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Contents

Communication

Kelly A. Davidson, Kelly J. Kilpin, Nicholas C. Lloyd, Brian K. Nicholson

J. Organomet. Chem. 692 (2007) 1871

A six-coordinate aryl-germanium complex formed by the Kläui ligand

The first structurally-characterised sixcoordinate aryl-germanium(IV) complex is described.



Regular Papers

Thengarai S. Venkatakrishnan, Swadhin K. Mandal, Raghuraman Kannan, Setharampattu S. Krishnamurthy, Munirathinam Nethaji

J. Organomet. Chem. 692 (2007) 1875

Ruthenium hydride complexes of chiral and achiral diphosphazane ligands and asymmetric transfer hydrogenation reactions Ruthenium(II) hydride complexes of chiral and achiral diphosphazanes and preliminary investigations on ruthenium catalyzed asymmetric transfer hydrogenation of 2-acetonaphthone in the presence of chiral diphosphazanes are reported.





Sudarsanan Varaprath, Debra H. Stutts

J. Organomet. Chem. 692 (2007) 1892

Utility of trichloroisocyanuric acid in the efficient chlorination of silicon hydrides

Silanes and siloxanes containing multiple hydrogen atoms can be very efficiently transformed to the corresponding chloro compounds using trichloroisocyanuric acid.



Kathi Halbauer, Helmar Görls, Tamara Fidler, Wolfgang Imhof

J. Organomet. Chem. 692 (2007) 1898

The reaction of manganese carbonyl with *tert*butylisocyanide: Synthesis and characterization of *cis*- and *trans*-[Mn^I(^tBuNC)₄(CN)(CO)] The reaction of $Mn_2(CO)_{10}$ with *tert*-butyl isocyanide proceeds either *via* the oxidation of manganese together with the concomitant reductive cleavage of isocyanides producing the coordination compounds *cis*- and *trans*-[Mn(¹BuNC)₄(CN)(CO)] (**1a** and **1b**), or *via* the oligomerization of isocyanides yielding the cyclopentene **2**. Additional side-products as well as coordination oligomers based on **1b** are also reported.



Ting-Ke Zhang, Ke Yuan, Xue-Long Hou

J. Organomet. Chem. 692 (2007) 1912

Palladacycle as highly efficient catalyst for ring opening of oxabicyclic alkenes with organozinc halides Palladacycle 3 is a highly active catalyst in ring opening reaction of oxabicylic alkenes 4 with in situ prepared organozinc halides 5. ^{31}P NMR study showed that the skeleton of 3 remained intact in the reaction, which implied that palladacycle 3 might be a real catalyst in the reaction.



58-80% yields





Ramaswamy Murugavel, Ramasamy Pothiraja, Swaminathan Shanmugan, Namrata Singh, Ray J. Butcher

J. Organomet. Chem. 692 (2007) 1920

First organotin complex of a phosphonic diamide RP(O)(NHR)₂

Organophosphonic diamide has been used for the first time as a ligand in organotin chemistry; the product obtained forms an interesting six-membered ring, through $N-H\cdots Cl$ hydrogen bonding, that contains six different elements, Sn, O, P, N, H, and Cl.

H en Cl P O

Hossein Tavakol, Saedeh Zakery, Akbar Heydari

J. Organomet. Chem. 692 (2007) 1924

Chemoselective addition of organometallics to oxime ethers

An efficient method for preparation of substitued hydroxylamines from aldehydes is reported. First *O*-trimethylsilyl oxime ether prepared from condensation reaction between aldehyde and *O*-trimethylsilyl hydroxylamine, then added organosilane or organotin nucleophile in the same vessel to preparing the corresponding α -substituted hydroxylamines in one-pot and chemoselective synthesis.



Inma Angurell, Cédric-Olivier Turrin, Régis Laurent, Valérie Maraval, Paul Servin, Oriol Rossell, Miquel Seco, Anne-Marie Caminade, Jean-Pierre Majoral

J. Organomet. Chem. 692 (2007) 1928

Decorating step-by-step and independently the surface and the core of dendrons

Dendrons are decorated step-by-step by several types of functional groups, in particular by phosphines at the end of the branches, then by amines at the core, and finally by metals complexed on the end groups. Such methodology affords nanometric "Christmas tree"-like compounds.



