Volume 694, Issue 5, 1 March 2009

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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



Contents

Communications

Zhiming Zhou, Weizhe Xue

J. Organomet. Chem. 694 (2009) 599

Manganese-catalyzed oxidative homocoupling of aryl Grignard chlorides Manganese-catalyzed homo-coupling of aryl magnesium chlorides to give biphenyls was successfully achieved using manganese chloride as catalyst. A variety of aryl magnesium chlorides were efficiently converted into the corresponding symmetrical biaryls using 10 mol% MnCl₂ as catalyst in the presence of a stoichiometric amount of 1,2-dichloroethane.



Stéphane Bellemin-Laponnaz, Richard Welter, Lydia Brelot, Samuel Dagorne

J. Organomet. Chem. 694 (2009) 604

Synthesis and structure of V(V) and Mn(III) NHC complexes supported by a tridentate *bis*-aryloxide-N-heterocyclic carbene ligand A novel tridentate *O,C,O-bis*-aryloxide-N-heterocyclic carbene proligand was efficiently synthesized in a two-step procedure. Preliminary studies suggest that this new ligand may exhibit a quite versatile coordination chemistry as it was found to form robust and air-stable NHC-based V(V) and Mn(III) metal complexes.



Regular Papers

Alexander A. Korlyukov, Konstantin A. Lyssenko, Mikhail Yu. Antipin, Ekaterina A. Grebneva, Aleksander I. Albanov, Olga M. Trofimova, Eleonora A. Zel'bst, Mikhail G. Voronkov

J. Organomet. Chem. 694 (2009) 607

Si-Fluoro substituted quasisilatranes (N \rightarrow Si) FYSi(OCH₂CH₂)₂NR

The title compounds were obtained by the reaction of fluorosilanes $XYSiF_2$ with diethanolamines or their O-trimethylsilyl derivatives. The quasisilatranes 3, 5 and 9 were characterized by the multinuclear NMR spectroscopy, X-ray diffraction method and quantum chemical calculations.



X = Y = F (3); X = Ph, Y = F (5);X = Me, Y = F (9)

Raúl Salas-Coronado. Raúl Colorado-Peralta, Sonia A. Sánchez-Ruiz. **Rosalinda Contreras**, Angelina Flores-Parra

J. Organomet. Chem. 694 (2009) 616

Seven membered ring chelates derived from γ -hydroxyamides and triphenyltin or diphenylboron

New diphenylboron and triphenyltin compounds derived from γ -hydroxy-amides were prepared. The crystalline structure

Ramesh Kapoor, Anand Gupta, Paloth Venugopalan, Aiav Pal Singh Pannu. Maninder Singh Hundal, Pratibha Kapoor

J. Organomet. Chem. 694 (2009) 623

Structural studies of diorganotin(IV) sulfonates: The synthesis of $[(n-C_4H_9)_2Sn\{OSO_2C_6H_3(CH_3)_2 [(n-C_4H_9)_2Sn\{OSO_2R\}_2 \cdot 2(hexa 2,5_2$ and methylphosphoric triamide)] [R = CH₃, 4-C₆H₄CH₃, 2,5-C₆H₃(CH₃)₂, 2,4,6-C₆H₂(CH₃)₃] and crystal structures of [(n-C₄H₉)₂Sn(μ-OH)- $(OSO_2C_6H_3(CH_3)_2-2,5)]_2$ and $(n-C_4H_9)_2 Sn{OSO_2R}_2 \cdot 2(hexamethylphosphoric triamide)]$ $[R = 4-C_6H_4CH_3, 2, 5-C_6H_3(CH_3)_2, 2, 4, 6-C_6H_2(CH_3)_3]$

Houjin Hachiya, Toshiyuki Kakuta, Makoto Takami, Yoshio Kabe

J. Organomet. Chem. 694 (2009) 630

Syntheses and crystal structures of azafulleroid and aziridinofullerene bearing silyl or germyl benzene

structures of two azafulleroids with the help of silvl and germylphenyl- C_{60} effective interactions. POAV analysis leads to a strong enhancement of homoconjugation in the bridged annulene moiety.

of (R)-4-hydroxy-2-methyl-N-[(R)-1-phenyl-ethyl]-butyramide is reported, as well as that of the first example of a X-ray diffraction analysis of a crystalline structure where a diphenylborinic ester forms a seven membered chelate diphenylborinic acid 3-benzylcarbamoyl-propyl ester. Structural studies of tin and boron esters were performed by NMR. The C=O internal coordination to tin atoms, affording seven membered rings, was observed by ¹¹⁹Sn NMR experiments at low temperature.

