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Communication

Wanda Ziemkowska, Magdalena Metelska, Przemysław Kruk, Romana Anulewicz-Ostrowska

J. Organomet. Chem. 693 (2008) 369

Reaction of methyl aluminium-(2,2'-methylene-*p*-chloro-bisphenoxide) with 2,2'-di(hydroxymethyl)biphenyl: A new aluminium complex bearing two kinds of diolate ligands Methyl aluminium-(2,2'-methylene-*p*-chlorobisphenoxide), Me₅Al₃[OC₆H₃(Cl)CH₂C₆H₃-(Cl)O]₂, (1) reacted with 2,2'-di(hydroxymethyl)biphenyl to form Me₃Al₃[OC₆H₃(Cl)CH₂C₆H₃-(Cl)OH₂C₁₂H₈CH₂O)₂ (2) bearing two kinds of diolate ligands.



Regular Papers

Ramasamy Jothibasu, Han Vinh Huynh, Lip Lin Koh

J. Organomet. Chem. 693 (2008) 374

Au(I) and Au(III) complexes of a sterically bulky benzimidazole-derived *N*-heterocyclic carbene

A *trans*-configured benzimidazolin-2-ylidene complex of gold(III) *trans*-[AuI₂(ⁱPr₂-bimy)₂]BF₄ (**3**) was obtained in a 2-step approach through oxidative addition of I₂ to the bis(carbene) Au(I) complex $[Au(^{i}Pr_2-bi$ $my)_2]BF_4$ (**2**), which in turn was obtained by halo substitution of neutral monocarbene Au(I) complex $[AuCI(^{i}Pr_2-bimy)_2]$ (**1**). Complex **3** shows electronic absorption and photoluminescence behavior owing to a charge transfer from the iodo ligands to the Au(III) metal center.



Peter Butler, Anthony R. Manning, C. John McAdam, Jim Simpson

J. Organomet. Chem. 693 (2008) 381

The reactions of some $\sigma\text{-alkynylnickel}$ complexes with 7,7,8,8-tetracyanoquinodimethane

The C=C bonds of Ni(η -C₃H₃)(PPh₃)-C=C-R (1), insert into the C=C(CN)₂ of TCNQ to give Ni(η -C₃H₃)(PPh₃)-C{=C₆H₄=C(CN)₂}-C{=C(CN)₂}-R (4), which have UV-Vis spectra that are independent of the group R; similar reactions of Ni(η -C₃H₃)(PPh₃)-C=C-X-C=CH take place only at the Ni-C=C and not at the H-C=C.



Clément Lansalot-Matras, Fabien Bonnette, Emmanuel Mignard, Olivier Lavastre

J. Organomet. Chem. 693 (2008) 393

N-tripodal ligands to generate copper catalysts for the syndiotactic polymerization of methylmethacrylate: Crystal structures of copper complexes A library of tripodal ligands, based on a central nitrogen atom connected to three different functionalized arms, was investigated via a parallel approach for the polymerization of methyl-methacrylate. Copper salts CuCl₂ and Cu(OAc)₂ in combination with N-(2-furanylmethyl)-N-(1-3,5-dimethyl-1H-pyrazolylmethyl)-N-(phenylmethyl)amine were detected as efficient catalysts for syndiotactic polymerization ([rr] up to 78%).





Kin Shing Chan, Kin Wah Mak, Man Kin Tse, Siu Kwan Yeung, Bao Zhu Li, Yun Wai Chan

J. Organomet. Chem. 693 (2008) 399

Reactions of nitroxides with metalloporphyrin alkyls bearing beta hydrogens: Aliphatic carbon–carbon bond activation by metal centered radicals Beta hydrogen elimination of alkyl rhodium porphyrins and subsequent carbon–carbon bond activation with nitroxides.



