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# Contents

## Communications

# Masanobu Wakasa, Yuya Takamori, Toshiyuki Takayanagi, Masayuki Orihara, Tsuyoshi Kugita

J. Organomet. Chem. 692 (2007) 2855

Re-examination of the photochemical reaction of octaisopropylcyclotetragermane

The photochemistry of octaisopropylcyclotetragermane was studied by laser flash photolysis and trapping experiments. Upon irradiation of the cyclotetragermane, the main reaction was a ring opening to form octaisopropyltetragermane-1,4-diyl biradical ( $\lambda_{max} =$ 310 and 550 nm), but generations of diisopropylgermylene and tetraisopropyldigermene are negligible.



## Review

### Issa M. El-Nahhal, Nizam M. El-Ashgar

J. Organomet. Chem. 692 (2007) 2861

A review on polysiloxane-immobilized ligand systems: Synthesis, characterization and applications

The two immobilized ligand systems, iminobis(N-2-aminoethylacetamide) and iminobis(N-diethylenetrimineacetamide) ligand systems were prepared by the reaction of the immobilized diethyliminoacetate polysiloxane with ethylenediamine and diethylenetriamine, respectively.



# **Regular Papers**

# Stefan Dilsky

J. Organomet. Chem. 692 (2007) 2887

Molybdenum and tungsten complexes of the neutral tripod ligands  $HC(pz)_3$  and  $MeC(CH_2\mbox{-}PPh_2)_3$ 

Seven-coordinated complexes of tungsten and molybdenum containing the facially coordinating ligands  $HC(pz)_3$  (1) and  $MeC(CH_2 PPh_2)_3$  (2) have a 4:3 piano stool geometry with almost perfect C<sub>S</sub> symmetry in the crystal. In solution, they show the typical fluxional behavior for seven-coordinated complexes. Complete oxidative decarbonylation occurs when [ $HC(pz)_3Mo(CO)_3$ ] (4) or [ $MeC(CH_2 PPh_2)_3Mo(CO)_3$ ] (6) are treated with an excess of I<sub>2</sub> or Br<sub>2</sub>.



# Supriya Biswas, Mahammad Ali

J. Organomet. Chem. 692 (2007) 2897

Transition metal carbene chemistry<sup>7</sup>: Nucleophilic substitution reactions of imidazolide and benzimidazolide ions with Fischer carbene complexes in MeOH Rate constants for the nucleophilic substitution reactions of imidazolide and benzimidazolide ions with **4-Cr-Z** and **5** in MeOH at 25 °C are reported. The Hammett  $\rho$  values are 1.50  $\pm$  0.10 and 1.51  $\pm$  0.08 for **4-Cr-Z-IZ**<sup>-</sup> and **4-Cr-Z-BIZ**<sup>-</sup> reactions, respectively. The comparable reactivity and also almost identical  $\rho$  values indicate that there is no difference in reactivity due to slightly bigger size of benzimidazolide over imidazolide ions and bond formation at the transition states are equally progressed.



## J.G. Małecki, M. Jaworska, R. Kruszynski

J. Organomet. Chem. 692 (2007) 2903

Synthesis, molecular, crystal and electronic structure of  $[(C_6H_6)RuCl(1,10-C_{12}H_8N_2)]Cl$ 

The  $[(C_6H_6)RuCl(1,10-C_{12}H_8N_2)]Cl$  complex has been prepared and studied by IR, UV–Vis, <sup>1</sup>H NMR spectroscopy and X-ray crystallography. The complex was obtained by reaction of  $[(C_6H_6)RuCl_2]_2$  with 1,10-phenatroline in acetone. The electronic spectrum of the compound has been calculated by the TDDFT method.



# Marina M. Tomashevskaya, Sergey P. Tunik, Ivan S. Podkorytov, Brian T. Heaton, Jonathan A. Iggo, Matti Haukka, Tapani A. Pakkanen, Päivi L. Pirilä, Jouni Pursiainen

J. Organomet. Chem. 692 (2007) 2911

A novel heterobidentate chiral phosphine and its coordination chemistry in transition metal clusters The optically active new ligand *R*,*R*-PHAZAN has been prepared and the products resulting from the reactions with  $Rh_6(CO)_{15}NCMe$ ,  $H_3RhOs_3(CO)_{12}$ , and  $H_4Ru_4(CO)_{12}$  have been investigated by X-ray crystallography and a variety of multinuclear NMR methods.

