

Available online at www.sciencedirect.com





Volume 692, issue 11, 1 May 2007

www.elsevier.com/locate/jorganchem

Contents

Communications

Isao Shimo, Tomoko Okumura, Kei Goto, Takayuki Kawashima

J. Organomet. Chem. 692 (2007) 2115

Syntheses and characterization of alkylzirconium complexes containing two silanolato ligands with a bowl-shaped framework

The first example of a cationic zirconium complex containing a silanolato ligand, $[(Ar_3SiO)_2ZrBn]^+[BnB(C_6F_5)_3]^-$, was synthesized by abstraction of a benzyl group from a neutral dibenzylbis(silanolato)zirconium complex containing bulky bowl-shaped silanolato ligands. Their structures have been characterized by X-ray crystallography.



Simonetta Orlandi, Maurizio Benaglia, Gianmaria Dell'Anna, Giuseppe Celentano

J. Organomet. Chem. 692 (2007) 2120

Synthesis of new C_1 -symmetric bis(oxazoline) ligands with a chelating sidearm for stereo-selective Mukaiyama aldol condensations

New enantiomerically pure C_1 -symmetric bis(oxazoline) ligands with a binding sidearm were synthesised in good yields and tested in the stereoselective Mukaiyama aldol condensation between the trimethylsilyl keteneacetal of methyl isobutyrate and a non-chelating substrate such as benzaldehyde to afford the product in up to 55% ee.



ee up to 55%

New enantiomerically pure C1-symmetric bis(oxazoline) ligands with a binding sidearm were synthesised in good yields and tested in stereoselective Mukaiyama aldol condensation.

Regular Papers

Alan K. Brisdon, Ian R. Crossley, Robin G. Pritchard, Ghazala Sadiq

J. Organomet. Chem. 692 (2007) 2125

Asymmetric fluoro-organomercurials. Part 2. The synthesis and characterisation of the fluorovinyl-mercurials RHgCX=CF₂ (R = Ph, Fc; X = F, Cl): The single crystal X-ray structures of PhHgCF=CF₂, FcHgCF=CF₂ and FcHgCCl=CF₂[Fc(η^5 -C₅H₅)Fe(η^5 -C₅H₄)]

The compounds RHgCX=CF₂ (R = Ph, Fc; X = F, Cl) have been prepared, in high yields, as the first fully characterised examples of asymmetric Hg(II) complexes of this type. The crystal structures of RHgCX=CF₂ reveal a series of short Hg...F and Hg... η^2 -arene interactions.



Ravi Shankar, Arti Joshi

J. Organomet. Chem. 692 (2007) 2131

Synthesis, characterization and UV spectral studies of copolysilanes, ${[RR'_2Si(CH_2)_2-SiMe]_x[PhR^1Si]_{1-x}}_n$ (R, R' = Me, Et or Ph; R¹ = Me or Ph) bearing carbosilyl side chains

The synthesis of copolysilanes 1-6 and their compositional effects on the NMR characteristics and UV spectra are described.



Gloria Sánchez-Cabrera, Francisco J. Zuno-Cruz, Berenice A. Ordóñez-Flores, María J. Rosales-Hoz, Marco A. Leyva

J. Organomet. Chem. 692 (2007) 2138

Reactivity of $[Os_3(CO)_{10}(NCMe)_2]$ and $[Os_3(CO)_{10}(\mu-Cl)(\mu-AuPPh_3)]$ with 4-mercaptopyridine: X-ray structure of $[Os_3(CO)_{10}(\mu-H)(\mu-SC_5H_4N)]$ and $[Os_3(CO)_{10}(\mu-AuPPh_3)-(\mu-SC_5H_4N)]$

The reaction between $[Os_3(CO)_{10}(NCMe)_2]$ (1) and $[AuClPPh_3]$ under mild conditions gave $[Os_3(CO)_{10}(\mu-Cl)(\mu-AuPPh_3)]$ (2) and its isolobal analog $[Os_3(CO)_{10}(\mu-Cl)(\mu-H)]$ (3). The reactions of compounds 1 and 2 with 4-mercaptopyridine gave compounds $[Os_3-(CO)_{10}(\mu-H)(\mu-SC_5H_4N)]$ (4) and $[Os_3(CO)_{10}-(\mu-AuPPh_3)(\mu-SC_5H_4N)]$ (5). The molecular structures of 4 and 5 were obtained by single crystal X-ray diffraction studies.