Contents

Reaction of (n-C₄H₉)₂SnO with 2,5-dimethylbenzenesulphonic acid yields [(n- $C_4H_9)_2Sn\{OSO_2C_6H_3(CH_3)_2-2,5\}_2\}$ which on crystallization yields a dimeric compound $[(n-C_4H_9)_2Sn(\mu-OH)(OSO_2C_6H_3(CH_3)_2-2,5)]_2$ containing bridging hydroxyl groups between Sn atoms and covalently bonded sulfonate anions.





X-ray crystal structures of two azafulleroid ([5,6]open)

Claire Jahier, Sylvain Nlate

J. Organomet. Chem. 694 (2009) 637

Dendritic polyallyl and polyferrocenyl bipyridine ligands: Synthesis, MALDI-TOF characterization and ruthenium(II) complexation studies

Dendritic polyallyl- and polyferrocenyl bipyridine ligands were synthesized by the coupling of 4,4'-bis(bromomethyl)-2,2'-bipyridine with AB3 and AB9 dendrons. The complexation studies indicates that in contrast to the bulky ferrocenyl ligand, the allyl counterparts react with Ru(bpy)₂Cl₂ to give the corresponding complexes. These compounds were successfully characterized by MALDI-TOF mass spectrometry.







Mothi Mohamed Ebrahim, Krishnaswamy Panchanatheswaran, Antonia Neels, Helen Stoeckli-Evans

J. Organomet. Chem. 694 (2009) 643

Mercury(II) complexes of stabilized phosphine-phosphonium ylide derived from bis(diphenylphosphino)methane: Synthesis, spectra and crystal structures The reaction of a mixed phosphine–phosphonium ylide, $PPh_2CH_2PPh_2=C(H)C(O)Ph$ with mercury(II) halides in methanol under mild conditions yielded the P, C-chelated complexes, $[HgX_2(PPh_2CH_2PPh_2C(H)C(O)-Ph)]$ where X = Cl (2), Br (3), I (4). The five-membered chelate rings in the two independent molecules present in the asymmetric unit of 4 adopt 'envelope' and 'twist' conformations.



Ari Lehtonen, Hynek Balcar, Reijo Sillanpää

J. Organomet. Chem. 694 (2009) 649

Aminobis(phenolate)s of imidomolybdenum(VI) and -tungsten(VI) Air-stable imidotungsten(VI) and imidomolybdenum(VI) complexes with tridentate aminobis(phenolate) ligands were prepared. A tungsten derivative [W(NPh)-(ONO^R)Cl₂] reacts further with MeMgI to yield air- and moisture-stable organometallic compound *cis*-[W(NPh)(ONO^R)(Me)₂].



Alexander Jakob, Petra Ecorchard, Michael Linseis, Rainer F. Winter, Heinrich Lang

J. Organomet. Chem. 694 (2009) 655

Synthesis, solid state structure and spectro-electrochemistry of ferroceneethynyl phosphine and phosphine oxide transition metal complexes The synthesis of compounds (FcC \equiv C)_n-Ph_{3-n}P (Fc = (η^5 -C₅H₅)(η^5 -C₅H₄)Fe) and their complexation behavior toward PtCl₂, AuCl and AuC \equiv CMc (Mc = Fc, Rc; Rc = (η^5 -C₅H₅)(η^5 -C₅H₄)Ru) is described. The structure of six molecules in the solid state and the spectro-electrochemical properties of *trans*-[((FcC \equiv C)Ph₂P)₂Pt(C \equiv CFc)₂], [((FcC \equiv C)Ph₂P)AuC \equiv C-Mc], [((FcC \equiv C)Ph₂P)AuCI], and [(Ph₃P)AuC \equiv CFc] for comparison, are reported.