Kevin R. Flower, Myles W. Garrould, Laura G. Leal, Claudia Mangold, Patrick J. O'Malley, Robin G. Pritchard

J. Organomet. Chem. 693 (2008) 408

The synthesis, reactivity and modelling studies of [RuCl(CO)(η^2 -*C*,*O*-C₆H₄-2-CHO)(PPh₃)₂]: Crystal and molecular structures of [RuCl-(CO)(η^2 -*C*,*O*-C₆H₄-2-CHO)(PPh₃)₂] · 3.5CHCl₃ and [Ru(NC'Bu)(CO)(η^2 -*C*,*O*-C₆H₄-2-CHO)-(PPh₃)₂][BF₄] · 2CHCl₃

A collection of cycloruthenated benzaldehyde complexes have been synthesised. The aldehyde C=O bond length increases significantly on going from neutral to cationic species. This has been seen in the solid state and modelled with DFT calculations (B3LYP LanL2DZ).



David Aguilar, Miguel Angel Aragüés, Raquel Bielsa, Elena Serrano, Tatiana Soler, Rafael Navarro, Esteban P. Urriolabeitia

J. Organomet. Chem. 693 (2008) 417

Synthesis and structure of orthopalladated complexes derived from prochiral iminopho-sphoranes and phosphorus ylides

The compounds $Ph_2MeP=NPh$ (1) and $Ph_2MeP=CHC(O)Ph$ (5) react with $Pd(OAc)_2$ to give the orthopalladated $[Pd(\mu-Cl)\{C_6H_4(PPh(Me)=NPh-\kappa-C,N)-2\}]_2$ (2), as the racemic mixture, and $[Pd(\mu-Cl)\{C_6H_4(PPh(Me)-CHC(O)Ph-\kappa-C,C)-2\}]_2$ (6), as a mixture of diastereoisomers with high d.e. The reactivity of 2 and 6 has been examined and the X-ray crystal structure of $[Pd(acac)\{C_6H_4(PPh(Me)=NPh-\kappa-C,N)-2\}]$ (3) has been determined.



Contents

Hayati Türkmen, Serpil Denizaltı, Ismail Özdemir, Engin Çetinkaya, Bekir Çetinkaya

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Synthesis and use of mono- or bisxylyl linked bis(benzimidazolium) bromides as carbene precursors for C–C bond formation reactions

Two benzimidazolium moieties linked by one or two xylyls (*m*-and *p*-) have been synthesized, characterized and then they were used for Heck coupling reactions as in situ formed catalysts. Mono bridged salts are more efficient as compared to bisbridged salts. In addition, mono bridged salts were converted to Rh– NHC complexes which were tested as catalysts for the arylation of aldehydes.



Ramón Macías, Mark Thornton-Pett, Josef Holub, Trevor R. Spalding, Yousafzai Faridoon, Bohumil Štíbr, John D. Kennedy

J. Organomet. Chem. 693 (2008) 435

Polyhedral metallathiaborane chemistry: Synthesis and characterisation of metallathiaboranes based on the twelve-vertex icosahedral $closo-\{MSB_{10}H_{10}\}$ unit, where M is Rh or Ir

A series of twelve-vertex *closo*-metallathiaboranes has been synthesized. Comparative analysis of NMR and X-ray diffraction data reveals metal-to-thiaborane bonding differences that have implications in the cluster structure and in the fluxional behaviour of some of the compounds.



Petr Štěpnička, Martin Lamač, Ivana Císařová

J. Organomet. Chem. 693 (2008) 446

Planar chiral alkenylferrocene phosphanes: Preparation, structural characterisation and catalytic use in asymmetric allylic alkylation Planar chiral alkenylferrocene phosphanes (S_p)-[Fe(η^5 -C₅H₃-1-PPh₂-2-CH=CR₂)(η^5 -C₅H₅)] (R = H, Ph) and (S_p)-[Fe(η^5 -C₅H₃-1-PPh₂-2-(E)-CH=CHR)(η^5 -C₅H₅)] (R = Ph, C(O)CH₃, and CO₂Et) form active catalysts for asymmetric palladium-catalysed allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate. However, the ee's are only modest (12–43%) and strongly depend on the properties of the double bond substitutents. The mechanism of stereodiscrimination is discussed in view of the solution and solid-state structural data for the cationic complex [Pd(η^3 -Ph₂C₃H₃){(S_p)-[Fe(η^5 -C₅H₃-1-PPh₂-2-CH=CH₂)(η^5 -C₅H₅]- η^2 : κP]CIO₄.



