Volume 693, issue 13, 15 June 2008

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



Contents

Review

SEVIER

Vincent O. Nyamori, Sabelo D. Mhlanga, Neil J. Coville

J. Organomet. Chem. 693 (2008) 2205

The use of organometallic transition metal complexes in the synthesis of shaped carbon nanomaterials

A review of the use of organometallic complexes in the synthesis of shaped carbon nanomaterials (SNCMs), in particular carbon nanotubes (CNTs) has been undertaken. This review reveals that a limited number of organometallic complexes have been used as catalysts to make carbon materials that have distinctive shapes.



Regular Papers

Katharina R. Nikolaides, Stephan D. Hoffmann, Jörg Eppinger

J. Organomet. Chem. 693 (2008) 2223

Synthesis of substituted 1,1'-diaminoferrocenes from cyclo-2-pentene imines The synthesis and characterisation of 1,1'diaminoferrocenes in two steps from a simple cyclopentenone precursor and primary amines is reported. Alternatively, LDA/FeCl₂ can be substituted by the less basic Fe[N(SiMe₃)₂]₂(thf) in the case of R = phenyl, where steric restrains are small.



Christian Taubmann, Evangeline Tosh, Karl Öfele, Eberhardt Herdtweck, Wolfgang A. Herrmann

J. Organomet. Chem. 693 (2008) 2231

Carbocyclic carbene ligands in palladiumcatalyzed C–N coupling reactions Palladium complexes supported by a cycloheptatrienylidene ligand showed significantly higher catalytic activities in Hartwig–Buchwald amination reactions than corresponding 2,3-diphenylcyclopropenylidene systems. The solid-state structure of *cis*-dibromo(cycloheptatrienyl-idene)(triphenylphosphane)palladium(II) was investigated and compared to the analogous chloro derivative.



Hassan Keypour, Reza Azadbakht, Sadegh Salehzadeh, Hamid Khanmohammadi, Hamidreza Khavasi, Harry Adams

J. Organomet. Chem. 693 (2008) 2237

Svnthesis. crvstal structure and spectroscopic properties of some cadmium(II) complexes with three polyamine and corresponding macroacyclic Schiff base ligands

Synthesis and characterization of six cadmium(II) complexes.



Stefan Köcher, Martin Lutz, Anthony L. Spek, Bernhard Walfort, Tobias Rüffer, Gerard P.M. van Klink, Gerard van Koten, Heinrich Lang

J. Organomet. Chem. 693 (2008) 2244

Oxime-substituted NCN-pincer palladium and platinum halide polymers through *non*-covalent hydrogen bonding (NCN = $[C_6H_2(CH_2NMe_2)_2-2,6]^-$) The synthesis of the oxime-substituted NCN-pincer molecules HON=CH-1-C₆H₃-(CH₂NMe₂)₂-3,5, HON=CH-4-C₆H₂(CH₂-NMe₂)₂-2,6-Br-1 and [(HON=CH-4-C₆H₂(CH₂NMe₂)₂-2,6)MBr] (M = Pd, Pt) is described. The solid state structures of these compounds are reported. By molecular recognition O-H···N and O-H···Br bonds are formed and hence, coordination polymers are set-up.



Sethuraman Kannan, M. Sivagamasundari, R. Ramesh, Yu Liu

J. Organomet. Chem. 693 (2008) 2251

Ruthenium(II) carbonyl complexes of dehydroacetic acid thiosemicarbazone: Synthesis, structure, light emission and biological activity Five new ruthenium(II) carbonyl complexes containing dehydroacetic acid thiosemicarbazone have been synthesized and characterized by analytical and spectral (IR, UV–Vis, and ¹H NMR) methods. The molecular structure of one of the complexes [Ru(dhatsc)(CO)(PPh₃)₂] (1) has been determined by single crystal X-ray diffraction. The complexes show better activity in inhibiting the growth of bacteria *Staphylococcus aureus* (209 P) and *Escherichia coli* (2231) and fungus *Candida albicans* and *Aspergillus niger*.



Donald S. Matteson, Davis Maliakal, Levente Fabry-Asztalos

J. Organomet. Chem. 693 (2008) 2258

Synthesis of a $(\beta$ -acetamido- α -acetoxyethyl)boronic ester via azido boronic esters

A (2-azido-1-chloroethyl)boronic ester resisted alkoxide substitution but yielded a mixture of epimeric acetates with sodium acetate via a carbocationic route. Azide hydrogenation in acid was accompanied by acetate cleavage to an α -hydroxy boronic ester that was unstable unless acylated promptly.



