me₃Si substituents in position(s) 1(3) or 1,2(1,3) is described. The result of the X-ray structure analysis of $[\eta^5-1,3-(Si-Me_3)_2C_9H_3]_2F_9$ is reported as well.

is approximately two times faster than the rate of isomerisation of 8 to 5 at r.t.



Attila Szorcsik, László Nagy, Jorunn Sletten, Gábor Szalontai, Erzsébet Kamu, Tiziana Fiore, Lorenzo Pellerito, Eszter Kálmán

J. Organomet. Chem. 689 (2004) 1145

Preparation and structural studies on dibutyltin(IV) complexes with pyridine mono- and dicarboxylic acids

Shigekazu Matsui, Yasunori Yoshida, Yukihiro Takagi, Thomas P. Spaniol, Jun Okuda

J. Organomet. Chem. 689 (2004) 1155

Pyrrolide-imine benzyl complexes of zirconium and hafnium: synthesis, structures, and efficient ethylene polymerization catalysis A number of organotin(IV) complexes formed with pyridine mono- and dicarboxylic acids were prepared in the solid state. Two $Bu_2Sn(IV)^{2+}$ complexes formed with 2-picolinic and pyridine-2,6dicarboxylic acid were obtained as singlecrystals. The X-ray diffraction studies performed on the complexes showed, that the central {Sn} atoms are in pbp surroundings, with bond distances characteristic of organotin(IV) compounds. The two butyl groups are located in *ax* positions.

The reaction of pyrrolyl-imine with a tertiary alkyl group at the imine nitrogen LH with $M(CH_2Ph)_4$ (M = Hf or Zr) gave dibenzyl hafnium and zirconium complexes (L)₂ $M(CH_2Ph)_2$. The complexes possess *cis*configured benzyl groups and exhibit high activity for ethylene polymerization of up to 2×10^4 kg-polymer/mol-M hbar, when activated with B(C₆F₅)₃ or methylaluminoxane.





Damian Plażuk, Agnieszka Rybarczyk-Pirek, Janusz Zakrzewski

J. Organomet. Chem. 689 (2004) 1165

 $\beta\mathchar`-Ferrocenyl-\alpha,\beta\mathchar`-nusaturated phosphonates and sulfones$

Ferrocene reacts with β -ketophosphonates and β -ketosulfones (or acetals of formylphosphonates and sulfones) in the presence of a strong acid (triflic or methanesulfonic) to afford β -ferrocenyl- α , β unsaturated phosphonates and β -ferrocenyl- α , β -unsaturated sulfones in good yield.



Oana Bumbu, Cristian Silvestru, M. Concepción Gimeno, Antonio Laguna

J. Organomet. Chem. 689 (2004) 1172

New organomercury(II) compounds containing intramolecular $N \rightarrow Hg$ interactions: crystal and molecular structure of $[2-(Me_2NCH_2)C_6H_4]HgCl$ and $[2-(Me_2N-CH_2)C_6H_4]Hg[S(S)PPh_2]$

New $[2-(Me_2NCH_2)C_6H_4]Hg[S(X)PR_2]$ [X = S, R = Me (2), Et (3), Ph (4), O'Pr (6); X = O, R = Ph (5)] derivatives were prepared and were characterized by IR and multinuclear NMR spectroscopy. The molecular structures of $[2-(Me_2NCH_2)-C_6H_4]HgCl$ (1) and 4 were determined by singlecrystal X-ray diffraction. Due to the strong intramolecular coordination of the N atom of the pendant CH₂NMe₂ arm both compounds exhibit a T-shaped (*C*,*N*)HgX core in the molecular unit, with almost linear arrangement of the covalent C-Hg and Hg–X (X = Cl, S) bonds. The crystals of 1 contain discrete monomeric molecules, while the crystals of 4 contain dimer associations built through asymmetric bridging dithiophosphinato ligands.