Errun Ding, Bin Du, Sheldon G. Shore

J. Organomet. Chem. 692 (2007) 2148

Preparation and crystal structures of an ionic triple-hydrogen-bridged derivative of 9-BBN hydroborate zirconium(IV)

An ionic dinuclear triple-hydrogen-bridged 9-BBN hydroborate zirconium complex, $[K(Et_2O)_4][{(\mu-H)_2BC_8H_{14}}_3Zr(\mu-H)_3Zr{(\mu-H)_2-BC_8H_{14}}_3]$ (1) was formed from the reaction of $Zr{(\mu-H)_2BC_8H_{14}}_4$ with KH and aniline in diethyl ether. Its molecular structure was determined. 9-BBN hydroborate ligands are coordinated to Zr atoms via bridging H atoms, with two Zr atoms bridged to each other by three hydrogens.



Clara Pampillón, Nigel J. Sweeney, Katja Strohfeldt, Matthias Tacke

J. Organomet. Chem. 692 (2007) 2153

Synthesis and cytotoxicity studies of new dimethylamino-functionalised and heteroaryl-substituted titanocene anti-cancer drugs

Bis-(*N*,*N*-dimethylamino-2(*N*-methylpyrrolyl)methylcyclopentadienyl) titanium (IV) dichloride is the most cytotoxic titanocene synthesised so far. It was synthesised starting from 2-(*N*-methylpyrrolyl) lithium and 6-*N*,*N*dimethylamino fulvene. Herein, we present the synthesis and DFT structure of the titanocene and two further derivatives followed by MTTbased cytotoxicity tests on LLC-PK cells.



Vadim A. Pestunovich, Svetlana V. Kirpichenko, Natal'ya F. Lazareva, Aleksander I. Albanov, Mikhail G. Voronkov

J. Organomet. Chem. 692 (2007) 2160

Pentacoordinate hydrochlorosilanes with lactamomethyl ligand A series of novel pentacoordinate amide-type silicon complexes $LCH_2SiRHCl$ (L-2-piperidonyl ligand, R = Me, Ph, Bn) (5-8) were synthesized and structurally characterized by multinuclear NMR spectroscopy.



Mothi Mohamed Ebrahim, Helen Stoeckli-Evans, Krishnaswamy Panchanatheswaran

J. Organomet. Chem. 692 (2007) 2168

Synthesis of monoorganotin(IV) chloride complexes of *cis*-1,2-bis(diphenylphosphino)ethylene: Solution and solid state structures The reaction of RSnCl₃ with *cis*-Ph₂PCH= CHPPh₂ yields chelate complexes [RSnCl₃(*cis*-*Ph*₂*PCH*=*CHPPh*₂)] [R = Me (1), "Bu (2), Ph (3)]. The complexes have been characterized both in solution and solid state. In solution, the complexes undergo redistribution to form [SnCl₄(*cis*-*Ph*₂*PCH*=*CHPPh*₂)] (4).



John P. Lee, J. Oscar C. Jimenez-Halla, Thomas R. Cundari, T. Brent Gunnoe

J. Organomet. Chem. 692 (2007) 2175

Reactivity of TpRu(L)(NCMe)R (L = CO, PMe₃; R = Me, Ph) systems with isonitriles: Experimental and computational studies toward the intra- and intermolecular hydroarylation of isonitriles

The Ru(II) phenyl complex TpRu(PMe₃)-(NCMe)Ph {Tp = hydridotris(pyrazolyl)borate} reacts with isonitriles to form complexes of the type TpRu(PMe₃)($C\equiv$ NR)Ph (R='Bu, CH₂Ph, CH₂CH₂Ph). Consistent with experimental studies, DFT calculations revealed that intramolecular hydroarylation of β -phenethylisonitrile to produce imine is a high energy process due to the strong coordinating nature of the isonitrile.



