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Volume 690, issue 16, 15 August 2005



www.elsevier.com/locate/jorganchem

Contents

Regular papers

Christelle Mauger, Olivier Buisine, Sylvain Caravieilhes, Gérard Mignani

J. Organomet. Chem. 690 (2005) 3627

Successful application of microstructured continuous reactor in the palladium catalysed aromatic amination

Microreactor technology was successfully applied in the palladium catalysed C–N cross-coupling reaction between 4-bromotoluene and piperidine. Excellent conversions and selectivities were obtained without any by-product formation in continuous reactor.



Stéphanie M. Cornet, Keith B. Dillon, Andrés E. Goeta, Judith A.K. Howard, Mark D. Roden, Amber L. Thompson

J. Organomet. Chem. 690 (2005) 3630

Synthesis and characterisation of the platinum complexes [PtCl(CCl=PAr)-(PPh_3)_2] and [PtCl(CCl=PAr')(PPh_3)_2] as potential intermediates in the preparation of phosphaalkynes

Oxidative addition reactions of $Cl_2C=PR$ (R = 2,4,6-tris(trifluoromethyl)phenyl (Ar) or 2,6-bis(trifluoromethyl)phenyl (Ar') with Pt(PPh_3)_4 yield the *cis* and *trans* (at platinum) complexes [PtCl(ClC=PAr)(PPh_3)_2] and [PtCl(ClC=PAr')(PPh_3)_2]. All starting materials and intermediates have been characterised by NMR spectroscopy. The crystal and molecular structures of the *trans*-platinum complexes have been determined by single-crystal X-ray diffraction at low temperature.



Alberto Fernández, José M. Vila

J. Organomet. Chem. 690 (2005) 3638

The cyclometallation of bis(di-p-methylbenzylphosphino)methane The new diphosphine $(4-MeC_6H_4CH_2)_2$ -PCH₂P(4-MeC_6H_4CH_2)₂, was reacted with [MnMe(CO)₅] to give a novel cyclometallated compound with the ligand as terdentate-[C,P,P].



Alessandro Toti, Piero Frediani, Antonella Salvini, Luca Rosi, Carlo Giolli

J. Organomet. Chem. 690 (2005) 3641

Hydrogenation of single and multiple N–N or N–O bonds by Ru(II) catalysts in homogeneous phase

The ruthenium(II) complexes $RuH_2(CO)_2$ -(PⁿBu₃)₂, $RuH_2(CO)_2(PPh_3)_2$, and RuH_2 -(PPh₃)₄ are catalytically active in the hydrogenation of organic substrates containing a N=N, N(O)=N or NO₂ group giving the corresponding amine i. A complete conversion was reached, depending on temperature, catalyst and substrate concentration. Also the hydrogenolysis of an N–N group giving the corresponding amine was obtained using $RuH_2(PPh_3)_4$ as catalyst. A catalytic cycle is suggested.



Dmitry V. Moiseev, Yulia B. Malysheva, Andrey S. Shavyrin, Yury A. Kurskii, Aleksey V. Gushchin

J. Organomet. Chem. 690 (2005) 3652

Study of homo- and cross-coupling competition in the reaction of triarylbismuth(V) dicarboxylates with methyl acrylate in the presence of a palladium catalyst $Ar_3Bi(O_2CR)_2$ are very active phenylating agents for the Pd-catalyzed C-arylation reaction of methyl acrylate under mild conditions. The carboxylic group, the palladium catalyst and oxygen affect the reactivity of the organobismuth compounds and the selectivity of the C-arylation reaction.



Ar = Ph, *m*-Tol, *p*-Tol R = H, Me, Et, *n*-Bu, *t*-Bu, *n*-C₅H₁₁, CF₃, CH₂Cl, CCl₃, Ph

José G. López-Cortés, Armando Samano-Galindo, M. Carmen Ortega-Alfaro, Alfredo Toscano, Henri Rudler, Andrée Parlier, Cecilio Alvarez-Toledano

J. Organomet. Chem. 690 (2005) 3664

Synthesis and X-ray structure of an unexpected bidentate allene–aminocarbene complex of tungsten

This contribution describes attempts at synthesizing 1,4-bidentate alkyne–ferrocenylaminocarbene complexes of tungsten, chromium and molybdenum. This led to the unexpected formation, upon base-induced propargyl bromide alkylation at nitrogen, of new allene–ferrocenylaminocarbene complexes **5a–c** of these metals.