Victoria Volkis, Claudia Averbuj, Moris S. Eisen

J. Organomet. Chem. 692 (2007) 1940

Reactivity of group 4 benzamidinate complexes towards mono- and bis-substituted silanes and 1,5-hexadiene

Cationic zirconium and titanium bis(benzamidinate) dimethyl complexes are active catalyst for the polymerization of 1,5-hexadiene producing poly(methyl-1,3-cyclopentane) and for the polymerization or the oligomerization of mono- and bis-substituted silanes. For polysilanes, the maximum polymerization index that was accomplished (n = 90) is by far the largest obtained with organometallic complexes.



Mustafa Keles, Ziya Aydin, Osman Serindag

J. Organomet. Chem. 692 (2007) 1951

Synthesis of palladium complexes with bis(diphenylphosphinomethyl)amino ligands: A catalyst for the Heck reaction of aryl halide with methyl acrylate Scheme 1. Synthesis of bis(diphenylphosphinomethyl)amino ligands and their Pd(II) complexes.

Scheme 2. Heck reaction of aryl halide with methyl acrylate.



Scheme 1.

Muralidhara Thimmaiah, Rudy L. Luck, Shiyue Fang

J. Organomet. Chem. 692 (2007) 1956

Novel benzoferrocenyl chiral ligands: Synthesis and evaluation of their suitability for asymmetric catalysis Four novel benzoferrocenyl phosphorus chiral ligands were prepared and fully characterized. The structure of one of them was further confirmed by X-ray analysis. These compounds were found chemically and configurationally stable and compatible with palladium catalyzed allylic alkylation reactions.



Contents

Thomas A. Zevaco, Jakub K. Sypien, Annette Janssen, Olaf Walter, Eckhard Dinjus

J. Organomet. Chem. 692 (2007) 1963

Synthesis, structural characterisation of new oligomeric alkyl aluminium (2,2'-methylene*p*-chloro-bisphenoxides) and application as catalysts in polymerisation reactions involving cyclohexene oxide The synthesis, spectroscopic characterisation and X-ray structure determination of the first aluminium *para*-chloro-bisphenoxides: a dinuclear $[Al_2(mbpcp)_2(C_2H_5)_2(THF)_2]$ and a trinuclear $[Al_3(mbpcp)_2(C_2H_5)_5]$ (mbpcp = 2,2'-methylenebis(4-chlorophenol) are reported. These compounds were tested as catalysts in polymerisation reactions involving cyclohexene oxide (CHO) as substrate. Both aluminium bisphenoxides are highly active in the ring opening polymerisation of CHO. These compounds are also active in the copolymerisation of CHO with CO₂ although the carbonate amounts in the copolymers remain low.



Lucie Červenková Šťastná, Kateřina Auerová, Jaroslav Kvíčala, Jan Čermák

J. Organomet. Chem. 692 (2007) 1974

Fluorophilic properties of (perfluorooctyl)ethyldimethylsilyl substituted and tetramethyl-(perfluoroalkyl) substituted cyclopentadienes and their Ti(IV), Rh(III), and Rh(I) complexes Fluorous partition coefficients, fluorophilicities, specific fluorophilicities, and fluorousnesses in perfluoromethylcyclohexane/ toluene system for 37 fluorinated silylcyclopentadienes, titanium(IV) complexes derived from them, perfluoroalkyl substituted tetramethylcyclopentadienes, and their Rh(III) and Rh(I) complexes are reported showing a relative unimportance of fluorine content parameter for fluorophilicity.



$f_i = In\{[c_i(CF_3C_6F_{11})]/[c_i(toluene)]\}$

Pelin Edinç, Ahmet M. Önal, Saim Özkar

J. Organomet. Chem. 692 (2007) 1983

Synthesis, characterization, and electrochemistry of tetracarbonyl(6-ferrocenyl-2,2'bipyridine)tungsten(0) 6-Ferrocenyl-2,2'-bipyridine, prepared by the reaction of lithiated ferrocene and bipyridine, reacts with pentacarbonyl[η^2 -bis(trimethylsilyl)ethyne]tungsten(0) to form tetracarbonyl-(6-ferrocenyl-2,2'-bipyridine)tungsten(0) which was isolated as analytically pure substance and characterized by elemental analysis, IR, UV– Vis, MS, ¹H and ¹³C NMR spectroscopies. Electrochemistry of 6-ferrocenyl-2,2'-bipyridine and its complex W(CO)₄(6-ferrocenyl-2,2'-bipyridine) was studied by cyclic voltammetry and controlled potential electrolysis combined with UV–Vis spectrometer.