Yun Wei, Zeyan Yu, Shaowu Wang, Shuangliu Zhou, Gaosheng Yang, Lijun Zhang, Guodong Chen, Huimin Qian, Jiaxi Fan

J. Organomet. Chem. 693 (2008) 2263

Synthesis, characterization and catalytic activity of organolanthanide(II) complexes with heterocyclic-functionalized fluorenyl ligands

New organolanthanide(II) complexes with tetrahydro-2H-pyranyl- or *N*-piperidine-ethyl-functionalized fluorenyl ligands were synthesized. The complexes exhibited a good catalytic activity on MMA and ε -caprolactone polymerization.



Mala Nath, Pramendra K. Saini, George Eng, Xueqing Song

J. Organomet. Chem. 693 (2008) 2271

Synthesis and solid-state spectroscopic investigation of some novel diorganotin(IV) complexes of tetraazamacrocyclic ligands Diorganotin(IV) complexes of general formula $[R_2Sn(L-1)/R_2Sn(L-2)]$ where R = Me, *n*-Bu and Ph; H₂L-1 = 5,12-dioxa-7,14-dimethyl-1,4,8,-11-tetraazacyclotetradeca-1,8-diene and H₂ L-2 = 6,14-dioxa-8,16-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene have been synthesized and characterized in the solid-state by elemental analysis, IR, recently developed DART-mass, solid-state ¹³C NMR, ^{119m}Sn Mössbauer spectroscopic studies. Thermal studies of all of the studied complexes have also been carried out in the temperature range 0–1000 °C using TG, DTG and DTA techniques.



Rehana Malgas-Enus, Selwyn F. Mapolie, Gregory S. Smith

J. Organomet. Chem. 693 (2008) 2279

Norbornene polymerization using multinuclear nickel catalysts based on a polypropyleneimine dendrimer scaffold Four novel dendritic salicylaldimine complexes of Ni were evaluated as catalyst precursors in the polymerization of norbornene. The catalysts activated by methylaluminoxane show moderate to high activity producing polynorbornenes with relatively low polydispersity indices.

Guy K.B. Clentsmith, F. Geoffrey N. Cloke, Matthew D. Francis, John R. Hanks, Peter B. Hitchcock, John F. Nixon

J. Organomet. Chem. 693 (2008) 2287

Synthesis and structural characterisation of lanthanide and actinide phosphaorganometallic complexes derived from the 3,5-di-*tert*-butyl-1,2,4-triphospholyl ring anion, $P_3C_2Bu_2^t$: Crystal and molecular structures of $[M(\eta^5-P_3C_2Bu_2^t)_2(\eta^2-P_3C_2-Bu_2^t)]$ (M = Sc, Y, Tm, and U)

$$\begin{split} &MI_3 + 3KP_3C_2Bu_2^t \to M(P_3C_2Bu_2^{-t})_3 + 3KI \\ &1 \ M = Sc, \ 2 \ M = Y, \ 3 \ M = Tm, \ 4 \ M = U \end{split}$$

(1)



(t-Bu groups removed for clarity)

Lise Baiget, Rami El Ayoubi, Henri Ranaivonjatovo, Jean Escudié, Heinz Gornitzka

J. Organomet. Chem. 693 (2008) 2293

Chlorophosphaalkenyl- and chloroalkenylstibanes Mono-, bis- and tris(chlorophosphaalkenyl)stibanes have been obtained from Mes*P=C(SiMe_3)Li (Mes* = 2,4,6-tri-*tert*butylphenyl) or from the phosphaalkene carbenoid Mes*P=C(X)Li (X = Cl) and SbF₃, Mes*Sb(OMes*)F or Mes*SbF₂. Bis[chloroalkenyl]stibanes [R₂C=C(Cl)]₂SbCl (R₂C = fluorenylidene and 2,7-di-*tert*-butylfluorenylidene) have also been obtained from R₂C=C(Cl)Li and SbCl₃.

$$E = C_{\downarrow} \xrightarrow{1}_{n} SbR_{(3-n)}$$

(E = -P, >C; X = Cl, SiMe₃; n = 1-3)