$\begin{array}{c} C13 \\ C14 \\ C15 \\ C15 \\ C15 \\ C15 \\ C17 \\ C17 \\ C19 \\ C19 \\ C19 \\ C19 \\ C10 \\$

Alberto Fernández, Digna Vázquez-García, Jesús J. Fernández, Margarita López-Torres, Antonio Suárez, José M. Vila

J. Organomet. Chem. 690 (2005) 3669

Cyclometallation of phenylhydrazones: Synthesis, reactivity, crystal structure analysis and novel trinuclear palladium(II) cyclometallated compounds with [C, N, N'] terdentate ligands The reactions of the phenylhydrazones $C_6H_5N(H)N=CMe(C_5H_4N)$ and 2-ClC₆H₄- $N(H)N=CMe(C_5H_4N) \cdot HCl$, with lithium tetrachloropalladate or palladium(II) acetate, as appropriate, give cyclometallated compounds with the organic ligand as terdentate [C, N, N], from which novel trinuclear species were obtained by reaction with the tertiary triphosphines MeC-(CH₂PPh₂)₃ (tripod) and (Ph₂PCH₂CH₂)₂-PPh (triphos).



Alexander D. Dilman, Dmitry E. Arkhipov, Alexander A. Korlyukov, Valentine P. Ananikov, Vitalij M. Danilenko, Vladimir A. Tartakovsky

J. Organomet. Chem. 690 (2005) 3680

Synthesis and structural characterization of carbon-centered tris(pentafluorophenyl)silyl derivatives

Carbon-centered tris(pentafluorophenyl)silyl derivatives have been prepared and studied by X-ray diffraction analysis.



Leszek Rupnicki,

Zofia Urbańczyk-Lipkowska, Anita Stępień, Piotr Cmoch, Zbigniew Pianowski, Krzysztof Staliński

J. Organomet. Chem. 690 (2005) 3690

New distannanes containing the chiral 2-(4isopropyl-2-oxazolinyl)-5-phenyl ligand The *N*-coordinated tin hydrides containing the oxazoline ligand in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium gave the corresponding distannanes in good yields. The $J(^{15}N-^{117/119}Sn)$, $J(^{117}Sn-^{119}Sn)$ couplings and single-crystal X-ray analysis of the distannanes revealed a tendency towards penta-coordination at the tin center as a result of the Sn–N interaction. N R₂Sn SnR₂N 57-87 % R = Me, *n*-Bu, Ph

Janusz Lewiński, Paweł Horeglad, Ewa Tratkiewicz, Iwona Justyniak, Zbigniew Ochal

J. Organomet. Chem. 690 (2005) 3697

Ring-opening of 2,3-epoxy-1-propanol with R_3Al : Unprecedented regiochemical switching simply achieved by changing alkyl substituents of aluminium reagent

Several control experiments were designed to optimise the reaction of 2,3-epoxy-1-propanol with R_3Al and to probe for the nature of aluminium-bound alkyl groups that influence the reactivity and selectivity. The reported studies revealed that the Et_3Al mediated reaction leads to the C-2 product in contrast to the well-known C-3 substitution promoted by Me_3Al .



Matthias Drexler, Thomas Haas, Sze-Man Yu, Henning S.g. Beckmann, Bernhard Weibert, Helmut Fischer

J. Organomet. Chem. 690 (2005) 3700

Bis(amino)allenylidene complexes by displacement of the MeO group in methoxy allenylidene complexes of chromium and tungsten. Synthesis, DFT calculations and solid-state structures of new bis(amino) allenylidene complexes The alkoxy substituent in pentacarbonyl dimethylamino(methoxy)allenylidene can easily be replaced by NH_2 , NHR, and NR_2 thus offering a convenient access to nearly any substitution pattern of bisamino-substituted allenylidene complexes.