Jan Honzíček, Petr Nachtigall, Ivana Císařová, Jaromír Vinklárek

J. Organomet. Chem. 689 (2004) 1180

Synthesis, characterization and structural investigation of the first vanadocene(IV) carboxylic acid complexes prepared from the vanadocene dichloride

Vanadocene dichloride with monocarboxylic and dicarboxilic acids forming Cp_2V -(OOCR)₂ (R = H, CCl₃ and CF₃) and Cp_2V (OOC–A–COO) (A = – and CH₂) respectively.



György Petöcz, Zoltán Berente, Tamás Kégl, László Kollár

J. Organomet. Chem. 689 (2004) 1188

Xantphos as *cis*- and *trans*-chelating ligand in square-planar platinum(II) complexes. Hydroformylation of styrene with platinum-*xantphos*-tin(II)chloride system Platinum(II) complexes of a diphosphine ligand *xantphos* (4,5-bis(diphenylphosphino)-9,9-dimethyl-xanthene) have been synthesised and characterised by NMR, conductivity and catalytic investigations.

Matthias Deppner, Ralf Burger, Helmut G. Alt

J. Organomet. Chem. 689 (2004) 1194

Alkylidenverbrückte dissymmetrische zweikernige Metallocenkomplexe als Katalysatoren für die Ethylenpolymerisation A series of dissymmetric alkylidene bridged dinuclear metallocene complexes of titanium, zirconium and hafnium was prepared and characterized. These complexes can be activated with methylalumoxane (MAO) and then be used as catalysts for the polymerization of ethylene to give resins with a broader molecular weight distribution than a mixture of the corresponding mononuclear components.

Cl. Zr Cl

n = **2–10**

Mei Wang, Hongjun Zhu, Deguang Huang, Kun Jin, Changneng Chen, Licheng Sun

J. Organomet. Chem. 689 (2004) 1212

Salen-type zirconium complexes with a labile coordination site and a robust skeleton: crystal structure of [(*t*-Bu₄-salen)ZrCl₂(H₂O)]

Water-coordinating salen-type zirconium complexes $[LZrCl_2(H_2O)]$ (L = $(t-Bu_4$ -salen, $t-Bu_4$ -salphen) were prepared. The association and disassociation of water molecule in $[LZrCl_2(H_2O)_n]$ (n = 0, 1) was studied. The crystal analysis reveals that a herringbone supramolecular assembly is constructed in the crystalline state of $[(t-Bu_4$ -salen)- $ZrCl_2(H_2O)]$ by intermolecular hydrogen bonds.



Xiangru Meng, Hongwei Hou, Gang Li, Baoxian Ye, Tiezhu Ge, Yaoting Fan, Yu Zhu, Hiroshi Sakiyama

J. Organomet. Chem. 689 (2004) 1218

Tetrametallic macrocyclic frameworks constructed from ferrocenedicarboxylato and 2,2'-bipyridine: synthesis, molecular structures and characteristics Four novel M–O₂CFcCO₂-2,2'-bpy (M = Cd, Zn, Co, Ni) tetranuclear macrocyclic compounds have been synthesized and characterized by single crystal diffraction. The magnetic measurements show that an antiferromagnetically coupling of Co^{II}–Co^{II} pairs occurs in compound (**3**), and unusual global ferromagnetic coupling between nickel(II) ions exists in compound (**4**). The solution-state differential pulse voltammetries of (**1**–(**4**) all show two peaks with large separations (ΔE) that indicate strong interactions between two ferrocene moieties.

Richard J. Bowen, Manuel A. Fernandes, Marcus Layh

J. Organomet. Chem. 689 (2004) 1230

Synthesis and crystal structures of novel lithium- and palladium-1-azaallyls

Treatment of the tetrasilyl pyridine derivative $(R_2HC)_2C_5H_3N-2,6 \ 1$ with Bu^nLi and PhCN gave the lithium-1-azaallyl $[Li\{N(R)C(Ph) C(R)(C_5H_3N-2,6)(CHR_2)]_2 \ 2 \ (R = SiMe_3)$, while the Pd(II) derivatives **3** and **4** were prepared from $[Li\{N(R)C(R')CH\}_2(C_5H_3N-2,6)]Li(tmen)_n (R = SiMe_3, R' = Bu', n = 1 \text{ or } R' = Ph, n = 2)$ and PdCl₂(PhCN)₂. The crystal structures of **1–4** are presented and discussed. Compound **3** is the first example of a crystallographically characterised PdNSiC heterocycle which is believed to be formed via an intramolecular CH-activation of a trimethylsilyl group by Pd(II).