#### Sergiusz Luliński, Janusz Serwatowski

J. Organomet. Chem. 692 (2007) 2924

A diverse structural behaviour of boronated *ortho*-phthalaldehydes: A crystal structure of 1,3-dihydro-1,3-dihydroxy-4-formylbenzo[c]-[2,1]oxaborole

Two isomeric boronated *ortho*-phthalaldehydes 3- and 4-[B(OH)<sub>2</sub>]-1,2-C<sub>6</sub>H<sub>3</sub>(CHO)<sub>2</sub> reveal a different structural behaviour in solution; the former compound undergoes a tautomeric rearrangement to form 1,3-dihydro-1,3-dihydroxy-4-formylbenzo[c][2,1]oxaborole.



#### Suman L. Jain, Sweety Singhal, Bir Sain

J. Organomet. Chem. 692 (2007) 2930

[Bmim]BF<sub>4</sub>-immobilized rhenium-catalyzed highly efficient oxygenation of aldimines to oxaziridines using solid peroxides as oxidants A variety of aldimines were selectively oxidized to the corresponding oxaziridnines in excellent yields using [bmim]BF<sub>4</sub> immobilized Re- catalysts and solid peroxy oxidants as oxygen source.



## Volker Langenhahn, Gerhard Beck, Gerhard Zinner, Dieter Lentz, Bernhard Herrschaft, Wolf Peter Fehlhammer

J. Organomet. Chem. 692 (2007) 2936

Reactions at the coordinated trichloromethyl isocyanide. Part VII.  $\alpha$ -Chloroalkenylisocyanide versus oxazolin-2-ylidene(ato) complex formation

The one-pot reactions of  $Cr^0(CO)_5CCl_3$ , phosphines and ketones proceed via intermediates which due to their double nature as phosphorus *and* metallo-nitrile ylids either cause Wittig carbonyl-(isocyano)methyleneation of *or* undergo [3+2] cycloaddition with the ketone. Which course is adopted depends on the phosphine (PPh<sub>3</sub> versus P(NMe<sub>2</sub>)<sub>3</sub>) [or the metal as demonstrated for the related system [Pt<sup>II</sup>]–CN–CH–PPh<sub>3</sub>/RR'C=O].



# Franz Dornhaus, Michael Bolte, Hans-Wolfram Lerner, Matthias Wagner

J. Organomet. Chem. 692 (2007) 2949

The first bidentate phosphanylborohydride: Synthesis, structure, and reactivity towards  $[CpFe(CO)_2I]$ 

Deprotonation of the phosphane-borane adduct (HP(BH<sub>3</sub>)(Ph)CH<sub>2</sub>)<sub>2</sub> with KH provides facile access to the bidentate phosphanylborohydride K<sub>2</sub>[(P(BH<sub>3</sub>)(Ph)CH<sub>2</sub>)<sub>2</sub>]. Treatment of K<sub>2</sub>[(P(BH<sub>3</sub>)(Ph)CH<sub>2</sub>)<sub>2</sub>] with two equivalents of [CpFe(CO)<sub>2</sub>I] gives the dinuclear complex [(CpFe(CO)<sub>2</sub>)<sub>2</sub>- $\mu$ -(P(BH<sub>3</sub>)(Ph)CH<sub>2</sub>)<sub>2</sub>].



# Huaxin Zhang, Sebastian Dechert, Jörg Maurer, Michael Linseis, Rainer F. Winter, Franc Meyer

J. Organomet. Chem. 692 (2007) 2956

Heterobimetallic Mn/Co hybrid complexes composed of proximate organometallic and classical coordination sites

Oxidation is confined to the organometallic Mn site and reduction occurs at the adjacent Werner-type Co subunit in a series of highly unsymmetric heterobimetallic Mn/Co hybrid complexes, as revealed by IR and UV–Visspectroelectrochemistry.



# M. Sarah Mohlala, Neil J. Coville

J. Organomet. Chem. 692 (2007) 2965

Floating catalyst CVD synthesis of carbon nanotubes from  $CpFe(CO)_2X$  (X = Me, I): Poisoning effects of I

MWCNTs were synthesized by an injection CVD method using  $CpFe(CO)_2Me$  and  $CpFe(CO)_2I$  as catalysts. The presence of iodine inhibited the growth of the carbon nanotubes.



# Frank Nitsche, Rudolf Aumann, Roland Fröhlich

J. Organomet. Chem. 692 (2007) 2971

Thiocarbene and alkoxycarbene tungsten complexes exhibit typically different reaction paths

The condensation of an (alkyl)thiocarbene tungsten complex with an  $\alpha$ , $\beta$ -unsaturated *secondary* acid amide gives a cyclopentadienimine, whilst an isostructural (alkyl)alkoxycarbene tungsten complex under similar conditions affords a (*N*-enamino)ethoxy-carbene compound.



