Volume 693, Issue 24, 15 November 2008

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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



Contents

Communications

SEVIER

Behrouz Notash, Nasser Safari, Hamid Reza Khavasi, Vahid Amani, Anita Abedi

J. Organomet. Chem. 693 (2008) 3553

C-H activation in bithiazole ring with thallium(III) ion

Two novel organometallic complex of 2,2'dimethyl-4,4'-bithiazole (dm4bt) ligand with formula [Tl(dm4bt)₂(NO₃)(H₂O)] (1) and [Tl(dm4bt)₂(NO₃)(DMSO)] (2) have been synthesized and structurally characterized by elemental analysis, FT-IR, ¹H NMR spectra and X-ray crystallography. These complexes also display the first transoid conformation in bithiazole ligands in which C-H bond activation in bithiazole ring is observed with Tl(III) ion.



Artur F. Keppler, Fernanda M. Prado, Giselle Cerchiaro, Paolo Di Mascio, João V. Comasseto

J. Organomet. Chem. 693 (2008) 3558

Mechanistic study of the addition reaction of TeCl₄ to alkynes: Participation of TeCl₃ centered-radical The mechanism of the addition reaction of TeCl₄ to alkynes was indirectly established by the detection of TeCl₃ centered radicals using EPR spin trapping, ESI-MS and ESI-MS/MS characterization.



Antonio L. Braga, Fábio Z. Galetto, Paulo S. Taube, Márcio W. Paixão, Claudio C Silveira, Devender Singh, Fabrício Vargas

J. Organomet. Chem. 693 (2008) 3563

Mild and efficient one-pot synthesis of chiral β -chalcogen amides via 2-oxazoline ring-opening reaction mediated by indium metal

A simple and efficient procedure for the synthesis of β -seleno and β -thio amides via the ring-opening reaction of chiral 2-oxazolines in the presence of indium metal has been developed.



Contents

Maryam Mirza-Aghayan, Rabah Boukherroub, Mahshid Rahimifard

J. Organomet. Chem. 693 (2008) 3567

Efficient method for the reduction of carbonyl compounds by triethylsilane catalyzed by PdCl₂

The versatility of the palladium(II) chloride and triethylsilane system has been tested in the reduction of aromatic carbonyl compounds. The reaction takes place under mild conditions and affords high yields. This facile and efficient method affords high yields for the reduction of aldehydes and Ketones to the corresponding alkanes.



Regular Papers

David J. Armitt, Michael I. Bruce, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 693 (2008) 3571

Reactions of cyano(alkynyl)ethenes with some alkynyl- and diynyl-ruthenium complexes

Reactions of $Ru(C \equiv CPh)(PPh_3)_2Cp$ with $(NC)_2C = CR^1R^2$ $(R^1 = H, R^2 = C \equiv CSiPr_3^i$ 8; $R^1 = R^2 = C \equiv CPh$ 9) have given η^3 -butadienyl

Show-Jen Chiou, Chien-Chu Wang, Chih-Ming Chang

J. Organomet. Chem. 693 (2008) 3582

Synthesis of dinitrosyl iron complexes (DNICs) with intramolecular hydrogen bonding

complexes Ru{ η^3 -C[=C(CN)₂]CPh=CR¹R²}(PPh₃)Cp (11, 12), respectively. Deprotection (tbaf) of 11 and subsequent reactions with RuCl(dppe)Cp and AuCl(PPh₃) afforded binuclear derivatives Ru{ η^3 -C[=C(CN)₂]CPh=CHC=C[ML_n]}(PPh₃)Cp [ML_n = Ru(dppe)Cp 19, Au(PPh₃) 20]. Reactions between 8 and Ru(C=CCC=CR)(PP)Cp [PP = (PPh₃)₂, R = Ph, SiMe₃, SiPrⁱ₃; PP = dppe, R = Ph] gave η^1 -dienynyl complexes Ru{C[=C(CN)₂]CR =CH[C=C(SiPrⁱ₃)]{PP}Cp (15–18), respectively. The phthalodinitrile C₆H(C=CSiMe₃)(CN)₂(NH₂)-(SiMe₃) (10) was obtained serendipitously from (Me₃SiC=C)₂CO and CH₂(CN)₂.

The water soluble complexes 2 and 3 with

and without intramolecular hydrogen bonding have been synthesized for peptide

bound mimic. Two complexes have the similar EPR signals as GSH-DNIC, the DNICs in biological system and rapidly release NO

upon illumination with visible or UV light.