Ashrafolmolouk Asadi, Anthony G. Avent, Martyn P. Coles, Colin Eaborn, Peter B. Hitchcock, J. David Smith

J. Organomet. Chem. 689 (2004) 1238

The ligands $C(SiMe_3)_2(SiMe_2H)$ and $C(SiMe_2Ph)_2(SiMe_2H)$ have been attached to lithium, potassium and aluminium. The compound $KC(SiMe_2Ph)_2(SiMe_2H)$ crystallizes with an ionic lattice in which the carbanionic centre, the hydrogen attached to silicon, and phenyl groups all interact with the potassium cation.



Sarjit Singh Keisham, Yurij A. Mozharivskyj, Patrick J. Carroll, Mohan Rao Kollipara

J. Organomet. Chem. 689 (2004) 1249

Syntheses and characterization of indenylruthenium(II) complexes containing N, N' donor Schiff base ligands. Molecular structures of $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)]$ BF₄ and $[(\eta^5-C_9H_7)Ru(PPh_3)(C_5H_4-N-2-CH=N-C_6H_4-p-CH_3)]BF_4$ The complex $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3-CN)]BF_4$ (2) reacts with a series of N, N' donor Schiff bases viz para substituted N-(pyrid-2-ylmethylene)phenylamines (ppa) in methanol yielding monocationic indenylruthenium(II) Schiff base complexes.



Contents

Simon J. Reid, Michael C. Baird

J. Organomet. Chem. 689 (2004) 1257

Reactions of free radicals with η^3 -allylpalladium(II) complexes: cyclohexyl radicals

Reactions of allylpalladium(II) compounds with cyclohexyl free radicals results in conversion of the allyl ligands to alkenes, but not as the thermodynamically favoured regioisomers.

 $Ph \checkmark Pd \checkmark Cl + R \rightarrow Ph \checkmark$ ≊-[⊢]dU PhCH₂CH=CH₂ + R-H

Jarosław Lewkowski, Monika Rzeźniczak, Romuald Skowroński

J. Organomet. Chem. 689 (2004) 1265

First synthesis of 1,1'-ferrocene bisaminophosphonic esters The series of aminophosphonates bearing the 1,1'-bis-substituted ferrocenyl moiety was obtained in the course of addition of phosphites to 1,1'-ferrocenedicarbaldehyde Schiff bases. It led to the formation of three isomers: a racemic mixture and a *meso*-form. Its stereochemistry is discussed.



Yasuhiro Morisaki, Hui Chen, Yoshiki Chujo

J. Organomet. Chem. 689 (2004) 1271

Synthesis and properties of PPE-type conjugated polymers containing tricarbonyl-(arene)chromium unit in the main chain

Novel π -conjugated polymers containing (η^6 arene)Cr(CO)₃ in the main chain based on poly(*p*-phenylene-ethynylene) are prepared. The polymers are soluble in common organic solvents and characterized by NMR and FT-IR spectra. Optical, electrochemical, and thermal properties of the polymer are discussed.



Handong Yin, Chuanhua Wang, Mei Hong, Daqi Wang

J. Organomet. Chem. 689 (2004) 1277

Three tin(IV) complexes with dithiomorpholincarbamate ligand $Br_2Sn[S_2CN(CH_2-CH_2)_2O]_2$ (1), (4-*F*-C₆H₄CH₂)₂Sn(Cl)S₂CN-(CH₂CH₂)₂O (2) and (2-*F*-C₆H₄CH₂)₃-SnS₂CN(CH₂CH₂)₂O (3) have been synthesized and their crystal and molecular structures have been determined.