Waly Diallo, Cheikh A.K. Diop, Libasse Diop, Mary F. Mahon, Kieran C. Molloy, Umberto Russo, Monique Biesemans, Rudolph Willem

J. Organomet. Chem. 692 (2007) 2187

Molecular structures of $[(Ph_3Sn)_2O_3Se]$ and $[(Ph_3Sn)_2O_4Cr](CH_3OH)$

Molecular structures of $[(Ph_3Sn)_2O_3Se]$ (1) and $[(Ph_3Sn)_2O_4Cr](CH_3OH)$ (2) consists of polymers containing two types of tin centres. In the case of the chromato derivative the pendant tin is also bonded to the oxygen atom of the solvent (methanol).Variable temperature Mössbauer spectroscopy data are consistent with the polymeric structure of the selenito derivative while NMR spectroscopy shows the presence of monomeric species in solution.



Contents

Maarit Risto, Esther M. Jahr, Milja S. Hannu-Kuure, Raija Oilunkaniemi, Risto S. Laitinen

J. Organomet. Chem. 692 (2007) 2193

Structural and spectroscopic trends in mononuclear arylchalcogenolato-palladium(II) and -platinum(II) complexes: Crystal structures of [M(TeAr)₂(dppe)] {M = palladium, platinum; Ar = phenyl, 2-thienyl; dppe = 1,2-bis(diphenylphosphino)ethane} Preparation, X-ray structures, and NMR spectroscopic properties of $[M(EAr)_2(dppe)]$ {E = Se, Te; Ar = Ph, 2-thienyl; dppe = 1,2-bis(diphenylphosphino)ethane} were systematically examined with a special emphasis on tellurolato complexes for which solid-state structural data are virtually non-existent.

Zhi-Gang Ren, Hong-Xi Li, Ling-Ling Li, Yong Zhang, Jian-Ping Lang, Jun-Yi Yang, Ying-Lin Song

J. Organomet. Chem. 692 (2007) 2205

Synthesis, crystal structures and third-order nonlinear optical properties of a new family of double incomplete cubane-like clusters $[(\eta^5-C_5Me_5)_2Mo_2(\mu_3-S)_3SCu_2X(\mu-X)]_2$ (X = Cl⁻, Br⁻, SCN⁻) and cubane-like clusters $[(\eta^5-C_5Me_5)_2Mo_2(\mu_3-S)_4(CuX)_2]$ (X = Br⁻, SCN⁻, CN⁻)

The reactions of *trans*- $[(\eta^5-C_5Me_5)_2Mo_2(\mu-S)_2S_2]$ with 2 equiv. of CuX (X = Cl⁻, Br⁻, SCN⁻, CN⁻) resulted in a set of double incomplete cubane-like clusters $[(\eta^5-C_5Me_5)_2-Mo_2(\mu_3-S)_3SCu_2X(\mu-X)]_2$ (X = Cl⁻ (2), Br⁻ (4), SCN⁻ (6)) and cubane-like clusters $[(\eta^5-C_5Me_5)_2Mo_2(\mu_3-S)_4(CuX)_2]$ (X = Br⁻ (3), SCN⁻ (5), CN⁻ (7)). All these compounds were fully characterized by elemental analysis, IR, UV–Vis, ¹H NMR and X-ray crystallography and their third-order nonlinear optical (NLO) properties of clusters were investigated.



Sven Dabek, Marc Heinrich Prosenc, Jürgen Heck

J. Organomet. Chem. 692 (2007) 2216

 $(\eta^4$ -Tetraarylcyclobutadiene) $(\eta^5$ -formylcyclopentadienyl)cobalt(I) complexes: Facilities to finetune the electron-donating capability in dipolar organometallics

 $(\eta^4$ -Tetraarylcyclobutadiene) $(\eta^5$ -formylcyclopentadienyl)cobalt(I) complexes (1a–1e) were synthesized. Compounds 1c and 1e were characterized by means of X-ray structure determination. Cyclic voltammetry studies were performed and the results are explained by DFT calculations on the $(\eta^4$ -cyclobutadiene) $(\eta^5$ -cyclopentadienyl)cobalt complex in its neutral, monocationic and dicationic state.