Sang Hoon Lee, Chun Ji Wu, Jina Yoo, Jung-eun Kwak, Hoseop Yun, Bun Yeoul Lee

J. Organomet. Chem. 693 (2008) 457

o-Phenylene-bridged Cp/amido titanium and zirconium complexes and their polymerization reactivity

o-Phenylene-bridged Me₃Cp/amido titanium and zirconium complexes were prepared and the structures were determined by X-ray crystallography. Some titanium complexes show comparable catalytic performance to the CGC ([Me₂Si(η^{5} -Me₄C₅)(N'Bu)]TiCl₂) in ethylene/ 1-octene copolymerization.



Tatiana Campos-Malpartida, Marianna Fekete, Ferenc Joó, Ágnes Kathó, Antonio Romerosa, Mustapha Saoud, Wojciech Wojtków

J. Organomet. Chem. 693 (2008) 468

Redox isomerisation of allylic alcohols catalysed by water-soluble ruthenium complexes in aqueous systems

The water-soluble ruthenium(II) complexes Na₄[{RuCl₂(*m*tppms)₂}₂], Na₄[{RuCl(μ -Cl)-(C=C=CPh₂)(*m*tppms)₂}₂], Na₂[RuClCp(*m*tppms)₂] and Na[Ru(CO)Cp(*m*tppms)₂] (*m*tppms = Ph₂P-C₆H₄-3-SO₃⁻) were found active catalysts of isomerization of allylic alcohols in water and in aqueous-organic biphasic systems with turnover frequencies up to 2226 h⁻¹. The reaction rates strongly depended on the pH with an optimum in the range pH 4–7.



Xiaojun Tan, Weihua Wang, Ping Li, Qiufen Wang, Gengxiu Zheng, Fei Liu

J. Organomet. Chem. 693 (2008) 475

Theoretical studies on the imine germylenoid HN=GeNaF and its insertion reaction with R-H (R = F, OH, NH_2 , CH_3)

The geometries and isomerization of the HN=GeNaF as well as its insertion reactions with R-H have been systematically investigated at the B3LYP/6-311+G^{*} level of theory. As a result, the relative reactivity among the four insertion reactions should be as follows: $H-F > H-OH > H-NH_2 > H-CH_3$.



Min Zhang, Peng Hao, Weiwei Zuo, Suyun Jie, Wen-Hua Sun

J. Organomet. Chem. 693 (2008) 483

2-(Benzimidazol-2-yl)-1,10-phenanthrolyl metal (Fe and Co) complexes and their catalytic behaviors toward ethylene oligomerization The $N^N N$ -tridentate metal complexes, LMCl₂ (M = Fe or Co; L represents a ligand of 2-(benzimidazol-2-yl)-1,10-phenanthrolines), were synthesized and fully characterized with spectroscopic and elemental analysis. Upon activation with modified methylaluminoxane (MMAO), these complexes performed good to high catalytic activities toward ethylene oligomerization.



Adrián Peña-Hueso, Adriana Esparza-Ruiz, Iris Ramos-García, Angelina Flores-Parra, Rosalinda Contreras

J. Organomet. Chem. 693 (2008) 492

Triphenyl lead, tin and germanium coordination compounds derived from 9H-3-thia-1,4a,9-triaza-fluorene-2,4-dithione Reactions of K 4-thioxo-3-thia-1,4a,9-triazafluorene-2-thiolate with Ph₃MCl, (Ge, Sn and Pb) provided metal pentacoordinated compounds. Addition of THF, DMSO, pyridine, Ph₃PO and CH₃OH afforded hexacordinated Sn and Pb compounds. A H₂O adduct was obtained for the Pb compound. In all cases the metal atom is chelated through S and N forming four membered rings. Compounds were identified by ¹H, ¹³C, ¹⁵N, ¹¹⁹Sn, ²⁰⁷Pb NMR and by X-ray diffraction.