Vaso N. Dokorou, Dimitra Kovala-Demertzi, Maria Louloudi, Anca Silvestru, Mavroudis A. Demertzis

J. Organomet. Chem. 693 (2008) 3587

Synthesis, characterization and catalytic properties of diorganotin derivatives. Crystal and molecular structure of the first complex of 2-(2-methyl-3-nitroanilino)benzoic acid of 1,2:3, 4-di-µ2-2-(2-methyl-3-nitroanilino)benzoato-0, 0-1,3-bis-2-(2-methyl-3-nitroanilino)benzoato-0-1,2,4:2,3,4-di-µ3-oxo-tetrakis[di-methyltin(IV)]

The complexes $[Me_2(MNAB)SnOSn-(MNAB)Me_2]_2$ (2) and $[Me_2Sn(MNAB)_2]$ (3), where HMNAB is 2-(2-methyl-3-nitroanilino)benzoic acid, (1), have been prepared and structurally characterized by means of vibrational, ¹H and ¹³C NMR spectroscopies. The catalytic activity of the prepared complexes in transesterification reactions has been studied. The diorganotin complexes efficiently catalyze the transesterification reaction of 2-phenylethanol without addition of free ligand or any promoting additive.



Richard D. Adams, Burjor Captain, Eszter Trufan

J. Organomet. Chem. 693 (2008) 3593

Ruthenium-tin complexes from the reaction of $HSnPh_3$ with $Ru_3(CO)_{10}(NCMe)_2$ and their reactions with bis(tri-t-butyl-phosphine)platinum

Three new triruthenium compounds: Ru₃-(CO)₉(SnPh₃)₂(NCMe)(μ -H)₂ (1), Ru₃(CO)₁₀-(SnPh₃)₂(μ -H)₂ (2) and Ru₃(CO)₇(SnPh₃)₃-(NCMe)₂(μ -H)₃ (5) were obtained by multiple oxidative additions of HSnPh₃ to Ru₃-(CO)₁₀(NCMe)₂. Compound 2 and the new compound Ru₃(CO)₉(SnPh₃)₃(μ -H)₃ (6) were obtained from reactions of 1 and 5 with CO, respectively. Compounds 2 and 6 eliminated benzene when heated to yield Ru₃-(CO)₁₀(μ -SnPh₂)₂ (7) and Ru₃(CO)₉(μ -SnPh₂)₃ (8). Compound 7 reacted with Pt(PBu'₃)₂ to yield Pt₂Ru₃(CO)₁₀(PBu'₃)₂(μ ₃-SnPh₂)₂ (9).



Wai-Yeung Wong, Xingzhu Wang, Hai-Liang Zhang, Kai-Yin Cheung, Man-Kin Fung, Aleksandra B. Djurišić, Wai-Kin Chan

J. Organomet. Chem. 693 (2008) 3603

Synthesis, characterization and photovoltaic properties of a low-bandgap platinum(II) polyyne functionalized with a 3,4-ethylenedioxythiophene-benzothiadiazole hybrid spacer The synthesis, characterization, and photovoltaic properties of a deep blue polyplatinyne are described, which shows a narrow bandgap of 1.76 eV due to the substantial donor–acceptor features along the main chain. It can give rise to photovoltaic spectral responses in the visible region at about 565 nm in bulk-heterojunction polymer solar cells.

$$E_{g} = 1.76 \text{ eV}$$

Arun K. Raha, Shishir Ghosh, Md. Manzurul Karim, Derek A. Tocher, Noorjahan Begum, Ayesha Sharmin, Edward Rosenberg, Shariff E. Kabir

J. Organomet. Chem. 693 (2008) 3613

A comparative study of the reactivity of unsaturated triosmium clusters $[Os_3(CO)_8-{\mu_3-Ph_2PCH_2P(Ph)C_6H_4}(\mu-H)]$ and $[Os_3(CO)_9-{\mu_3-\eta^2-C_7H_3}(2-Me)NS}(\mu-H)]$ with ^tBuNC

Kazem D. Safa, Akbar Hassanpour, Shahin Tofangdarzadeh

J. Organomet. Chem. 693 (2008) 3622

Synthesis of 1,1-bis(silyl)-1-alkene derivatives bearing Si–H functional groups via Peterson protocol