X = Cl (1a), H (1b), Me (1c), OMe (1d), NMe₂ (1e)

Mohammad El-khateeb, Khawla Damer, Helmar Görls, Wolfgang Weigand

J. Organomet. Chem. 692 (2007) 2227

Pyridine- and pyrimidine-2-thiolate complexes of ruthenium

 $CpRu(PPh_3)(\kappa^2 S, N-SR)$ Compounds (1)(SR = pyridine-2-thiolate (a), pyrimidine-2thiolate (b)) were prepared by reacting the thiolato anions (RS⁻) with CpRu(PPh₃)₂Cl. Complexes 1 readily react with NOBF₄ or CO to give $[CpRu(PPh_3)(NO) (\kappa^1 S-HSR)][BF_4]_2$ (2) and CpRu(PPh₃)(CO)($\kappa^{1}S$ -SR) (3), respectively. The one-pot reaction of CpRu-(PPh₃)₂Cl, thiolato anions and dppe gave $CpRu(dppe)(\kappa^1 S-SR)$ (4). The complex salts [CpRu(dppe)(ĸ¹S-HSR)]BPh₄ (5) are prepared by mixing CpRu(PPh₃)₂Cl, HSR and NaBPh₄. The structures of 1a, 2a and 3a have been determined.



Contents

J.S. Casas, M.V. Castaño, M.C. Cifuentes, J.C. García-Monteagudo, A. Sánchez, J. Sordo, A. Touceda

J. Organomet. Chem. 692 (2007) 2234

Interaction of organolead(IV) derivatives with formyl- and acetylferrocene thiosemicarbazones: Coordination versus dephenylation or reductive elimination processes The reaction of diphenyllead(IV) derivatives with the title ligands (HTSC) in methanol afforded either 1:2 adducts or 1:1 complexes (see scheme). With triphenyllead(IV), dephenylation occurred leading to diphenyllead(IV) compounds. The reaction of Me₂Pb(OAc)₂ and HTSC afforded only Pb(II) derivatives.



Luigi Busetto, Fabio Marchetti, Mauro Salmi, Stefano Zacchini, Valerio Zanotti

J. Organomet. Chem. 692 (2007) 2245

C–C bond formation through olefin–thiocarbyne coupling in diiron complexes Activated olefins, in the presence of NaH and Me_3NO , give regio- and stereo-specific addition at the bridging thiocarbyne ligand, in diiron complexes, affording novel bridging methylthio-functionalized allylidene complexes. The reactivity of these complexes is also reported.



Yong Leng Kelvin Tan, Weng Kee Leong

J. Organomet. Chem. 692 (2007) 2253

Ditertiary phosphine derivatives of the heteronuclear cluster $RuOs_3(\mu\mathchar`-H)_2(CO)_{13}$

The heteronuclear cluster $RuOs_3(\mu-H)_2(CO)_{13}$ (1) reacted readily with a number of ditertiary phosphines under chemical activation with TMNO. The solid-state and solution structures of these derivatives have been examined. Six structural types have been characterized crystallographically. There are many more isomers present in solution, most of which are rapidly inter-converting via hydride migrations.



Mhamed Lemhadri, Ahmed Battace, Touriya Zair, Henri Doucet, Maurice Santelli

J. Organomet. Chem. 692 (2007) 2270

Heck arylations of pent-4-enoates or allylmalonate using a palladium/tetraphosphine catalyst cis,cis,cis,cis-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane/1/2[PdCl(C₃H₅)]₂ system catalyses the Heck reactions of pent-4-enoates or dimethyl allylmalonate with a wide range of aryl bromides with medium to high selectivity and in high ratio substrate/catalyst.



