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Contents

Communications

Akinobu Naka, Shinsuke Ueda, Mitsuo Ishikawa

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The reactions of germenes generated thermally from pivaloyl- and adamantoyltris(trimethylsilyl)germane with 1,3-butadienes The thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)germane in the presence of 2,3-dimethyl- and 2,3-diphenyl-1,3-butadiene gave the respective adducts derived from [2+4] cycloaddition of the germenes with butadienes in good yields.



Ari Lehtonen, Reijo Sillanpää

J. Organomet. Chem. 692 (2007) 2361

Synthesis and structure of stable *cis*-dimethyl complex of oxotungsten(VI)

Transmetallation reaction of oxotungsten(VI) complex [WO(L^{tBu})Cl₂] (L^{tBu} = methylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) dianion) with methyl magnesium iodide leads to the formation of *cis*-[WO-(L^{tBu})Me₂]. Both *cis* and *trans* isomers of initial dichloro complex yield identical product. This unexpectedly stable dialkyl complex can be activated by Et₂AlCl to catalyze the ring-opening metathesis polymerization of norbornene.



Regular Papers

Brenna L. Ghent, Sarah L. Martinak, Lauren A. Sites, James A. Golen, Arnold L. Rheingold, Chip Nataro

J. Organomet. Chem. 692 (2007) 2365

Electrochemistry and complexation of Josiphos ligands

The oxidative electrochemistry of 11 chiral bis-phosphinoferrocene ligands, all within the Josiphos class of ligands, was examined in methylene chloride. In addition, palladium(II) and palatinum(II) complexes with the general formula [MCl₂(P–P)] (M = Pd or Pt; P–P = Josiphos) were prepared, characterized by NMR and cyclic voltammetry and the X-ray structures of two complexes reported.



Contents

Fu-Chen Liu, Shou-Chon Chen, Gene-Hsian Lee, Shie-Ming Peng

J. Organomet. Chem. 692 (2007) 2375

Effect of solvent on reactions of $Cp_2Zr\{(\mu\text{-}H)_2\text{-}BHR\}_2$ and $Cp_2ZrH\{(\mu\text{-}H)_2BHR\}$ (R = CH₃, Ph) with $B(C_6F_5)_3$

The effect that a solvent has on reactions of $Cp_2Zr\{(\mu-H)_2BHR\}_2$ and $Cp_2ZrH\{(\mu-H)_2BHR\}$ (R = CH₃, Ph) with $B(C_6F_5)_3$ has been studied. In the case of benzene a metathesis product was isolated. In the case of diethyl ether different hydride abstraction ionic products were isolated from each reaction. The time-elapsed ¹¹B NMR spectra were used to investigate the course of reactions.



Takao Shibasaki, Nobuyuki Komine, Masafumi Hirano, Sanshiro Komiya

J. Organomet. Chem. 692 (2007) 2385

Synthesis of di-, tri-, tetra- and pentacyclic arene complexes of ruthenium(II):[Ru(η^6 -polycyclic arene)-(1-5- η^5 -cyclooctadienyl)]PF₆ and their reactions with NaBH₄

Polycyclic arene complexes, $[Ru(\eta^6-arene)(1-5-\eta^5-cyclooctadienyl)]PF_6$ (2) [arene = benzene, naphthalene, phenanthrene, anthracene, triphenylene, pyrene and perylene], are prepared. The coordination ability of arenes is as follows: benzene ~ triphenylene > phenanthrene > naphthalene > perylene > anthracene. These observations indicate that the benzo fused rings, particularly those of acenes, decrease the thermal stability.



coordination ability to cationic Ru fragment

Bing Yan, Fang-Fang Wang

J. Organomet. Chem. 692 (2007) 2395

Molecular design and photo-physics of quaternary hybrid terbium centered systems with novel functional di-urea linkages of strong chemical bonds through hydrogen transfer addition Two kinds of crosslinking reagents, 3-aminopropyl-methyl-diethoxylsiliane $(H_2N(CH_2)_3Si-CH_3(OC_2H_5)_2$, abbreviated as APMES) and *N*-2-aminoethyl-3-aminopropyltriethoxylsiliane $(H_2N(CH_2)_2HN(CH_2)_3Si(OC_2H_5)_3$, abbreviated as AEAPES) are modified by 3-(triethoxysilyl)-propyl isocyanate (TEPIC) to afford two novel crosslinking molecular derivatives as bridge ligands. Then the ternary and quaternary organic–inorganic molecular-based hybrid material with these functional and bridge ligands and 1,10-phenanthroline (phen) are constructed with the two components equipped with covalent bonds are reported.