Zekeriya Bıyıklıoğlu, Halit Kantekin

J. Organomet. Chem. 693 (2008) 505

A novel metal-free and metallophthalocyanines containing four 19-membered dithiadiazadioxa macrocycles by microwave irradiation: Synthesis and characterization The novel tetrasubstituted metal-free phthalocyanine (5) and metallophtalocyanines (6, 7 and 8) bearing four 19-membered dithiadiazadioxa macrocyclic moieties on peripheral positions have been synthesized by cyclotetramerization reaction of phthalonitrile derivative (4) in a multi-step reaction sequence. The new compounds were characterized by a combination of IR, ¹H NMR, ¹³C NMR, UV– Vis, elemental analysis and MS spectral data.

Dorota Duraczynska, Ewa M. Serwicka, Anna Waksmundzka-Gora, Alicja Drelinkiewicz, Zbigniew Olejniczak

J. Organomet. Chem. 693 (2008) 510

Immobilization of a cationic ruthenium(II) complex containing the hemilabile phosphaallyl ligand in hexagonal mesoporous silica (HMS) and application of this material as hydrogenation catalyst The cationic ruthenium(II) complex $[(\eta^5-Me-C_5H_4)Ru(\eta^3-PPh_2CHCH_2)(\eta^1-PPh_2CHCH_2)]^+$ (1) has been immobilized inside the pores of aluminated hexagonal mesoporous silica HMS(Si/Al = 40) by direct ion exchange method. This material was characterized and used as catalyst in the hydrogenation of phenylacetylene.

Igor B. Sivaev, Nadezhda Yu. Kulikova, Evgeniya A. Nizhnik, Maxim V. Vichuzhanin, Zoya A. Starikova, Andrei A. Semioshkin, Vladimir I. Bregadze

J. Organomet. Chem. 693 (2008) 519

Practical synthesis of 1,4-dioxane derivative of the *closo*-dodecaborate anion and its ring opening with acetylenic alkoxides ane derivative of the *closo*-dodecaborate anion was developed. The cleavage of the dioxonium ring in $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ with acetylenic alcohols give rise to *closo*-dodecaborate derivatives with terminal acetylene group. The click reaction of the acetylene derivatives with phenylazide results in the corresponding triazoles. The structures of $(Bu_4N)[B_{12}H_{11}O(CH_2-CH_2)_2O]$ and $(Bu_4N)_2[B_{12}H_{11}(OCH_2CH_2)_2-OCH_2C\equiv CH] \cdot 0.5HOCH_2C\equiv CH$ were determined by single-crystal X-ray diffraction.

MTT-based cytotoxicity tests on pig kidney epithelial (LLC-PK) cells completed.

Practical method of synthesis of the 1,4-diox-

James Claffey, Megan Hogan, Helge Müller-Bunz, Clara Pampillón, Matthias Tacke

J. Organomet. Chem. 693 (2008) 526

Synthesis and cytotoxicity studies of methoxy benzyl substituted titanocenes

Four benzyl substituted titanocenes were synthesised through the hydridolithiation reaction of 6-aryl substituted fulvenes with LiBEt₃H. Within the synthesis of the four titanocene derivatives are reported along with a structural discussion of either their X-ray diffraction or calculated structure. Each compound had







Fu-Chen Liu, Pei-Shan Yang, Chun-Yu Chen, Gene-Hsian Lee, Shie-Ming Peng

J. Organomet. Chem. 693 (2008) 537

Syntheses, structures, and dynamic properties of $M(CO)_2(\eta^3-C_3H_5)(L-L)(NCBH_3)$ (M = Mo, W; L-L = dppe, bipy, en) The cyanotrihydroborate complexes $M(CO)_2$ -(η^3 -C₃H₅)(L–L)(NCBH₃) (M = Mo, W; L–L = dppe, bipy, en) were prepared and characterized. Those with dppe or en ligands are fluxional in solution and possess asymmetric structures in the solid state. For the complexes with bipy ligand both *endo-* and *exo*-isomers coexist in solution while only *endo-* form has been found in the solid state.

Notes

Ying-Feng Han, Wei-Guo Jia, Yue-Jian Lin, Guo-Xin Jin

J. Organomet. Chem. 693 (2008) 546

Stepwise formation of metallo-prisms of iridium and rhodium complexes bearing pentamethylcyclopentadienyl ligands

Iridium and rhodium metallo-prisms **3a** and **3b** bearing pentamethylcyclopentadienyl and bridging chloro ligands, connected by two 2,4,6-tripyridyl-1,3,5-triazine (tpt) subunits have been synthesized and characterized structurally (black: C; green: Rh; red: Cl; blue: N).