Tell Tuttle, Dongqi Wang, Walter Thiel, Jutta Köhler, Marco Hofmann, Johann Weis

J. Organomet. Chem. 692 (2007) 2282

Mechanism of olefin hydrosilylation catalyzed by $[RuCl(NCCH_3)_5]^+$: A DFT study

Chloropenta(acetonitrile)ruthenium(II)⁺ (C1) is able to catalyze the hydrosilylation reaction between methyldimethoxysilane and methylvinyldimethoxysilane. The Chalk–Harrod, Glaser–Tilley and σ -bond metathesis mechanism were compared. We predict that a σ -bond metathesis mechanism involving the formation of a hydride analogue of C1 is most favored, in contrast to the commonly accepted Chalk–Harrod mechanism of hydrosilylation.



Manuel Gómez, Pilar Gómez-Sal, José Manuel Hernández

J. Organomet. Chem. 692 (2007) 2291

Synthesis of new chloro methyl niobium and tantalum complexes with silyl-cyclopentadienyl ligands: X-ray crystal structure of $[Ta\{\eta^5C_5-H_3(SiMe_3)_2\}Cl_2Me_2]$

We report herein the results obtained in the reactivity studies of the tetrachloro silylcyclopentadienyl niobium and tantalum complexes $[M{\eta^5-C_5H_3(SiXMe_2)(SiMe_3)}Cl_4]$ (M = Nb, X = Cl, 1a; Me 1b; M = Ta, X = Cl, 1c; Me, 1d) towards alkylating reagents and the structural characterization of the new methyl, dimethyl, trimethyl and tetramethyl derivatives synthesized.



Igor Novak, Branka Kovač

J. Organomet. Chem. 692 (2007) 2299

Photoelectron spectroscopy of metal $\beta\mbox{-diketo-nato}$ complexes

We discuss the metal–ligand bonding in the series of metal β -diketonato complexes on the basis of empirical arguments derived from photoelectron spectra. The photoionization cross-sections and orbital energies of metal atoms must both be taken into account in order to rationalize changes in relative band intensities of the HeI/HeII spectra.



Z.K. Yu, F.L. Zeng, X.J. Sun, H.X. Deng, J.H. Dong, J.Z. Chen, H.M. Wang, C.X. Pei

J. Organomet. Chem. 692 (2007) 2306

Two $pseudo\text{-}N_3$ ligands and the catalytic activity of their ruthenium(II) complexes in transfer hydrogenation and hydrogenation of ketones

Complex $RuCl_2(PPh_3)(iBu-BTP)$ (5) exhibited moderate to good and excellent catalytic efficiency in the transfer hydrogenation of ketones, and $RuCl_2(PPh_3)(Me_4BPPy)$ (1) showed good to excellent catalytic activity in hydrogenation of ketones. These results suggest that *iBu-BTP* and Me_4BPPy are promising *pseudo-N*₃ ligands to construct highly active transition-metal catalysts.



Sander G.A. van Assema, Petr B. Kraikivskii, Stanislav N. Zelinskii, Vitaly V. Saraev, G. Bas de Jong, Frans J.J. de Kanter, Marius Schakel, J. Chris Slootweg, Koop Lammertsma

J. Organomet. Chem. 692 (2007) 2314

Building blocks for phospha[n]pericyclynes

Amino-substituted bisethynylphosphines are building blocks for the synthesis of phospha[*n*]pericyclynes. The formation of tetraphospha[4]pericyclynes is demonstrated. Triethynylphosphines, bearing differently substituted alkynes, are reported as starting point toward novel three-dimensional phosphaacetylenic scaffolds for which DFT calculated structures are presented.



Teng-Yuan Dong, Mei-Ching Lin, Shu-Wei Chang, Chih-Chien Ho, Shu-Fan Lin, Liangshiu Lee

J. Organomet. Chem. 692 (2007) 2324

Synthesis, electrochemistry, and photophysical properties of binuclear ruthenium(II)–terpyridine complexes comprising redox-active ferrocenyl spacer

In attempting to perturb the electronic properties of the spacer, we now describe an interesting example of Ru^{2+} -terpyridine complexes with 1,1'-bis(ethynyl)ferrocenes moiety attached directly to the 4'-position of terpyridine ligand which have room-temperature luminescence in H₂O/CH₃CN (4/1) solution.