Han Dong Yin, Min Hong, Gang Li, Da Qi Wang

J. Organomet. Chem. 690 (2005) 3714

Synthesis, characterization and structural studies of diorganotin(IV) complexes with Schiff base ligand salicylaldehyde isonicotinylhydrazone

Eight diorganotin(IV) complexes of salicylaldehyde isonicotinylhydrazone (H₂SalN) R₂Sn(SalN) R = *t*-Bu **1**, Ph **2**, PhCH₂ **3**, *o*-*ClC*₆H₄CH₂ **4**, *p*-*ClC*₆H₄CH₂ **5**, *m*-*Cl*-C₆H₄CH₂ **6**, *o*-FPhCH₂ **7**, *p*-*F*C₆H₄CH₂ **8** were prepared. All the complexes **1–8** have been characterized by elemental, IR, ¹H, ¹³C and ¹¹⁹Sn NMR analyses. The crystal structures of H₂SalN and complex **1** were determined by X-ray crystallography diffraction analyses.



Keisham Sarjit Singh, Yurij A. Mozharivskyj, Carsten Thöne, Mohan Rao Kollipara

J. Organomet. Chem. 690 (2005) 3720

New mononuclear ruthenium complexes of η^5 -cyclichydrocarbon containing azine ligands: Syntheses, spectral and structural studies

A series of indenyl and pentamethylcyclopentadienyl ruthenium(II) complexes of azine ligands have been prepared by the reaction of $[(\eta^5-C_9H_7)Ru(PPh_3)_2(CH_3CN)]$ -PF₆ or $[(\eta^5-C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ with the appropriate azine ligands. The complexes were fully characterized with the help of spectroscopic data.



Giuliana Gervasio, Domenica Marabello, Enrico Sappa, Andrea Secco

J. Organomet. Chem. 690 (2005) 3730

Reactions of $Ru_3(CO)_{12}$ with 2-pentynaldiethyl-acetal. The crystal structure of $Ru_2(CO)_6[\mu-\eta^4-\{EtC_2C(H)(OEt)_2\}CO\{EtC_2-C(H)(OEt)_2\}]$ and its reactivity towards tetraethyl-orthosilicate
$$\begin{split} Ru_2(CO)_6[\mu-\eta^4-\{EtC_2C(H)(OEt)_2\}CO\{EtC_2C(H)-(OEt)_2\}] has been obtained in considerable yield by reacting Ru_3(CO)_{12} with 2-pentynal-diethyl-acetal [CH_3CH_2C=CC(H) (OEt)_2](PDA) in hydrocarbon solvents. The complex contains ethoxy-groups which could potentially undergo hydrolysis in the presence of tetraethyl orthosilicate (TEOS) in the presence of catalysts. Reactions of complex Ru_2(CO)_6[\mu-\eta^4-\{EtC_2C(H)(OEt)_2\}CO\{EtC_2C(H)-(OEt)_2\}] with TEOS in the presence of HCl or of NaF (as catalysts) have been attempted. An inorganic-organometallic sol-gel material containing the skeleton of the complex has been obtained and characterized.$$

Horacio Reyes, José María Rivera, Norberto Farfán, Rosa Santillan, Pascal G. Lacroix, Christine Lepetit, Keitaro Nakatani

J. Organomet. Chem. 690 (2005) 3737

Synthesis and quadratic molecular hyperpolarizabilities of two new chiral boronates: Computational and experimental study The molecular hyperpolarizabilities of two chiral boronates were investigated by the electric field induced second harmonic (EFISH) technique and semi-empirical calculations. The dimeric oxobridge derivative is two times more efficient than the monomeric specie.



6

Debaprasad Mandal, B.D. Gupta

J. Organomet. Chem. 690 (2005) 3746

Pyrazine bridged benzyl dicobaloximes: Competition between π -interaction and steric crowding in crystal structure A one-pot synthesis of pyrazine (Pz) bridged benzyl dicobaloximes [ArCH₂Co(dioxime)₂]₂- μ -Pz [dioxime = dmgH, dpgH] has been described. Two cobaloxime units attain the eclipsed conformation in [PhCH₂Co(dpgH)₂]₂- μ -Pz due to the π - π interaction between the axial benzyl group and phenyl ring of the equatorial dpgH group whereas both *cis* and *trans* isomers crystallize together in [PhCH₂Co(dpgH)(dmgH)]₂- μ -Pz. The cyclic voltammetry study in [PhCH₂Co(dioxime)₂]₂- μ -Pz [dioxime = dmgH, dpgH] shows two cobalt center are mixed together due to electron delocalization through pyrazine and behave like a monocobaloxime and the monocobaloximes.