Sonia Pérez, Concepción López, Amparo Caubet, Xavier Solans, Mercè Font-Bardía, Martí Gich, Elies Molins

J. Organomet. Chem. 692 (2007) 2402

Versatility in the mode of coordination $\{(N), (N,O)^-, (C,N)^- \text{ or } (C,N,O)^{2-}\}$ of $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2OH)\}]$ to palladium(II)

The experimental strategies to control selectively the formation of a wide variety of novel palladium(II) complexes containing the ferrocenyliminoalcohol $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(C_6H_4-2OH)\}]$ (**1b**) acting as a (N)⁻, (N,O)⁻, $[C(sp^2, \text{ ferrocene}),N]^-$ or $[C(sp^2, \text{ ferrocene}),N]^-$ ferrocene),N,O]²⁻ ligand are described.



Bianka Muschalek, Ingo Weidner, Holger Butenschön

J. Organomet. Chem. 692 (2007) 2415

Synthesis of tricarbonyl(*N*-methylisatin)chromium(0) and an unanticipated transformation of a *N*-MEM to a *N*-MOM group The synthesis and some reactions of tricarbonyl(*N*-methylisatin)chromium(0) are reported.



Mario Rodríguez, Ma. Eugenia Ochoa, Cristina Rodríguez, Rosa Santillan, Víctor Barba, Norberto Farfán

J. Organomet. Chem. 692 (2007) 2425

Imino Diels–Alder reaction of boronates. Preparation and characterization of new 3,4dihydroquinoline and 1,2,3,6-tetrahydropyridine derivatives The preparation of 3,4-dihydroquinolines and 1,2,3,6-tetrahydropyridines by imino Diels–Alder reaction of boronates derived from Schiff bases with 2,3-dimethylbutadiene is reported. The results show that the dienophile or diene behavior of these boronates is influenced by the substituent *para* to the imine fragment.



Zekeriya Bıyıklıoğlu, Halit Kantekin, Musa Özil

J. Organomet. Chem. 692 (2007) 2436

Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 14-membered tetraaza macrocycles The novel tetrasubstituted metal-free phthalocyanine (6) and metallophthalocyanines (7, 8) bearing four 14-membered tetraaza macrocycles moieties on peripheral positions have been synthesized by cyclotetramerization reaction of phthalonitrile derivative (5) 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.



Michito Shiotsuka, Yasuhiro Inui, Yasushi Sekioka, Youhei Yamamoto, Satoru Onaka

J. Organomet. Chem. 692 (2007) 2441

Synthesis, photochemistry, and electrochemistry of ruthenium(II) polypyridyl complexes anchored by dicobalt carbonyl units A novel hybrid complex system of ruthenium polypyridyl complexes containing dicobalt carbonyl units is prepared and shows obvious emission quenching, as evidenced by the efficient intramolecular energy transfer from the MLCT excited state in the ruthenium polypyridyl unit to the dicobalt carbonyl units.



Anthony Birri, Benjamin Harvey, Graeme Hogarth, Elif Subasi, Fadime Uğur

J. Organomet. Chem. 692 (2007) 2448

Allyl palladium dithiocarbamates and related dithiolate complexes as precursors to palladium sulfides

Dithiocarbamate complexes, $[Pd(\eta^3-ally])$ -(S₂CNR₂)], have been prepared and TGA and DSC studies carried out in order to assess their potential as MOCVD precursors to palladium sulfides. For comparison $[(\eta^3-C_4H_7)Pd(S_2PPh_2)]$ and $[Pd(S_2CNMeR)_2]$ (R = Bu, Hex) have been prepared and tested as precursors. The crystal structures of $[(\eta^3-C_4H_7)Pd(S_2CNMe_2)]$, $[(\eta^3-C_4H_7)Pd(S_2CNPr_2)]$, $[(\eta^3-C_4H_7)Pd(S_2PPh_2)]$ and $[Pd(S_2CNMeBu)_2]$ are reported.