The reactivity of the unsaturated cluster [Os₃(CO)₈- $\{\mu_3-Ph_2PCH_2P(Ph)C_6H_4\}(\mu-H)\}$ (2) and $[O_{S_2}(CO)_{0^{-1}}]$ $\{\mu_3 - \mu_2^2 - (\Gamma_{12} - (\Pi_{12} -$ ^tBuNC are $(CO)_8(CNBu')$ $(\mu_3-Ph_2PCH_2P(Ph)C_6H_4)(\mu-H)$ (3) which on decarbonylation affords [Os₃(CO)₇(CNBu[']){u₃- $Ph_2PCHP(Ph)C_6H_4\}(\mu-H)_2$ (4). Treatment of the labile complex [Os₃(CO)₉(µ-dppm)(NCMe)] (5) with ^tBuNC gives the substitution product [Os3(CO)9(µ-dppm)-(CNBu')] (6) which on decarbonylation also furnishes 4. Reaction of 7 with 'BuNC yields the addition product $[Os_3(CO)_9(CNBu')\{\mu-\eta^2-C_7H_3(2-Me)NS\}(\mu-H)]$ (8) which on decarbonylation gives unsaturated Os₃(CO)₈(CNBu'){μ₃-η²-C₇H₃(2-Me)NS}(μ-H)] (9). Compound 9 reacts with PPh₃ at room temperature to give the adduct [Os₃(CO)₈(PPh₃)(CNBu'){μ-η²-C₇H₃-(2-Me)NS(µ-H)] (10).



A variety of non-enolizable benzaldehyde derivatives and polymers containing formyl groups are converted to the corresponding 1,1-bis(silyl)-1-alkenes in onepot procedure involving the addition of (HMe₂Si)₃CLi to carbonyl groups.



vi

Contents

Robin Haunschild, Gernot Frenking

J. Organomet. Chem. 693 (2008) 3627

Quantum chemical study of ethylene addition to group-7 oxo complexes $MO_2(CH_3)(CH_2)$ (M = Mn, Tc, Re)

Quantum chemical calculations using DFT at the B3LYP level suggest rather complex scenarios with numerous pathways for the reaction of ethylene with the group-7 compounds $\text{ReO}_2(\text{CH}_3)(\text{CH}_2)$, $\text{TcO}_2(\text{CH}_3)(\text{CH}_2)$ and $\text{MnO}_2(\text{CH}_3)(\text{CH}_2)$.



Sen-ichi Aizawa, Takahiro Sano, Yoshiaki Fujita

J. Organomet. Chem. 693 (2008) 3638

High selectivity for L-cysteine residue at axial solvated site of trigonal-bipyramidal palladium(II) complex with tripodal tetradentate phosphine High selectivity for the thiolate sulfur atom in L-cysteinate was observed at the solvated coordination site in the trigonalbipyramidal palladium(II) complex, $[Pd(pp_3)(CH_3CN)]^{2+}$ (pp₃ = tris[2-(diphenylphosphino)ethyl]phosphine). The selectivity was applied to extractions of L-cysteinate from a mixture of amino acids and the reduced form of glutathionate from a mixture of the reduced and oxidized forms of glutathione.



Jacques Lalevée, Nicolas Blanchard, Bernadette Graff, Xavier Allonas, Jean Pierre Fouassier

J. Organomet. Chem. 693 (2008) 3643

Tris(trimethylsilyl)silyl versus tris(trimethylsilyl)germyl: Radical reactivity and oxidation ability A comparison of the tris(trimethylsilyl)silyl I and tris(trimethylsilyl)germyl II radical reactivity is provided. A large variety of chemical processes (addition to double bond, halogen abstraction, peroxyl radical formation...) is examined by Laser Flash Photolysis, quantum mechanical calculations and electron spin resonance (ESR) experiments.

Tris(trimethylsilyl)silylvs. Tris(trimethylsilyl)germyl radical reactivity



Svetlana V. Amosova, Alexander V. Martynov, Maxim V. Penzik, Natalia A. Makhaeva, Vladimir A. Potapov, Alexander I. Albanov, Larisa V. Zhilitskaya, Mikhail G. Voronkov

J. Organomet. Chem. 693 (2008) 3650

4,4-Diorganyl-1,1,3,6-tetrachloro-1,4-tellura-(IV)silafulvenes – New class of telluriumsilicon containing heterocycles Reaction of TeCl₄ with diorganyl diethynyl silanes 1 in CHCl₃ at room temperature leads to regio- and stereoselective formation in high yields of a new class of unsaturated five-membered heterocycles, 4,4-diorganyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes 2, exclusively or predominantly, as *E*-isomers. The structures of the heterocycles 2 were confirmed by the multinuclear (¹H, ¹³C, ²⁹Si, ¹²⁵Te) NMR spectroscopy, 2D NOESY NMR spectroscopy and mass-spectrometry. Long-range, through five bonds, spin-spin interaction of *exo-* and *endo*-cyclic olefinic protons was revealed in *Z*-isomers. In the mass spectra the heterocycles manifest themselves as the fragment ions [M-Cl₂]⁺.