Michael A. Scharwitz, Ingo Ott, Yvonne Geldmacher, Ronald Gust, William S. Sheldrick

J. Organomet. Chem. 693 (2008) 2299

Cytotoxic half-sandwich rhodium(III) complexes: Polypyridyl ligand influence on their DNA binding properties and cellular uptake The DNA binding of half-sandwich complexes of the types $[(\eta^5-C_5Me_5)RhCl(pp)]^+$ and $[(\eta^5-C_5Me_5)Rh\{(MeN)_2CS\}(pp)]^{2+}$ has been studied by spectroscopic and viscosity measurements. Strong intercalation is observed for the dpq and dppz complexes. The uptake and cytotoxicity for human MCF-7 and HT-29 cells increase with increasing polypyridyl (pp) ligand size in the order dpq < dppz < dppn.



Su Jing, Christopher P. Morley, Christopher A. Webster, Massimo Di Vaira

J. Organomet. Chem. 693 (2008) 2310

Synthesis and characterisation of Group 6 metal carbonyl complexes of bis(ferrocenylchalcogeno)propanes: X-ray crystal structures of [Cr(CO)₄{FcTe(CH₂)₃-TeFc}], [Mo(CO)₄{FcE(CH₂)₃E'Fc}] (E = E' = Se; E = Se, E' = Te; E = E' = Te), and [W(CO)₄{FcTe(CH₂)₃TeFc}](Fc = [Fe(η^5 -C₃H₅)-(η^5 -C₅H₄)]) Five complexes $[M(CO)_4{FcE(CH_2)_3E'Fc}]$ have been prepared and fully characterised. Electronic communication between the ferrocenyl groups is observed in the case of $[Mo(CO)_4{FcSe(CH_2)_3SeFc}]$, where the through-bond Fe…Fe distance is 13.17 Å, but in the other four complexes the longer through-bond Fe…Fe distances (\geq 13.56 Å) preclude it.



Mark R.J. Elsegood, Andrew J. Lake, Roger J. Mortimer, Martin B. Smith, George W. Weaver

J. Organomet. Chem. 693 (2008) 2317

Synthesis, coordination studies and redox properties of a novel ditertiary phosphine bearing two ferrocenyl groups

The new ferrocenyl functionalised ditertiary phosphine 1 along with some transition metal complexes of this ligand were prepared and studied by multinuclear NMR spectroscopy, single crystal X-ray diffraction and cyclic voltammetry. Solution and structural studies show that 1 can function as a chelating or bridging ligand upon metal coordination.



Simon G. Bott, Huafeng Shen, Shih-Huang Huang, Michael G. Richmond

J. Organomet. Chem. 693 (2008) 2327

CO substitution in $HRu_3(CO)_{10}(\mu$ -COMe) by the unsaturated diphosphine ligand 4,5bis(diphenylphosphino)-4-cyclopenten-1,3dione (bpcd): Synthesis and reactivity studies of the face-capped cluster $Ru_3(CO)_7(\mu_3$ -COMe)[μ -P(Ph)C=C(PPh_2)C(O)-CH_2C(O)] Thermolysis of HRu₃(CO)₁₀(μ -COMe) (1) with the unsaturated diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) affords the bpcd-chelated cluster HRu₃(CO)₈(μ -COMe)(bpcd) (2), which is unstable and transforms into the face-capped cluster Ru₃(CO)₇(μ ₃-CO-Me)[μ -P(Ph)C=C(PPh₂)C(O)CH₂C(O)] (4). The kinetics for the conversion of 2 to 4 have been investigated by UV–Vis spectroscopy, and the reactivity of 4 with H₂, PPh₃, and PMe₃ has been investigated, with the resulting triruthenium product clusters fully characterized in solution and X-ray crystallography.



Piotr Smoleński, Chiara Dinoi, M.Fatima C. Guedes da Silva, Armando J.L. Pombeiro

J. Organomet. Chem. 693 (2008) 2338

Synthesis of the water-soluble [Rh(Tpms)(CO)(PTA)] compound, the first transition metal complex bearing the 1,3,5-triaza-7-phosphaadamantane (PTA) and the tris(1-pyrazolyl)methanesulfonate (Tpms) ligands

The water-soluble [Rh(Tpms)(CO)(PTA)] complex has been prepared by a singlepot reaction of [{Rh(CO)₂(μ -Cl)}₂], PTA and Li(Tpms), in CH₂Cl₂/MeOH, and characterized by NMR spectroscopies, cyclic voltammetry, elemental and single crystal X-ray diffraction analyses.