Evans O. Changamu, Holger B. Friedrich, Melanie Rademeyer

J. Organomet. Chem. 692 (2007) 2456

Synthesis and characterization of transition metal stabilized carbocations of the types $[Cp^*(CO)_2Fe\{\mu-(C_nH_{2n-1}\}M(CO)_xCp]PF_6(x = 2, M = Fe or Ru; x = 3, M = W, Cp^* = \eta^5-C_5-(CH_3)_5; Cp = \eta^5-C_5H_5; n = 3-6)$ and $[Cp(CO)_2-Ru\{\mu-(C_nH_{2n-1})\}W(CO)_3Cp]PF_6$ (n = 3-5) and the crystal structures of the complexes $[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp], [Cp^*(CO)_2-Fe(CH_2)_5Ru(CO)_2Cp], [Cp^*(CO)_2-Fe-(CH_2)_5-W(CO)_3Cp], and <math>[Cp(CO)_2Ru(CH_2)_5W(CO)_3Cp]$

The complexes $[Cp^*(CO)_2Fe(CH_2)_n-M(CO)_x-Cp]$ (n = 3-6, $Cp^* = \eta^5-C_5(CH_3)_5$, $Cp = \eta^5-C_5H_5$, x = 2, M = Fe or Ru; x = 3, M = W), undergo hydride abstraction selectively from the CH₂ β to Cp^{*}(CO)₂Fe to give the cationic metallocycles $[Cp^*(CO)_2Fe \{\mu-(C_nH_{2n-1})\}-M(CO)_xCp]PF_6$ upon reaction with Ph₃CPF₆. Similarly, $[Cp(CO)_2Ru(CH_2)_nW(CO)_3Cp]$ (n = 3-5) undergo hydride abstraction from the CH₂ β to Cp(CO)₂Ru to give $[Cp(CO)_2Ru + \{\mu-(C_nH_{2n-1})\}W(CO)_3Cp]PF_6$.



Fatma Karipcin, Saliha Ilican, Yasemin Caglar, Mujdat Caglar, Bülent Dede, Yücel Sahin

J. Organomet. Chem. 692 (2007) 2473

Synthesis, structural and optical properties of novel borylated Cu(II) and Co(II) metal complexes of 4-benzylaminobiphenylglyoxime

Two novel BF_2^+ -bridge containing 4-benzylaminobiphenylglyoxime Co(II) and Cu(II) complexes have been synthesized by replacing of the bridging protons of the dioxime complexes with BF_2 group. These compounds were characterized using elemental analysis, IR, ICP-OES, magnetic susceptibility, thermal gravimetry techniques. The optical band gaps, optical dispersion parameters, optical constants such as optical conductivity, dielectric constant, refractive index were determined for the complexes.



Prakash C. Srivastava, Sangeeta Bajpai, Chhabi Ram, Rajesh Kumar, Ray J. Butcher

J. Organomet. Chem. 692 (2007) 2482

Synthesis, spectral and structural characterisation of ditelluroxanes: µ-oxo-bis[nitrato-; 2,4,6-trinitrophenolato-dialkyl tellurium (IV)] The synthesis of ditelluroxanes has been achieved by convenient routes. Their X-ray structures show that they possess Ψ TBP geometry with stereochemically active electron lone pair. Their supramolecular associations are organised through cooperative participation of Te···O secondary bonds, C-H···O hydrogen bonds and π -stacking of the organic substituents.



Mitsushiro Nomura, Marc Fourmigué

J. Organomet. Chem. 692 (2007) 2491

Isostructural diamagnetic cobalt(III) and paramagnetic nickel(III) dithiolene complexes with an extended benzenedithiolate core $[CpM^{III}(bdtodt)]$ (M = Co and Ni)

The isostructural diamagnetic [CpCo(bdtodt)] and paramagnetic [CpNi(bdtodt)] (Cp = η^5 cyclopentadienyl, bdtodt: benzo[1,3]dithiol-2one-5,6-dithiolato) complexes were prepared by starting from benzo[1,2-d;4,5-d']bis[1,3]dithiole-2,6-dione. Both Co and Ni complexes are isostructural and crystallize in the orthorhombic system with *Pbca* space group. The structural similarities, but the electrochemical, spectroscopic and magnetic differences between various [CpCo(dithiolene)] and [CpNi(dithiolene)] complexes are described.



Seyyed Javad Sabounchei, Alireza Dadrass, Mojtaba Jafarzadeh, Sadegh Salehzadeh, Hamid Reza Khavasi

J. Organomet. Chem. 692 (2007) 2500

Synthesis of a new carbbenzyloxymethylenetriparatolylphosphorane ylide and study of its reaction with mercury(II) halides: Spectral and structural characterization The reaction of a new phosphorus ylide, carbbenzyloxymethylenetriparatolylphosphorane, $\{(p\text{-tolyl})_3\text{PCHCOOCH}_2\text{C}_6\text{H}_5\}$, with a mercury(II) halide yields a dimeric complex of the form $[\{(p\text{-tolyl})_3\text{PCHCOOCH}_2\text{C}_6\text{H}_5\}(\text{HgX}_2)]_2$ (where X = Cl, Br or I). Single crystal X-ray analyses of **2** reveals the presence of centrosymmeteric dimeric structure containing the ylide and HgBr₂.