S. Jafar Hoseini, S. Masoud Nabavizadeh, Sirous Jamali, Mehdi Rashidi

J. Organomet. Chem. 692 (2007) 1990

Ligand substitution reaction at a binuclear organoplatinum(II) complex

The kinetics of substitution reactions of the Ndonor ligand in the binuclear dimethylplatinum(II) complex **1**, in which dppm = bis-(diphenylphosphino)methane and NN = phthalazine, by different nucleophilic phosphorous-donors L, L = $P(O^{-i}Pr)_3$ or PPh₃ and L₂ = dppm, to form the dinuclear complexes **2** are studied.



Krishna K. Pandey

J. Organomet. Chem. 692 (2007) 1997

Structure and coordinate bonding nature of the manganese– σ –borane complexes

The calculated electronic and molecular structures of the complexes [(Cp')Mn(CO)2-[(Cp')Mn(CO)₂(HBpin)] (HBcat)], and [(Cp')Mn(CO)₂(HBMe₂)] at DFT B3LYP and BP86 levels are consistent with [(Cp)Mn(CO)2- $(\eta^2$ -HBR₂)] being Mn(I) complexes in which both hydrogen and boron of the [HBR₂] ligands have a bonding interaction with the manganese preserving B-H bond character. Upon coordination of [HBR₂] ligand, an approximate 34% reduction in B-H bond order has been observed. The [(Cp')Mn(CO)2]- $[\eta^2$ -H-BR₂] bonding in σ -borane complexes is more than half electrostatic.



Jun-Fang Gong, Xin-Heng Fan, Chen Xu, Jin-Lei Li, Yang-Jie Wu, Mao-Ping Song

J. Organomet. Chem. 692 (2007) 2006

New cycloplatinated complexes with 2arylimidazolines: Synthesis, crystal structures and photophysical properties The synthesis, crystal structures and photophysical properties of a series of cycloplatinated complexes are presented. The complexes have the general formula (C^N)Pt(O^O), where O^O is acetylacetonate and C^N represents 2-arylimidazoline ligands. All of them are luminescent in CH_2Cl_2 solution at room temperature. Different aryl group on N-1 of the ligand has no significant effect on the emission properties of the platinum complexes. While introducing alkyl group on N-1 or electron-donating group on 2-aryl ring does result in a blue shift of emission maxima or even an increase in emission intensity.



Bo Xiao, Hongwei Hou, Yaoting Fan

J. Organomet. Chem. 692 (2007) 2014

Catalytic applications of Cu^{II}-containing MOFs based on N-heterocyclic ligand in the oxidative coupling of 2,6-dimethylphenol Two Cu^{II}-containing MOFs were synthesized and found to be highly effective catalysts for the oxidative coupling of 2,6-dimethylphenol (DMP) to poly(1,4-phenylene ether) (PPE) and diphenoquinone (DPQ) with H_2O_2 as oxidant and NaOMe as co-catalyst at room temperature. Under the optimized conditions, the selectivity to PPE is almost up to 90% for both complexes, and the conversion of DMP is 85% for 1 and 90% for 2, which can match those observed for the reported well-known catalysts.



Lirong Zhang, Kin Shing Chan

J. Organomet. Chem. 692 (2007) 2021

Activation of aliphatic carbon-carbon bonds of esters and amides by rhodium(II) porphyrin

Aliphatic carbon–carbon bonds of esters and amides were activated successfully with rhodium(II) porphyrin radical to give rhodium(III) porphyrin alkyls in moderate yields. Rh(tmp) + or amide Ph_3P , benzene $100-130 \ ^{\circ}C$, Rh(tmp)R $6-24 \ h$

Contents

Ken-ichi Suyama, Takanori Nakatsuka, Takahiro Gunji, Yoshimoto Abe

J. Organomet. Chem. 692 (2007) 2028

Synthesis and crystal structure of disiloxane-1,3-diols and disiloxane-1,1,3,3-tetraol Titled disilxoanepolyols were synthesized by hydrolysis of the corresponding diisocyanatodisiloxanes and tetrachlorodisiloxane. X-ray crystallography showed that the disiloxane-1,3-diols in the crystal feature a 1.21 nm diameter columnar array with intermolecular hydrogen bonding. The disiloxane-1,1,3,3-tetraol, on the other hand, revealed molecules with a *gauche-* and *anti*-conformation depending on crystallization method which formed a columnar array and a sheet-like array, respectively.