U. Deva Priyakumar, M. Punnagai, G. Narahari Sastry

J. Organomet. Chem. 689 (2004) 1284

Facile valence isomerization among bis(silacyclopropenyl), disila(Dewar benz-ene) and disilabenzvalene

Isomerization from bis(silacyclopropenyl) is very facile either to disila(Dewar benzene) or disilabenzvalene.



David P. Gallasch, Susan L. Woodhouse, Louis M. Rendina

J. Organomet. Chem. 689 (2004) 1288

Synthesis and redistribution reactions of asymmetric σ -arylplatinum(II) complexes containing 4,7-phenanthroline

The synthesis of asymmetric, mono- and dinuclear σ -arylplatinum(II) complexes containing the 4,7-phenanthroline ligand is reported. The dinuclear species undergo an unusual redistribution reaction that is essentially thermoneutral at 298 K. The exchange process involves facile cleavage of a Pt–N bond and the rapid exchange of *trans*.[PtL₂(σ -aryl)] units in the equilibrium mixture.



Ya-Zheng Zhu, Jing-Yu Liu, Yue-Sheng Li, Yue-Jin Tong

J. Organomet. Chem. 689 (2004) 1295

Synthesis, structure and norbornene polymerization behavior of nickel complexes bearing two β -ketoiminato chelate ligands

A new class of nickel complexes with two nonsymmetric bidentate 1,1,1-trifluoro- β ketoiminato or 1-benzoyl- β -ketoiminato as ligands **4a**–**d** has been synthesized and characterized, and shown to be high active catalysts for vinylic polymerization of norbornene in the presence of modified methylaluminoxane.

Sanjiv Prashar, Mariano Fajardo, Andrés Garcés, Iván Dorado, Antonio Antiñolo, Antonio Otero, Isabel López-Solera, Carmen López-Mardomingo

J. Organomet. Chem. 689 (2004) 1304

Isocyanide insertion reactivity of dinuclear niobium and tantalum imido complexes: X-ray crystal structure of $[{Nb(\eta^5-C_5H_4-SiMe_3)(CH_2Ph)_2}_2(\mu-1,4-NC_6H_4N)]$

The reactivity of dinuclear niobium and tantalum imido alkyl complexes with the isocyanide compound 2,6-Me₂C₆H₃NC and the characterization of the subsequent η^2 -iminoacyl derivatives is described.



Janine T. Chantson, Simon Lotz

J. Organomet. Chem. 689 (2004) 1315

C-H and N-H activation by Pt(0) in N- and O-heteroaromatic compounds

Oxidative insertion reactions of $[Pt(PEt_3)_4]$ with N- and O-heteroaromatic compounds were studied. N–H activation of (azoles) and C–H activation (of furan derivatives) led to the isolation of *trans*-[PtHR(PEt_3)_2] complexes, where R = 1-indolyl, 1-imidazolyl, 1-pyrazolyl, 1-benzimidazolyl, 1-indazolyl, 2-furyl, 2-benzoxazolyl and 2-benzothiazolyl.



Note

Pradeep Mathur, Vidya D. Avasare, Abhijit K. Ghosh, Shaikh M. Mobin

J. Organomet. Chem. 689 (2004) 1325

Formation of 5-phenyl-1,2-dithiole-3-thione from molybdenum dithiopropiolato complexes Molybdenum dithiopropiolato complexes, $[(\eta^5-C_5R_4R')Mo(CO)_2(\eta^2-S_2CC\equiv CPh)]$ react with trimethylamine-*N*-oxide (TMNO-2H₂O) to form 5-phenyl-1,2-dithiole-3thione. The reaction proceeds through the formation of the oxo-complexes, $[(\eta^5-C_5R_4R')Mo(O)(\eta^3-S_2CC\equiv CPh)]$ which also react with TMNO-2H₂O to form **2**.



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