Marcus L. Cole, Aaron J. Davies, Cameron Jones, Peter C. Junk

J. Organomet. Chem. 692 (2007) 2508

Persistent π -arene interactions in bulky formamidinate complexes of potassium

The reaction of potassium hexamethyldisilazide with N(Diep)=C(H)NH(Diep) (Diep-FormH, Diep = 2,6-Et₂C₆H₃) in THF yields the half deprotonated compound [K(Diep-Form)(DiepFormH)] (1), which exhibits suppressed reactivity with the hexamethyldisilazide anion. Reaction of 1 with *n*-BuLi gives [{Li(THF)₂K(DiepForm)₂}_{*n*]} (2). Preparation of 1 in the presence of chelating ethers or amines gives fully deprotonated polymeric species.



Rosalyn J. Evans, Kevin R. Flower, Laura G. Leal, Patrick J. O'Malley, Claudia Mangold, Robin G. Pritchard, John E. Warren

J. Organomet. Chem. 692 (2007) 2519

Hemilabile orthometallated acetals: Synthesis, spectroscopic characterization and crystal and molecular structures of $[RuCl\{\eta^2-C,O-C_6H_4-2-CH(O_2C_2H_4)\}(CO)(PPh_3)_2]$ and $[HgBr\{\eta^2-C,O-C_6H_4-2-CH(O_2C_2H_4)\}]$

The cyclometallated acetal-containing complexes [RuCl{ η^2 -*C*,*O*-C₆H₄-2-CH(O₂C₂H₄)}-(CO)(PPh₃)₂] (X = F, Cl, Br, I) have been prepared. The solid state structure (X = Cl) shows four independent molecules which consist of an enantiomeric (planar oxygen) and diasteromeric pair (pyramidal oxygen). Theoretical calculations suggest that ether ligands should be planar unlike thioether ligands which are pyramidal. The electrostatic potential for simplified model compounds suggests this is due to the nature of the lone pairs at oxygen and sulfur respectively.



Masaru Sato, Yuta Miyagawa, Yuko Shigetoh

J. Organomet. Chem. 692 (2007) 2529

The synthesis and properties of ferroceno-[1',2';1'',2'']bis(1,3-dithiol-2-thione and -2-one) derivatives

Ferrocene, t-Bu- and 1.1'-bis(t-Bu)ferrocenes fused with 1,3-dithiol-2-thione ring were prepared. In spite of the presence or absence of t-Bu groups, the 1,3-dithiol-2-thione rings are heaped on top of each other. In the anodic scan, the 1,3-dithiol-2-thione part is oxidized likely to cause a coupling of the S atoms.



Wee-Chuan Yeo, Shuli Chen, Geok-Kheng Tan, Pak-Hing Leung

J. Organomet. Chem. 692 (2007) 2539

Synthesis of P-chiral phosphines via chiral metal template promoted asymmetric furan Diels-Alder reaction

The organoplatinum complex containing *ortho*-metalated (S)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary promoted the asymmetric furan Diels–Alder reaction between phenyldivinylphosphine and 2-diphenylphosphinofuran (E)-2-diphenylphosphinostyrene, for the synthesis of P-chiral phosphines.

$M_{a_{i}} = \begin{pmatrix} 1 & A_{i} BF_{i} & MeCN \\ (S) & 1 \\ 2 & 0 \\ (S) & 1 \\ 2 & 0 \\ (S) & 1 \\ (S) & 1$

Lloyd T.J. Evans, Martyn P. Coles, F. Geoffrey N. Cloke, Peter B. Hitchcock

J. Organomet. Chem. 692 (2007) 2548

Main group complexes incorporating 1,3bis(furyl)-1,1,3,3-tetramethyldisilazide ligands The bis-furyl substituted disilazide anion, $[N(SiMe_2R)_2]^-$ (R = 2-methylfuryl) has been coordinated to aluminium and magnesium centres. In the case of the aluminium dichloride fragment, both the THF adduct and the base-free complexes have been structurally characterized, the latter of which shows a previously unreported $\kappa^1 N, O, O'$ -bonding mode.



Michael Nonnenmacher, Doris Kunz, Frank Rominger, Thomas Oeser

J. Organomet. Chem. 692 (2007) 2554

Palladium(II) complexes bearing methylene and ethylene bridged pyrido-annelated *N*heterocyclic carbene ligands as active catalysts for Heck and Suzuki–Miyaura cross-coupling reactions Bridged pyrido annelated *N*-heterocyclic bis-(carbenes) are generated and serve as bidentate ligands for palladium(II) complexes that are fully characterized and act as catalyst precursor in C–C coupling reactions.