Dobrochna Matkowska, Maciej Gola, Marcin Śnieżek, Piotr Cmoch, Krzysztof Staliński

J. Organomet. Chem. 692 (2007) 2036

Structural assignment of organotin hydrides containing the oxazoline ligand

In the corresponding triorganotin hydrides and diorganotin dihydrides containing the optically active 2-(4-isopropyl-2-oxazolinyl)-5phenyl ligand values of the ${}^{1}J({}^{1}H_{-}^{117/119}Sn)$ couplings appeared to be temperature dependent, supporting a pseudo-axial/equatorial position of the hydrogen attached to the tin.



Jennifer A. Shaw-Taberlet, Jean-René Hamon, Thiery Roisnel, Claude Lapinte, Michaela Flock, Thomas Mitterfellner, Harald Stueger

J. Organomet. Chem. 692 (2007) 2046

Electronic interactions in 1-ethynyl-2-phenyltetramethyldisilanes HC=CSiMe₂CiMe₂C₆H₄X Experimental and calculated (time-dependent DFT B3LYP/TZVP) UV absorption data of 1-ethynyl-2-phenyltetramethyldisilanes $HC\equiv CSiMe_2SiMe_2C_6H_4X$ show pronounced electronic interactions of the $HC\equiv C$ - and the C₆H₄X π -systems with the central Si–Si bond. The observed absorption bands can be assigned to $\sigma(Si–Si) \rightarrow \pi^*(ph)$ or $\pi(ph) \rightarrow \pi^*(ph)$ electron transitions depending on the substituents attached to the benzene ring.





Antonella Leone, Sebastian Gischig, Cornelis J. Elsevier, Giambattista Consiglio

J. Organomet. Chem. 692 (2007) 2056

High-pressure NMR study of migratory CO-insertion in palladium–methyl complexes modified with C_s-symmetrical 1,4-diphosphines

Carbonylation of the palladium complexes $[PdCH_3(P^P)'CI]$ (P^P' = 1a, 1b, 1c, 1d, 1e) and $[PdCH_3(P^P)'(CH_3CN)](OTf)$ was investigated by means of high-pressure NMR with the determination of the half-life times $t_{1/2}$. The results were rationalized on the basis of the electronic properties of the diphosphines and the nature of the solvento ligand in the first coordination sphere. The crystal structures of the complexes $[Pd(1b)Cl_2]$ and $[Pd(1b)(H_2O)_2](OTf)_2$ are described (1b = 1-(diphenylphosphinomethyl)-2-[bis(3-trifluoromethylphenyl)phosphinomethyl]benzene).



Jiří Pinkas, Vojtech Varga, Ivana Císařová, Jiří Kubišta, Michal Horáček, Karel Mach

J. Organomet. Chem. 692 (2007) 2064

The first thermally stable half-sandwich titanium zwitterionic complex

Thermally stable zwitterionic complex $[(\eta^5 C_5Me_5)Ti(Ot-Bu)_2]^{(\delta+)}[(\mu-Me)B(C_6F_5)_3]^{(\delta-)}$ (5) forms from equimolar quantities of $[(\eta^5 C_5Me_5$)TiMe(Ot-Bu)₂] and [B(C₆F₅)₃]. The ¹H, ¹⁹F and 1D NOESY NMR spectra in C₆D₆ solution proved the inner sphere ion pair structure of 5. The X-ray crystal structure of 5 revealed that the C-H bonds of bridging methyl group fulfil criteria for agostic bonding interaction with the titanium atom.



