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Regular papers

Agustín Galindo, Diego del Río, Carlo Mealli, Andrea Ienco, Carles Bo

J. Organomet. Chem. 689 (2004) 2847

Folded 2,5-diazapent-3-ene metallacycle in ene-diamido group 4 metal compounds: DFT and AIM analyses The electronic implications for the folding of the five-membered 2,5-diazapent-3-ene metallacycle moiety in ene-diamido Group 4 metal compounds has been analyzed by DFT and AIM methods.





Manuel Jiménez-Tenorio, M. Dolores Palacios, M. Carmen Puerta, Pedro Valerga

J. Organomet. Chem. 689 (2004) 2853

Activation of alkynes by $\{[Cp^*Ru(CO)-(PMe^iPr_2)]^+\}$: X-ray crystal structures of $[Cp^*Ru=C=CH'Bu(CO)(PMe^iPr_2)][BAr'_4]$ and $[Cp^*Ru(CO)_2(PMe^iPr_2)][BAr'_4]$ The complex $[Cp^*Ru\{OCMe_2\}(CO)(PMe'-Pr_2)][BAr'_4]$ (2, $Ar'_4 = 3, 5 \cdot C_6H_3(CF_3)_2$) reacts with HCCPh at -40 °C in CD_2Cl_2 furnishing the π -alkyne adduct $[Cp^*Ru-(\eta^2-HC\equiv CPh)(CO)(PMe'Pr_2)][BAr'_4]$ (3), which rearranges to the vinylidene complex $[Cp^*Ru=C=CHPh(CO)(PMe'Pr_2)][BAr'_4]$ (4a) when the temperature is raised to 25 °C.



Michael I. Bruce, Frédéric de Montigny, Martyn Jevric, Claude Lapinte, Brian W. Skelton, Mark E. Smith, Allan H. White

J. Organomet. Chem. 689 (2004) 2860

Synthesis, structures and some reactions of $Ru(C \equiv CC \equiv CFc)(PP)Cp$ (PP=dppm, dppe) and related compounds

The compound Ru(C=CC=CFc)(dppe)Cp reacts with Co₂(CO)₆(L₂) [L₂=(CO)₂, dppm] to add the Co₂(CO)₄(L₂) group to the outer C=C triple bond, whereas tetracyanoethene adds to either C=C triple bond. The reaction of RuCl(dppe)Cp with HC=CC=CFc carried out in a thf/NEt₃ mixture in the presence of Na[BPh₄] gave [Ru{C=CC (NEt₃)=CHFc}(dppe)Cp]BPh₄ which reacts with I₂ to give [RuI(dppe){ η -C₅H₄C=C(NEt₃)=CHFc}]I₃.



Martin J. Brown, John F. Corrigan

J. Organomet. Chem. 689 (2004) 2872

Synthesis, characterization and electrochemistry of ferrocenylselenolate bridged palladium(II) and platinum(II) complexes The dimeric ferrocenyl-selenolate complexes of Pd and Pt, $[\{\mu-\eta^1-Fe(\eta^5-C_5H_4Se)_2\}M(P^nBu_3)]_2$ (M = Pd 2, Pt 3 shown), and the monomeric ferrocenyl(bis-selenolate) complex of platinum, $[\{\eta^2-Fe(C_5H_4Se)_2\}Pt(P^nBu_3)_2]$ 4, have been prepared from 1,1'-bis(trimethysilylseleno)ferrocene 1 and trans- MCL_2(P^nBu_3)_2 and cis-PtCL_2(P^nBu_3)_2, respectively. Complexes 2 and 3 contain two edge-sharing, square-planar metal centres forming a planar M_2Se_2 four-membered ring and exhibit two one-electron redox waves indicating electronic communication between the two Fe centers.



Irene E. Beck, Anatoli V. Golovin, Vladimir A. Likholobov, Elena V. Gusevskaya

J. Organomet. Chem. 689 (2004) 2880

Propylene oxidation by palladium nitro and nitrato complexes: in situ NMR and IR studies The mechanism of the propylene oxidation by $Pd(NO_n)_mCl_{2-m}(CH_3CN)_2$ complexes (n=2; m=0, 1, 2) in chloroform solutions has been studied by ¹H NMR and IR spectroscopy. Various new organopalladium intermediates have been observed and monitored in situ. In the presence of dioxygen, which re-oxidizes the nitrosyl groups, the acetone formation becomes a catalytic reaction with respect to both palladium and nitrogen.



Chiu Brenda Ka-Wen, Lam Michael Hon-Wah, Lee Derek Yiu-Kin, Wong Wai-Yeung

J. Organomet. Chem. 689 (2004) 2888

Synthesis, characterization and spectroscopic studies of cyclometalated platinum(II) complexes containing *meta*-bis(2-pyridoxy)-benzene

A series of mononuclear and binuclear cyclometalated platinum(II) complexes containing new "pincer-like" terdentate *meta*bis(2-pyridoxy)benzene ligands have been synthesized, characterized and their spectroscopic properties studied.

 $\begin{array}{c} C_{i} = CH_{i}; R_{i} = H; Y \quad Y = \infty dppm; n = 2\\ c_{i} = H; R_{i} = C_{i}H_{i}; Y \quad Y = \infty dppm; n = 2\\ c_{i} = CH_{i}; R_{i} = H; Y \quad Y = \infty pyrazoly; n = 1\\ c_{i} = H; R_{i} = C_{i}H_{i}; Y \quad Y = \infty pyrazoly; n = 1 \end{array}$

Kainthan Rajesh Kumar, Anca Penciu, Mark J. Drewitt, Michael C. Baird

J. Organomet. Chem. 689 (2004) 2900

Isobutene–isoprene copolymerization initiated by $[Cp^*MMe_2][(n-C_{18}H_{37}E)-B(C_6F_5)_3]$ (M = Ti, Hf; E = O, S) and related compounds The highly electrophilic borane $B(C_6F_5)_3$ reacts with n- $C_{18}H_{37}SH$ (E = O, S) to form the acidic 1:1 adducts (n- $C_{18}H_{37}EH$) $B(C_6F_5)_3$ (E = O, S) which react with Cp^{*}MMe₃ (M = Ti, Hf) to give the unstable complexes [Cp^{*}MMe₂][(n- $C_{18}H_{37}E$) $B(C_6F_5)_3$]; these are very good initiators for the copolymerization of isobutene with isoprene.