Peter B. Hitchcock, Michael F. Lappert, Mikko Linnolahti, Rafaël Sablong, John R. Severn

J. Organomet. Chem. 694 (2009) 667

Synthesis and structures of the transition metal(II) β -diketiminates $[ML_2]$ (M = Mn, Fe, Ni, Cu, Pd), $[ML_2']$ (M = Ni, Cu) and $[M(\eta^3-C_3H_5)L]$ (M = Ni, Pd); L or L' = $[\{N(SiMe_3 \text{ or } H)C(Ph)\}_2CH]$

The X-ray analysis of the homoleptic metal(II) β -diketiminates showed three structural types: (i) pseudo-tetrahedral complexes with planar rings formed by the metal atom M and the κ^2 -N,N'-coordinated ligand (M = Mn, Fe, Ni, Cu), (ii) square-planar complexes with planar metal-ligand rings (M = Ni, Cu), and (iii) a square-planar complex with boat-shaped M–L rings (M = Pd).



Boris A. Trofimov, Nina K. Gusarova, Svetlana N. Arbuzova, Nina I. Ivanova, Alexander V. Artem'ev, Pavel A. Volkov, Igor' A. Ushakov, Svetlana F. Malysheva, Vladimir A. Kuimov

J. Organomet. Chem. 694 (2009) 677

Stereoselective free-radical addition of secondary phosphine selenides to aromatic acetylenes

Reported herein are the stereoselective free-radical additions (AIBN, 65–70 °C) of secondary phosphine selenides to aromatic and heteroaromatic acetylenes. UV irradiation of the reactants distorts stereoselectivity due to isomerization of the primary *Z*-adducts. Microwave activation of the process allows the reaction time to be reduced significantly.



NC Palladacycle

NMP, 110⁰C, NaOAc

AcOH

Shashi B. Atla, Ashutosh A. Kelkar, Vedavati G. Puranik, Wolfgang Bensch, Raghunath V. Chaudhari

J. Organomet. Chem. 694 (2009) 683

NC palladacycles in the Heck arylation of ethylene: Synthesis, structure and their reactivity

New NC palladacycles have been prepared and used in the arylation of ethylene with industrially important substrate 2-bromo-

Qiuwen Wang, Li Xiang, Haibin Song, Guofu Zi

J. Organomet. Chem. 694 (2009) 691

Synthesis, structure, and catalytic activity of binuclear lanthanide complexes with chiral NOBIN-based NNO ligands

6-methoxynaphthalene to give 2-vinyl-6methoxynaphthalene, an intermediate for the synthesis of anti-inflammatory drug naproxen. The structures of new palladacycles have been determined by single crystal X-ray diffraction studies. The NC palladacycles exhibit excellent catalytic activity with TOF > 4000 h⁻¹. Finally the NC palladacycles have also been demonstrated in the arylation of ethylene with 3bromo-benzophenone and 4-bromo-isobutylbenzene, the precursors of Ketoprofen and Ibuprofen, respectively.

Two new binuclear lanthanide amides with chiral NNO ligands have been prepared. They are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes and the ring-opening polymerization of *rac*-lactide, affording cyclic amines in excellent conversions with moderate ee values and isotactic-rich polylactides, respectively.

Jin Zhou, Xuming Guo, Changzheng Tu, Xiaoyan Li, Hongjian Sun

J. Organomet. Chem. 694 (2009) 697

Aqueous Suzuki coupling reaction catalyzed by water-soluble diimine/Pd(II) systems

A series of water-soluble diimine ligands were applied for the Suzuki reaction of arylbromide in different media. Low loading of catalyst (0.01 mol%) were necessary for the coupling reaction to proceed in water or water/ethanol. The catalytic system was found to tolerate a broad range of functional groups.







Renan Cariou, Vernon C. Gibson, Atanas K. Tomov, Andrew J.P. White

J. Organomet. Chem. 694 (2009) 703

Group 4 metal complexes bearing new tridentate (NNO) ligands: Benzyl migration and formation of unusual C-C coupled products

A series of Group 4 metal complexes bearing new phenoxy(benzimidazolyl)imine, -amine and -amide ligands has been synthesized. Derivatives containing benzyl ligands undergo benzyl migration and an unusual C-C coupling process to afford binuclear species in which the metals are linked by a central piperazine unit. Deuterium labelling experiments have been employed to determine the mechanistic pathways for these reactions.