James Moss, Jemima Thomas, Andrew R. Cowley, Dermot O'Hare

J. Organomet. Chem. 692 (2007) 2071

The synthesis of $[(\eta^6-Flu^*H)Mn(CO)_3]PF_6$, and its deprotonation to yield a novel coordination mode of fluorene

Deprotonation of $[(\eta^6 - Flu^*H)Mn(CO)_3]PF_6$ gives a neutral zwitterionic complex containing a previously unknown coordination mode of fluorene.

Robert C.J. Atkinson, Louisa J. Hope-Weeks, Martin J. Mays, Gregory A. Solan

J. Organomet. Chem. 692 (2007) 2076

Medium size macrocycles incorporating combinations of coordinated-1,3-divne units, oxygen donors and group 14 elements

Both an acid-catalysed condensation route and a metathesis-type approach have been employed to prepare strained eight- and ninemembered macrocycles incorporating combinations of coordinated-1,3-diyne units, oxygen donors and group 14 elements (C, Si, Ge).

Lydie Viau, Anthony C. Willis, Mark G. Humphrey

J. Organomet. Chem. 692 (2007) 2086

Ruthenium cluster chemistry: Monodentate bis(diphenylphosphino)acetylene-ligated cluster modules in chain and dendrimer formation

Reaction of Ru₃(CO)₉(NCMe)₃ with excess $Ru_3(\mu$ -dppm)(CO)₉(η^1 -dppa), which possesses a monodentate dppa ligand, or reaction of excess Ru₃(µ-dppm)(CO)₁₀ with Ru₃(CO)₉(η¹dppa)3, which possesses three monodentate dppa ligands, affords the dodecanuclear firstgeneration dendrimer Ru₃(CO)₉{PPh₂C₂- $PPh_2Ru_3(\mu-dppm)(CO)_9\}_3.$ Reaction of $WIr_3(\mu-CO)_3(CO)_8(\eta-C_5Me_5)$ with excess $Ru_3(\mu$ -dppm)(CO)₉(η^1 -dppa) affords the decanuclear tri-cluster WIr₃(CO)₉{PPh₂C₂- $PPh_2Ru_3(\mu$ -dppm)(CO)₉}₂(\eta-C₅Me₅).







Hongping Ren, Peiyuan Yao, Shansheng Xu, Haibin Song, Baiquan Wang

J. Organomet. Chem. 692 (2007) 2092

A new class of *o*-hydroxyaryl-substituted *N*heterocyclic carbene ligands and their complexes with palladium A facile synthesis of *o*-hydroxyaryl-substituted *N*-heterocyclic carbene ligands and their complexes with palladium is presented. This kind of salicylaldimine-like NHC ligands expands the class of available NHC ligands for organometallic catalysts.



Shaowu Wang, Shaoyin Wang, Shuangliu Zhou, Gaosheng Yang, Wei Luo, Nan Hu, Zhihong Zhou, Hai-Bin Song

J. Organomet. Chem. 692 (2007) 2099

Synthesis, characterization, and catalytic activity of divalent organolanthanide complexes with new tetrahydro-2*H*-pyranyl-functionlized indenyl ligands

Two series of new divalent organolanthanide complexes with the general formula $[\eta^5:\eta^1-\{1-R-3-(C_5H_9OCH_2)C_9H_5\}]_2Ln^{II}$ were prepared and characterized. Their catalytic activities on the MMA and ϵ -caprolactone polymerization were examined.



R = H, Ln = Yb (3), Eu (5); R = Me₃Si-, Ln = Yb (4), Eu (6)

Note

V.A. Bhirud, A. Uzun, P.W. Kletnieks, R. Craciun, J.F. Haw, D.A. Dixon, M.M. Olmstead, B.C. Gates

J. Organomet. Chem. 692 (2007) 2107

Synthesis and crystal structure of $Ir(C_2H_4)_2-(C_5H_7O_2)$

Erratum

We report a new synthesis and a full experimental and theoretical characterization of $Ir(C_2H_4)_2(C_5H_7O_2)$ [(acetylacetonato)-bis(η^2 -ethene)iridium(I)]. The crystal structure of $Ir(C_2H_4)_2(C_5H_7O_2)$ is isostructural to that of $Rh(C_2H_4)_2(C_5H_7O_2)$, but there is a substantial difference in the ethylene binding energies in these two compounds, which are valuable as precursors of oxide-supported catalysts with reactive ethylene ligands.





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