Giuliana Gervasio, Domenica Marabello, Enrico Sappa, Andrea Secco

J. Organomet. Chem. 690 (2005) 3755

The reactions of Fe₃(CO)₁₂ with but-2-yn-1,4-diol (BUD), 1,4-dichloro-but-2-yne (DCB), propargyl alcohol (PA) and propargyl chloride (PC) in KOH/CH₃OH solutions (followed by acidification with HCl) and under thermal conditions have been examined. The complexes Fe₂(CO)₆ {H₂CCC-CH₂}, Fe₂(CO)₆{H₂CCC(H)C(OMe)O} and Fe₃(CO)₁₀{H₂CCC(H)C(O)C{CH₂(O)CH₃}-CCH₂} are the main products and their structures have been determined by means of X-ray analysis.

Wei Fan, Rui Zhang, Weng Kee Leong, Chit Kay Chu, Yaw Kai Yan

J. Organomet. Chem. 690 (2005) 3765

Rhenium carbonyl complexes with monodentate-coordinated diphosphines: activation of terminal phosphino groups towards amine-oxide oxidation Terminal phosphino groups of $[Re_2(CO)_9-(\eta^1-P-P)]$ (P-P = diphosphines) are activated towards oxidation by Me₃NO, possibly via an interaction with a carbonyl ligand.

Ling Ling Ouh, Thomas Ernst Müller, Yaw Kai Yan

J. Organomet. Chem. 690 (2005) 3774

Intramolecular hydroamination of 6aminohex-1-yne catalyzed by Lewis acidic rhenium(I) carbonyl complexes The synthesis of pyridine-substituted triflato tricarbonyl rhenium(I) complexes of the type fac-[Re(CF₃SO₃)(CO)₃L₂] (L = py-Cl, py, py-Me and py-NMe₂) and their use in the catalysis of the intramolecular hydroamination of 6-aminohex-1-yne is described.





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Yinghua Chen, Zhenyu Zhu, Jie Zhang, Jianzhong Shen, Xigeng Zhou

J. Organomet. Chem. 690 (2005) 3783

Modification of mesoporous silicate SBA-15 with tris[bis(trimethylsilyl)amido]samarium and its utility in Tishchenko reaction Treatment of mesoporous silicate SBA-15 with $Sm[N(SiMe_3)_2]_3$ led to the formation of a novel organolanthanide/inorganic hybrid material [SBA-15]Sm[N(SiMe_3)_2]_x, which is an efficient and mild catalyst for Tishchenko reaction.



Ahmed Battace, Touriya Zair, Henri Doucet, Maurice Santelli

J. Organomet. Chem. 690 (2005) 3790

Selective synthesis of (*E*)-triethyl(2-arylethenyl)silane derivatives by reaction of aryl bromides with triethyl vinylsilane catalysed by a palladium–tetraphosphine complex Cis, cis, cis-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane / 0.5 $[PdCl(C_3H_5)]_2$ system catalyses the Heck reaction of vinyltriethysilane with a range of aryl bromides with high selectivities in favour of the formation of (*E*)-triethyl(2-arylethenyl)silane derivatives. High ratio substrates/catalyst were used in most cases.



M. Andreina Moreno, Matti Haukka, Sirpa Jääskeläinen, Sauli Vuoti, Jouni Pursiainen, Tapani. A. Pakkanen

J. Organomet. Chem. 690 (2005) 3803

Synthesis, characterization, reactivity and theoretical studies of ruthenium carbonyl complexes containing *ortho*-substituted triphenyl phosphanes

A series of ruthenium complexes containing substituted phosphanes was synthesized and used as catalysts for the hydroformylation of 1-hexene. The activities were found to depend on binding mode of the phosphane and on the strength of the metal–phosphane interaction. Strongly coordinated chelating phosphanes showed poor activity, while weakly chelated and non-chelating phosphanes led to higher activities.



Renata Dreos, Lassaad Mechi, Giorgio Nardin, Lucio Randaccio, Patrizia Siega

J. Organomet. Chem. 690 (2005) 3815

Alternative cocrystallization of "almost" enantiomers and true enantiomers in some cis- β -organocobalt salen-type complexes with α -amino acids

The reaction of a racemic *cis*- β -organocobalt salen-type complex with L-histidine and a second non-chiral cobalt complex resulted in the cocrystallization of diastereomers. The reaction of the same cobalt complexes with DL-histidine led to the formation of two pairs of enantiomers, which crystallized separately as racemic compounds.