Michel Guerro, Emmanuel Di Piazza, Xin Jiang, Thierry Roisnel, Dominique Lorcy

J. Organomet. Chem. 693 (2008) 2345

Dithiafulvenylphosphine as P- and P,Sligand towards metal carbonyl fragments The ability of the dithiafulvenylphosphine (P-DTF) to react as a monodentate (P) or a bidentate (P,S) ligand with metal carbonyl complexes such as $Mo(CO)_6$ and $MnBr(CO)_5$ allowed us to prepare a series of metal carbonyl complexes.



$ML_4 = Mo(CO)_4 \text{ or } MnBr(CO)_3$

Anu Ploom, Dmitri Panov, Jaak Järv, Ants Tuulmets

J. Organomet. Chem. 693 (2008) 2351

Rate and equilibrium constants for Grignard reaction with alkoxysilanes and ketones

Rate and equilibrium constants were determined for the reactions of alkoxysilanes with Grignard reagents specifically solvated with a variety of donors in toluene solutions. Thermodynamic parameters were determined from some rate and equilibrium constants and the implication of steric effects is discussed.



Wanli Nie, Longyu Liao, Wenqing Xu, Maxim V. Borzov, Dmitrii P. Krut'ko, Andrei V. Churakov, Judith A.K. Howard, Dmitri A. Lemenovskii

J. Organomet. Chem. 693 (2008) 2355

A novel bidentate 2-methylimidazolyl side-chain functionalized ligand, $LiC_5H_4CPh_2CH_2-(1-Me-C_3H_4N_2)$, has been prepared and characterized along with a set of its tin, titanium and zirconium derivatives.



Michael Werner, Clemens Bruhn, Dirk Steinborn

J. Organomet. Chem. 693 (2008) 2369

Diacetylplatinum(II) complexes (II) with chelating N^N ligands like 2,2'-bipyridine, 1,10-phenanthroline, 2,2'-bipyrimidine and 2,2'-bipyrazine were synthesized in a straightforward two step reaction starting from the platina- β -diketone [Pt₂{(CO-Me)₂H}₂(μ -Cl)₂] (I). The airstable complexes II were fully characterized by NMR and microanalysis. In the solid-state structures π - π stacking and hydrogen bonding were found to be important packing motifs.



M.D. Jones, M.F. Mahon

J. Organomet. Chem. 693 (2008) 2377

Synthesis of Rh(I) diamine complexes and their exploitation for asymmetric hydrogen transfer processes The synthesis, characterisation and catalytic activity of three new Rh(I) complexes are reported, together with the unusual product obtained from the recrystallisation of one of the diamine ligands in acetone.



Luigi Busetto, Marco Dionisio, Fabio Marchetti, Rita Mazzoni, Mauro Salmi, Stefano Zacchini, Valerio Zanotti

J. Organomet. Chem. 693 (2008) 2383

Zwitterionic diiron vinyliminium complexes: Alkylation, metalation and oxidative coupling at the S and Se functionalities Zwitterionic bridging vinyliminium complexes (I) easily and selectively undergo *S*alkylation and *S*-metalation affording type II complexes. Oxidative coupling is produced upon treatment of I with I₂, generating the tetranuclear species III. Similar reactions have been observed in zwitterionic complexes analogues to I, containing selenium in the place of sulphur.



Note

Wen-Yann Yeh, Meng-Jin Yu

J. Organomet. Chem. 693 (2008) 2392

Reaction of multifunctional molecule $(Ph_2P(o-C_6H_4)CH{=}NCH_2CH_2)_3N$ with triosmium carbonyl clusters

Reaction of $(Ph_2P(o-C_6H_4)CH=NCH_2CH_2)_3N$ with 3 equiv. of $Os_3(CO)_{10}(NCMe)_2$ affords the tripodal cluster $[Os_3(CO)_{10}Ph_2P(o-C_6H_4)CH=NCH_2CH_2]_3N$ (1), and thermolysis of which leads to decarbonylation and C-H/C-N bond activation of the ligand to generate $(\mu$ -H)Os_3(CO)_8(μ_3 -Ph_2P(o-C₆H₄)-CH=NC=CH₂) (2).





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