Michael I. Bruce, Paul A. Humphrey, Martyn Jevric, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 692 (2007) 2564

Preparation, structure and some chemistry of FcC=CC=CC=CRu(dppe)Cp

The synthesis of $Fc(C \equiv C)_3 Ru(dppe) Cp$ (2) from Fc(C=C)₃SiMe₃ and RuCl(dppe)Cp is described, together with its reactions with tcne to give the tetracyano-dienvl $FcC \equiv CC \equiv C \{C\}$ [=C(CN)₂]}₂Ru(dppe)Cp (3) and -cyclobutenyl $FcC \equiv CC \equiv C\{C = CC(CN)_2C(CN)_2\}Ru(dppe)$ Cp (4), with $Co_2(\mu$ -dppm)_n(CO)_{8-2n} (n = 0, 1) to give $FcC_2\{Co_2(CO)_6\}C_2\{Co_2(CO)_6\}C\equiv C$ Ru(dppe)Cp (5) and $FcC \equiv CC \equiv CC_2$ $\{Co_2(\mu-dppm)(CO)_4\}Ru(dppe)Cp$ (6), respectively, and with Os₃(CO)₁₀(NCMe)₂ to give $Os_3{\mu_3-C_2C \equiv CC \equiv C[Ru(dppe)Cp]}(CO)_{10}$ (7). On standing in solution, the latter isomerises to the cyclo-metallated derivative $Os_3(\mu-H){\mu_3}$ - $C[Ru(dppe)Cp]CCC[(\eta-C_5H_3)FeCp]\}(CO)_8(8).$

Dialkenyl-substituted 1,1-bis(silyl)ethenes of the general formulae $(CH_2=CH(CH_2)_nMe_2-Si)_2C=CH_2$ and $(CH_2=CH(CH_2)_nOMe_2-Si)_2C=CH_2$, (where n = 1-3) have been successfully converted into new silacyclic or silamacrocyclic compounds in the presence of ruthenium benzylidene complex (first generation Grubbs catalyst).



Grzegorz Hreczycho, Piotr Pawluć, Maciej Kubicki, Bogdan Marciniec

J. Organomet. Chem. 692 (2007) 2575

New cyclic and macrocyclic silaolefins *via* ringclosing metathesis of 1,1-bis(silyl)ethenetethered dienes

Attila Kovács, Katalin Mészáros Szécsényi, Vukadin M. Leovac, Zoran D. Tomić, György Pokol

J. Organomet. Chem. 692 (2007) 2582

Synthesis under self-controlled reaction conditions: Reaction of tetraamminezinc(II) chloride with 3,5-dimethyl-1-thiocarboxamide pyrazole The trinuclear $[Zn_3(Hdmpz)_2(dmpz)_4(NCS)_2]$ complex (Hdmpz: 3,5-dimethylpyrazole) has been synthesized by the title reaction. The complex has been characterized by X-ray diffraction, FT-IR spectroscopy, thermal analysis and quantum chemical computations.



H.J. Breunig, T. Borrmann, E. Lork, C.I. Rat

J. Organomet. Chem. 692 (2007) 2593

Syntheses, structures and DFT study of $[W(CO)_5(Ph_2SbX)] X = Cl, Br, I$

The syntheses and the molecular structures of $[W(CO)_5(Ph_2SbX)]$, X = Cl, Br, I are reported. The complexes are readily prepared in high yields and they are remarkably stable. The bonding in $[W(CO)_5(Ph_2SbCl)]$ has been investigated by DFT methods.



Note

Chiara Dinoi, Petr Prikhodchenko, Funda Demirhan, Jenny Gun, Ovadia Lev, Jean-Claude Daran, Rinaldo Poli

J. Organomet. Chem. 692 (2007) 2599

Reduction of $[Cp_2*Mo_2O_5]$ by mercaptopropionic acid in an aqueous medium. Isolation and characterization of a dinuclear oxo- and 3-sulfido-proprionato(2-)-bridged molybdenum(IV) compound Compound HSCH₂CH₂COOH reduces and coordinates molybdenum upon interaction with Cp₂*Mo₂O₅, to yield Cp₂*Mo₂(μ -O)(μ -SCH₂CH₂CO₂)₂ but, unlike the closely related HSCH₂COOH substrate, does not lead to C–S bond cleavage.





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