J. Organomet. Chem. 690 (2005) 3822

The Heck-type arylation of allylic alcohols with arenediazonium salts

The Heck coupling of ArN_2BF_4 with allylic alcohols has been carried out in methanol using Pd(dba)₂ as catalyst in the absence of extra ligand and base.



Nicholas P. Robinson, Gary J. Depree, Rene W. de Wit, Lyndsay Main, Brian K. Nicholson

J. Organomet. Chem. 690 (2005) 3827

Indenols, indenones and (arylcyclohexadienyl)Mn(CO)₃ π -complexes from the thermally promoted reactions of alkynes with *ortho*-Mn(CO)₄ aryl ketone, amide, ester and aldehyde derivatives Alkynes normally react with orthomanganated aryl ketones to give 1*H*-inden-1-ols and with other orthomanganated arylcarbonyl compounds to give related cyclopentaannulation products, but in some cases triple alkyne insertion leads to (cyclohexadienyl)Mn(CO)₃ complexes; the crystal structure of $[(1,2,3,4,5-\eta)-2-(3-acetylthien-2-yl)-$ 1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese is reported.



Simon G. Bott, Huafeng Shen, Michael G. Richmond

J. Organomet. Chem. 690 (2005) 3838

Reversible aryl C–H bond activation in the reaction between $HRu_3(CO)_{9,10}(\mu$ -PPh₂) and the diphosphine ligand 4,5-bis(diphenyl-phosphino)-4-cyclopenten-1,3-dione (bpcd): X-ray diffraction structures of $H_2Ru_3(CO)_7$ -(bpcd)[μ , σ -PPh(C₆H₄)] and $Ru_3(CO)_6(\mu$ -CO)(μ -PPh₂)[μ , η^2 , η^1 -PPhC=C(PPh₂)C(O)-CH₂C(O)]

The triruthenium cluster HRu₃(CO)₁₀(µ-PPh₂) (1) reacts with the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) under thermal and Me₃NO activation to give $H_2Ru_3(CO)_7(bpcd)[\mu,\sigma-PPh(C_6H_4)]$ (3) as the major isolable product. The same product is obtained from the reaction between $HRu_3(CO)_9(\mu-PPh_2)$ (2) and bpcd at room temperature. Thermolysis of $H_2Ru_3(CO)_7(bpcd)[\mu,\sigma-PPh(C_6H_4)]$ regenerates the µ-PPh2 moiety and leads to P-Ph bond cleavage in the bpcd ligand to furnish Ru3(CO)6(µ-CO)(µ- $PPh_2[\mu,\eta^2,\eta^1-PPhC=C(PPh_2)C(O)CH_2C(O)] \quad (4)$ as the major isolable product. Clusters 3 and 4 have been fully characterized in solution and their molecular structures have been established by Xray crystallography.

Anna Johansson, Erica Wingstrand, Mikael Håkansson

J. Organomet. Chem. 690 (2005) 3846

Chiral diethylzinc complexes with diamine ligands: synthesis, crystal structure and enantioselective solvent-free alkylation

Conformationally chiral reagents can be subjected to total spontaneous resolution and the resulting chiral crystals may be used in enantioselective solid-state reactions.





Han Vinh Huynh, Joanne Hui Hui Ho, Tiong Cheng Neo, Lip Lin Koh

J. Organomet. Chem. 690 (2005) 3854

Solvent-controlled selective synthesis of a trans-configured benzimidazoline-2-ylidene palladium(II) complex and investigations of its Heck-type catalytic activity

A trans-configured benzimidazole-2-ylidene complex of palladium(II) (trans-2) was selectively obtained from the reaction of precursor A with $Pd(OAc)_2$ in DMSO and structurally characterized. The novel complex and its cis-isomer show high catalytic activities in the Mizoroki-Heck reaction comparable to imidazole-derived carbene complexes.





Note

Chunxiang Li, Mei Ying Doreen Lai, Weng Kee Leong

J. Organomet. Chem. 690 (2005) 3861

ToF-SIMS analysis of surface-anchored organometallic clusters

The organometallic cluster Os₃(µ-H)(CO)₁₀-(µ-SCH₂CH₂SH) chemically attached onto a silver or gold surface has been analysed by ToF-SIMS. This allows identification of the surface organometallic species, and also gives information on its reactivity. A similar analysis also afforded identification of the cluster fragment Os₃(µ-H)(CO)₁₀(µ-OSi≡) on a silica surface.





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