Carolina Valdebenito, María Teresa Garland, Raul Quijada, Rene Rojas

J. Organomet. Chem. 694 (2009) 717

Acetamidine complexes as catalysts for ethylene polymerization

New (N)-imidoylamidine nickel complexes polymerize ethylene in good yield and afford a polymer of high molecular weight $(80-169 \times 10^3 \text{ g mol}^{-1})$ and a monomodal molecular weight distribution (M_w/M_n 1.8). Variation of the polymerization conditions (increasing polymerization temperature) results in a bimodal molecular weight distribution, likely indicating the activation of a secondary active site.



Carlos Camacho-Camacho, Adriana Esparza-Ruiz, Aurora Vásquez-Badillo, Heinrich Nöth, Angelina Flores-Parra, Rosalinda Contreras

J. Organomet. Chem. 694 (2009) 726

Fused hexacyclic tin compounds derived from 3-(3,5-di-*t*-butyl-2-hydroxy-phenylimino)-3H-phenoxazin-2-ol The template synthesis of dimethyl (1) and diphenyl tin (2) compounds $[N \rightarrow Sn]$ 3-(2-oxo-phenylimino)-3Hphenoxazin-2-oxo-tin (1) is reported. They are fused delocalized planar hexacyclic systems bearing a pentacoordinated diorganyl tin and were identified by NMR, IR, TOF mass spectra and, for 1, by X-ray diffraction analysis.



Osman Akba, Feyyaz Durap, Murat Aydemir, Akın Baysal, Bahattin Gümgüm, Saim Özkar

J. Organomet. Chem. 694 (2009) 731

Synthesis and characterizations of *N*,*N*,*N'*,*N'*-tetrakis (diphenylphosphino)-ethylendiamine derivatives: Use of palladium(II) complex as pre-catalyst in Suzuki coupling and Heck reactions

Metal complexes {Ni (II), Pd (II) and Pt (II)} and oxidation products (sulfide and selenide) of N,N,N',N'-tetrakis(diphenylphosphino)ethylendiamine, [(Ph₂P)₂NCH₂CH₂-N(PPh₂)₂] (1) have been prepared and characterized. The catalytic behaviour of the Pd(II) complex was investigated in the Suzuki coupling and Heck reactions.



Dongfang Qiu, Jiang Wu, Zhiyuan Xie, Yanxiang Cheng, Lixiang Wang

J. Organomet. Chem. 694 (2009) 737

Synthesis, photophysical and electrophosphorescent properties of mononuclear Pt(II) complexes with arylamine functionalized cyclometalating ligands Novel orange phosphorescent emitter: The neutral-charged C^N^N Pt(II) halide with arylamine functionalized cyclometalating ligand displays an efficient phosphorescent emission with a current efficiency of 11.3 cd A^{-1} and no apparent voltage-dependence from 6 V to 10 V.



Luis Adrio, José M. Antelo, Jesús J. Fernández, King Kuok (Mimi) Hii, M^a Teresa Pereira, José M. Vila

J. Organomet. Chem. 694 (2009) 747

The trinuclear cyclometalated palladium-(II) compound (2), with σ carbon(sp³)-metal bonding, contains a non-planar hexagonal metallated ring plus a central six-membered core of alternating palladium and sulfur atoms.

Reaction of the electron-deficient $[Os_3-(CO)_8(\mu-H)(\mu_3-Ph_2PCH_2P(Ph)C_6H_4)](1)$ with Ph₃GeSPh at 80 °C led to two triosmium compounds, $[Os_3(CO)_8(\mu-H)(\mu-SPh)(\mu-dp-pm)](2)$ and $[Os_3(CO)_7(\mu-H)(\mu-SPh)(\mu_3-SC_6H_4)(\mu-dppm)](3)$. Compound 3 represents a rare example of a structurally characterized orthometallated arylthiolate ligand on a triosmium cluster.



J. Organomet. Chem. 694 (2009) 752

Shariff E. Kabir, Brian K. Nicholson,

Arun K. Raha, Shishir Ghosh,

Derek A. Tocher

Cleavage of Ge–S and C–H bonds in the reaction of electron-deficient $[Os_3(CO)_8(\mu-H)(\mu_3-Ph_2PCH_2P(Ph)C_6H_4)]$ with Ph_3GeSPh : Generation of thiophenol derivatives $[Os_3-(CO)_8(\mu-H)(\mu-SPh)(\mu-dppm)]$ and $[Os_3-(CO)_7(\mu-H)(\mu-SPh)(\mu_3-SC_6H_4)(\mu-dppm)]$