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Craig Streu, Patrick J. Carroll, Rakesh K. Kohli, Eric Meggers

J. Organomet. Chem. 693 (2008) 551

Synthesis of cyclopentadienyl ruthenium complexes bearing pendant chelating picolinates through an electrophilic precursor The facile synthesis of two ruthenium cyclopentadienyl half-sandwich complexes functionalized with coordinating α -picolinates is reported. The synthetic approach involves the $(\eta^5$ -chloromethylcyclopentadienyl)(η^6 -benzene)-ruthenium(II) cation as a useful common building block for cyclopentadienyl complexes bearing anchored ligands.



Ludmila Vigo, Merja J. Poropudas, Raija Oilunkaniemi, Risto S. Laitinen

J. Organomet. Chem. 693 (2008) 557

 $\label{eq:preparation} \begin{array}{l} Preparation \mbox{ and structural characterization of } [RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2] \mbox{ and } [RuCl_2-(CO)\{Te(CH_2SiMe_3)_2\}_3] \end{array}$

The reaction of Te(CH₂SiMe₃)₂ and [RuCl₂-(CO)₃]₂ affords a mixture of mononuclear ruthenium complexes [RuCl₂(CO)₂{Te(CH₂-SiMe₃)₂}₂] (1) and [RuCl₂(CO){Te(CH₂SiMe₃)₂}₃] (2). The X-ray structures show the formation of the *cis*(Cl), *cis*(C), *trans*(Te) isomer of 1 and the *cis*(Cl), *mer*(Te) isomer of 2.



Sonia G. Thangavelu, Kathryn E. Hocker, Shayna R. Cooke, Clare N. Muhoro

J. Organomet. Chem. 693 (2008) 562

Synthetic, spectroscopic and structural studies of two novel phosphanyl(organyl)borane compounds

The titanium (II) complex, Cp₂Ti(HBcat)₂, catalyzes the hydroboration of diphenylvinylphosphine by catecholborane and pinacolborane to afford exclusive anti-Markovnikov phosphanyl(organyl)boranes cleanly, rapidly and in good yields. Spectroscopic and X-ray studies of the phosphanyl(organyl)borane products show no evidence of boron–phosphorus interaction, indicating that the compounds preclude formation of Lewis pairs.



Piyali Datta Chaudhuri, Ruiyun Guo, Helena C. Malinakova

J. Organomet. Chem. 693 (2008) 567

Formation of benzofurans in a stoichiometric annulation reaction between stable Pallada (II) Cycles hypervalent vinyl- and alkynyl(phenyl)iodonium salts Stable pallada(II)cycles reacted with vinyl- and alkynyl(phenyl)iodonium salts to afford substituted benzofurans via a pathway presumed to involve transient Pd(IV) intermediates.



Jean-Cyrille Hierso, David Evrard, Dominique Lucas, Philippe Richard, Hélène Cattey, Bernard Hanquet, Philippe Meunier

J. Organomet. Chem. 693 (2008) 574

"Through-space" ${}^{31}P$ spin–spin couplings in ferrocenyl tetraphosphine coordination complexes: Improvement in the determination of the distance dependence of J_{PP} constants

The study of a new palladium dibromide ferrocenyl tetraphosphine complex of blocked conformation (solution NMR correlated with solid state X-ray) lead to a confirmation and a mathematic refinement of the $P \cdots P$ throughspace distances dependence of J_{PP} spin–spin coupling constants.



François Jean-Baptiste dit Dominique, Heinz Gornitzka, Catherine Hemmert

J. Organomet. Chem. 693 (2008) 579

N-functionalised heterocyclic dicarbene complexes of silver: Synthesis and structural studies A series of alcohol functionalised diimidazolium salts bridged by an alkyl arm was synthesized, using a modular strategy. The corresponding silver–carbene complexes were obtained. X-ray structures of two dinuclear Ag(I) complexes, involving a trimethylenebridged bis-carbene ligand and non-coordinating anions TsO⁻ or PF_6^- , showed crossed and parallel conformations, respectively.



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