1,2: $R+R^{1} = (CH_{2})_{4}$ (**a**), $(CH_{2})_{5}$ (**b**), $R = R^{1} = Me$ (**c**), R = Me, $R^{1} = Me_{3}Si(CH_{2})_{2}$ (**d**)

Contents

Raquel Ares, Digna Vázquez-García, Margarita López-Torres, Alberto Fernández, Nina Gómez-Blanco, José M. Vila, Jesús J. Fernández

J. Organomet. Chem. 693 (2008) 3655

Synthesis, characterization and crystal structures of cyclometallated palladium (II) compounds containing difunctional ligands with [*P*,*P*], [*As*,*As*], [*N*,*N*], [*P*,*As*], [*P*,*N*] and [*P*,*O*] donor atoms

The synthesis and characterization of the new cyclometallated palladium(II) complexes bearing ligands with [P,P], [As,As], [N,N], [P,As], [P,N] and [P,O] donor atoms is described. Ligands bearing amino groups may give condensation reactions with the solvent. The crystal and molecular structure of 3 has been determined and shows the palladium atom is bonded to four different donor atoms: C, N, S and Cl. Treatment of 3 with tertiary phosphines generates a series of mono- and dinuclear complexes and the reaction conditions may be regulated to give compounds where the Pd-S bond either remains or is cleaved. The reactivity of compound 3 is described.



Huy V. Nguyen, Mebuba R. Yeamine, Jahangir Amin, Majid Motevalli, Christopher J. Richards

J. Organomet. Chem. 693 (2008) 3668

Synthesis and ^1H NMR spectroscopic properties of substituted (η^4 -tetraaryl-cyclobutadiene)(η^5 -cyclopentadienyl)cobalt metallocenes

The complex CoCl(PPh₃)₃ is transformed into aryl substituted metallocenes 1–2 *via* the intermediacy of cobaltacyclopentadiene complexes 9–10 (R = H, CO₂Me, Ar = p-CF₃C₆H₄, p-FC₆H₄, p-MeOC₆H₄). The influence of the aryl substituents and the R substituent (18 examples) on the ¹H NMR spectra of the metallocenes is tabulated.



Notes

Chan Sik Cho, Jun Uk Kim, Heung-Jin Choi

J. Organomet. Chem. 693 (2008) 3677

Synthesis of alkyl 2,5-dihydro-5-oxofuran-2-carboxylates via palladium-catalyzed carbonylative cyclization of β -bromovinyl aldehydes in alcohols

 β -Bromovinyl aldehydes are carbonylatively cyclized under carbon monoxide pressure in alcohols at 125 °C in the presence of a catalytic amount of a palladium catalyst along with a base to give the corresponding alkyl 2,5-dihydro-5-oxofuran-2-carboxylates in good yields.



Paloma Paredes, Josefina Díez, M. Pilar Gamasa

J. Organomet. Chem. 693 (2008) 3681

Alkene and alkyne insertion into the Ir-H bond: Synthesis of new mono- and dinuclear alkyl and alkenyl iridium-pybox complexes The complex $[IrClH(\eta^2-C_2H_4)\{\kappa^3-N,N,N-(S,S)-^iPr-pybox\}][PF_6]$ evolves spontaneously to give the dinuclear complex $[Ir_2(\mu-Cl)_2(C_2H_5)_2\{\kappa^3-N,N,N-(S,S)-^iPr-pybox\}_2]-[PF_6]_2$ which in turn reacts with NaCl to afford the complex $[Ir_2(\mu-Cl)(C_2H_5)_2Cl_2\{\kappa^3-N,N,N-(S,S)-^iPr-pybox\}_2][PF_6]$. The X-ray crystal structure of the latter is reported. Novel mono and dinuclear alkyl and alkenyl iridium–pybox complexes are stereoselectively prepared through the insertion reaction of olefins and activated alkynes into the Ir–H bond of the mononuclear hydride precursors.





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