A. Dzambasky, J. Baumgartner, K. Hassler

J. Organomet. Chem. 694 (2009) 757

Phosphanes with bulky oligosilyl substituents By reaction of the dichloroheptasilane [(SiMe₃)₂MeSi]₂SiCl₂ with the bulky phosphanes RHPLi with R either supermesityl or hypersilyl, the sterically hindered oligosilyl-substituted phosphanes [(SiMe₃)₂Me-Si]₂SiClPHR have been prepared. Subsequent lithiation afforded the unusually stable phosphanides [(SiMe₃)₂Me-Si]₂SiClPLiR which showed no bias for LiClelimination.





Ya Chen, Wei Liu, Jian-Shi Jin, Bin Liu, Zhi-Gang Zou, Jing-Lin Zuo, Xiao-Zeng You

J. Organomet. Chem. 694 (2009) 763

Rhenium(I) tricarbonyl complexes with bispyridine ligands attached to sulfur-rich core: Syntheses, structures and properties Rhenium(I) tricarbonyl complexes with bispyridine ligands incorporating with delocalized sulfur-rich units, Re(CO)₃(Medpydt)X and Re(CO)₃(MebpyTTF)X, have been prepared. Hydrolysis of the above complexes affords the analogue products with carboxylate derivatives. Complexes 3– 6 exhibit blue to red emissions. The performance of some typical complexes as photosensitizers for anatase TiO₂ solar cells has been preliminarily investigated.



Yuhua Qi, Dacheng Feng, Rui Li, Shengyu Feng

J. Organomet. Chem. 694 (2009) 771

Theoretical study on the substitution and insertion reactions of silylenoid H₂SiLiF with CH₃XH_{*n*-1} (X = F, Cl, Br, O, N; n = 1, 1, 1, 2, 3)

The substitution reactions of H_2SiLiF (A) with CH_3XH_{n-1} (X = F, Cl, Br, O, N; n = 1, 1, 1, 2, 3) proceed via two reaction paths, forming the same product H_2SiFCH_3 . The insertion reactions of A with CH_3XH_{n-1} form $H_2SiXH_{n-1}CH_3$. The substitution reactions occur more readily than the insertion reactions for A with CH_3XH_{n-1} systems.



Jorge Torres-Nieto, Juventino J. García

J. Organomet. Chem. 694 (2009) 780

Catalytic desulfurization of dibenzothiophene using nickel supported on crosslinked polystyrene-PPh₃ catalysts Nickel catalysts supported on polystyrene-PPh₃ (0.1 mol% Ni) were used for the desulfurization of dibenzothiophene (DBT) quantitatively yielding 2,2'-dimethylbiphenyl as the sulfur-free product.



Gagik G. Melikyan, Boghos Mikailian, Ruth Sepanian, Pogban Toure

J. Organomet. Chem. 694 (2009) 785

High-temperature reaction of a $\text{Co}_2(\text{CO})_6$ complexed propargyl cation The novel high-temperature reaction of $Co_2(CO)_6$ -propargyl cations (up to 147 °C), occurring in the spontaneous and stereo-selective (90–97% *d*,*l*-) manner and yield-ing the radical dimers, *d*,*l*-3,4-diaryl-1,5-hexadiynes, is described.



Note

Hideo Kondo, Takashi Sue, Akira Kageyama, Yoshitaka Yamaguchi, Yusuke Sunada, Hideo Nagashima

J. Organomet. Chem. 694 (2009) 795

Two coordination modes of TCNE in the ruthenium amidinates: The first example providing experimental evidence for κ^1-N to η^2-C rearrangement

A stable ruthenium amidinate having a " κ^{1} -N"-coordinated TCNE, Cp ^{*}Ru(κ^{2} -N('Bu)=C(Mes)N'Bu)(κ^{1} (N)-TCNE) (2c), is synthesized by treatment of Cp ^{*}Ru(κ^{2} -N('Bu)=C(Mes)N'Bu) (1c) with TCNE, and the charge transfer nature is supported by ESR analysis. Close analogy in IR and UV-Vis spectroscopy of 2c with the intermediary species formed from the Ph analogue of 1c suggests that this intermediary product is " κ^{1} -N TCNE" ruthenium amidinate, which is rearranged to the " η^{2} -C TCNE" complex.





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