Youhei Yamamoto, Michito Shiotsuka, Satoru Onaka

J. Organomet. Chem. 689 (2004) 2905

rhenium(I)-gold(I) hetero Luminescent organometallics linked by ethynylphenanthrolines

The first luminescent rhenium(I)-gold(I) heterometallics, fac-Re{phen=Au(PPh₃)}-(CO)₃Cl and fac-Re{(PPh₃)Au=phen- \equiv -Au(PPh₃)}(CO)₃Cl, have been prepared and these heterometallics have shown the phosphorescence from the ³MLCT excited state because of the efficient intramolecular energy transfer from the Au unit to the Re unit.



Andriy B. Zaborovskiy, Daria S. Lutsyk, Ruslan E. Prystansky, Vladimir I. Kopylets, Vitaliy I. Timokhin, Chryssostomos Chatgilialoglu

J. Organomet. Chem. 689 (2004) 2912

A mechanistic investigation of (Me₃Si)₃SiH oxidation

O2 abstracts hydrogen from (Me3Si)3SiH spontaneously, initiating a radical chain oxidation of this silane. The resulting silyl radical adds to oxygen to form a peroxyl radical that undergoes three consecutive unimolecular steps. Evidence is provided that the rate determining step is the formation of a dioxiran-like pentacoordinated silyl radical.

$(Me_3Si)_3SiH + O_2 \longrightarrow (Me_3Si)_3Si^{\bullet} + HOO^{\bullet}$
$(Me_3Si)_3Si^{\bullet} + O_2 \longrightarrow (Me_3Si)_3SiOO^{\bullet}$
$(\text{Me}_3\text{Si})_3\text{SiOO}^\bullet \longrightarrow \begin{array}{c} \text{SiMe}_3\\ \text{O}_{\text{SiMe}_3} \\ \text{O}_{\text{SiMe}_3} \\ \text{SiMe}_3 \end{array} \longrightarrow (\text{Me}_3\text{Si})_2\text{Si}(\text{O}^\bullet)\text{OSiMe}_3$
$(Me_3Si)_2Si(O^{\bullet})OSiMe_3 \longrightarrow (Me_3SiO)_2Si(\bullet)SiMe_3$
$\begin{array}{rrr} (Me_3SiO)_2Si(\bullet)SiMe_3 &+ (Me_3Si)_3SiH & \longrightarrow \\ & (Me_3SiO)_2Si(H)SiMe_3 &+ (Me_3Si)_3Si^\bullet \end{array}$
2 (Me ₃ Si) ₃ SiOO• products

(1)

Irina P. Beletskaya, Vladimir I. Bregadze, Vasily A. Ivushkin, Pavel V. Petrovskii, Igor B. Sivaev, Stefan Sjöberg, Galina G. Zhigareva

J. Organomet. Chem. 689 (2004) 2920

New B-substituted derivatives of mcarborane, p-carborane, and cobalt bis(1,2dicarbollide) anion

The Pd-catalyzed cross-coupling reactions of B-I bond in *m*- and *p*-carboranes and cobalt bis(1,2-dicarbollide) anion with organomagnesium and organozinc compounds were studied. Carboranyl derivatives of furan, thiophene, indole, pyridine and quinoline were synthesized. 2-Pyridylethynyl and 3-quinolylethynyl derivatives of *p*-carborane were prepared by Pd-catalyzed crosscoupling reactions using corresponding alkynes or their magnesium derivatives.



R = furyl, thienyl, indolyl, pyridyl, quinolyl

Wanda Ziemkowska, Szymon Kucharski, Aleksandra Kołodziej, Romana Anulewicz-Ostrowska

J. Organomet. Chem. 689 (2004) 2930

Reactions of alkylalane diolates with water synthesis, characterisation and ɛ-caprolactone polymerisation activity of novel alane benzopinacolates

Reaction of trinuclear alane benzopinacolates $[R_5Al_3(OC(C_6H_5)_2C(C_6H_5)_2O)_2]$ [R = Me (1), R = Et (2)] with water results in an elimination of R3Al and formation of unusual binuclear products [R2Al2(TH-F) $[OC(C_6H_5)_2C(C_6H_5)_2O]_2$ [3 (R = Me), 4 (R = Et)]. Compounds 3 and 4 demonstrate catalytic activity in ring-opening polymerisation (ROP) of ɛ-CL.



Horst Kunkely, Arnd Vogler

J. Organomet. Chem. 689 (2004) 2940

Optical properties of bis(cyclopentadienyl)magnesium: excimer-type luminescence of the bis(cyclopentadienyl) ligand frame

The electronic spectra of solid MgCp₂ (Cp = cyclopentadienyl) show features which indicate the presence of intramolecular interligand interactions. The fluorescence of MgCp₂ (λ_{max} = 363 nm) undergoes a considerable Stokes shift which is apparently caused by a bonding attraction between both Cp rings in the excited state. An additional phosphorescence of the (Cp⁻)₂ fragment $(\lambda_{\text{max}}=535 \text{ nm})$ appears at 77 K.



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