Francesca Micoli, Werner Oberhauser, Antonella Salvini, Claudio Bianchini

J. Organomet. Chem. 692 (2007) 2334

Chemoselective hydrogenation of α , β -unsaturated ketones to allylic alcohols, catalyzed by a mononuclear ruthenium complex containing *trans* P^{*n*}Bu₃ and PPh₃ ligands

Ru(CO)₂(OAc)₂(P^n Bu₃)(PPh₃) (OAc = acetate) containing two different *trans* phosphine ligands, has been employed as pre-catalyst for the chemoselective hydrogenation of α , β -unsaturated ketones to allylic alcohols. Batch catalytic reactions and *operando* high-pressure NMR experiments have contributed to establish that the hydrogenation of the C=O group is performed by the monohydride RuH-(CO)₂(OAc)(P^n Bu₃)(PPh₃).



Notes

Luciano Canovese, Fabiano Visentin, Gavino Chessa, Paolo Uguagliati, Claudio Santo, Lucia Maini

J. Organomet. Chem. 692 (2007) 2342

The synthesis of palladacyclopentadienyl derivatives from rigid bis-alkynes and their use as precursors in the synthesis of fluoroanthene-like cycles under mild condi-tions. A reactivity investigation The palladium(0) derivatives of the type $[Pd(\eta^2 ol)(LL')]$ (ol = dmfu: dimethylfumarate, fn: fumaronitrile, tmetc: tetramethylethylenetetracarboxylate, LL' = HNSPh: 2-(phenylthiomethyl)pyridine, BiPy: 2,2'-bipyridyl, DPPE: bis-diphenylphosphinoethane) were reacted in CH₂Cl₂ with 1,8-bis(methylpropynoate)naphthalene (1) and 2,2'-bis(methylpropynoate)biphenyl (1'). At variance with the flexible 1' derivative, the rigid bis-alkyne 1 reacts smoothly to give the corresponding cyclopalladate complexes [PdC₄-(COOMe)₂(Ph)₂(LL')] (3).



Arif Kivrak, Metin Zora

J. Organomet. Chem. 692 (2007) 2346

Efficient one-pot synthesis of cyanoferrocene from ferrocene carboxaldehyde using $\rm NH_2OH \cdot HCl/KI/ZnO/CH_3CN$ system A new and efficient one-pot synthesis of cyanoferrocene from ferrocenecarboxaldehyde is described by employing the NH₂OH \cdot HCl/KI/ ZnO/CH₃CN system.

Contents



Libor Dostál, Roman Jambor, Ivana Císařová, Ludvík Beneš, Aleš Růžička, Robert Jirásko, Jaroslav Holeček

J. Organomet. Chem. 692 (2007) 2350

Unexpected product formed by the reaction of $[2,6-(MeOCH_2)_2C_6H_3]$ Li with SbCl₃: Structure of Sb–O intramolecularly coordinated organoantimony cation The reaction of $[2,6-(MeOCH_2)_2C_6H_3]Li$ with SbCl₃ in 1:1 molar ratio yielded besides the intended product $[2,6-(MeOCH_2)_2C_6H_3]SbCl_2$ an unexpected complex consisting of antimony anion $[Sb_6Cl_{22}]^{4-}$ compensated by four intramolecularly coordinated organoantimony cations $[2,6-(MeOCH_2)_2C_6H_3]_2Sb^+$.



Holger Braunschweig, Fabian Seeler, Rainer Sigritz

J. Organomet. Chem. 692 (2007) 2354

Alternative synthesis and crystal structure of a [2]boraferrocenophane

The [2]boraferrocenophane $[(\eta^5-C_5H_4)-B(NMe_2)-B(NMe_2)-(\eta^5-C_5H_4)Fe]$ (1) was obtained from the reaction of FeCl₂ and $(Me_2N)_2B_2(\eta^1-C_5H_5)_2$ as a diborane(4) based ligand precursor in very good yields and fully characterized in the solid by single crystal X-ray diffraction.





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