# Zhou Li-Ying, Sheng Hong-Ting, Yao Ying-Ming, Zhang Yong, Shen Qi

J. Organomet. Chem. 692 (2007) 2990

A series of new anionic lanthanocene complexes  $\{[o-(Me_3SiN)_2C_6H_4]Ln(MeC_5H_4)_2\}$  {Li-(DME)<sub>3</sub>} [Ln = Yb (1), Sm (2), Nd(3)] have been successfully synthesized. These anionic complexes were found to be efficient singlecomponent initiators for the polymerization of MMA under mild conditions, giving syndiotactic-rich polymers with relatively narrow molecular weight distributions.



# Anna Pla-Quintana, Anna Roglans, Teodor Parella, Jordi Benet-Buchholz

J. Organomet. Chem. 692 (2007) 2997

Synthesis and structure of a chiral dinuclear palladium(0) complex with a 30-membered hexaolefinic macrocyclic ligand

The synthesis and the structural characterization of a chiral dinuclear palladium(0) complex with a 30-membered hexaolefinic azamacrocycle has been achieved.



# Florian Kessler, Normen Szesni, Chaya Maaß, Christiane Hohberger, Bernhard Weibert, Helmut Fischer

J. Organomet. Chem. 692 (2007) 3005

Transfer of heterocyclic carbene ligands from chromium to gold, palladium and platinum The heterocyclic carbene ligand in pentacarbonyl(pyrazolin-3-ylidene)chromium complexes is readily transferable to gold, palladium and platinum thus affording pyrazolin-3-ylidene gold complexes and bis(pyrazolin-3-ylidene)palladium and -platinum complexes in high yield.



## Farkhanda Shaheen, Amin Badshah, Marcel Gielen, Michal Dusek, Karla Fejfarova, Dick de Vos, Bushra Mirza

J. Organomet. Chem. 692 (2007) 3019

Synthesis, characterization, antibacterial and cytotoxic activity of new palladium(II) complexes with dithiocarbamate ligands: X-ray structure of bis(dibenzyl-1-S:S'-dithiocarbamato)Pd(II) Six palladium(II) dithiocarbamates of general formula Pd(AmDTC)<sub>2</sub>, where HAmDTC = aminedithiocarbamic acid, [Pd(II) piperidinedithiocarbamate (1), Pd(II) 4-methylpiperidinedithiocarbamate (2), Pd(II) N-methylbenzyldithiocarbamate (3), Pd(II) dibenzyldithiocarbamate (4), Pd(II) dicyclohexyldithiocarbamate (5), Pd(II) N-cyclohexyl-Nmethyldithiocarbamate (6) have been synthesized and characterized by elemental analyses, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR. The X-ray structure of Pd(II), compounds 3 and 4, showed that the ligands are chelated by both sulfur atoms with bond angles S1-Pd- $S4 = 179.24(2)^{\circ}$  and  $S2-Pd-S3 = 179.09(5)^{\circ}$ , with a distorted square planar geometry around Pd. All these complexes were screened for cytotoxic and antibacterial effects and showed significant activities.



# M. Helena Garcia, Paulo J. Mendes, M. Paula Robalo, A. Romão Dias, Jochen Campo, Wim Wenseleers, Etienne Goovaerts

# J. Organomet. Chem. 692 (2007) 3027

Compromise between conjugation length and charge-transfer in nonlinear optical  $\eta^5$ -monocyclopentadienyliron(II) complexes with substituted oligo-thiophene nitrile ligands: Synthesis, electrochemical studies and first hyperpolarizabilities

New organometallic complexes [FeCp(P\_P)-(NC{SC<sub>4</sub>H<sub>2</sub>}<sub>n</sub>NO<sub>2</sub>)][PF<sub>6</sub>] (P\_P = dppe, (+)-diop; n = 1-3) were prepared and fully characterized. Quadratic hyperpolarizabilities have been determined by hyper-Rayleigh scattering, at 1.064 and 1.550 µm, to reveal the resonant enhancement effects. The quasi-independence of  $\beta_0$  with conjugation length is attributed to the competing effects of charge-transfer efficiency and conjugation length.



$$P_P = dppe, (+) - diop; n = 1 - 3$$

# Leslie D. Field, Warren J. Shaw, Guy K.B. Clentsmith

J. Organomet. Chem. 692 (2007) 3042

A quantitative measure of the ionicity of selected iron hydride species by examination of the deuterium quadrupole coupling constant (DQCC)

The ionicity of the metal hydride bonds of a series of iron hydrides supported by multidentate phosphine donors has been determined by measurement of deuterium quadrupolar coupling constant (DQCC) of the isotopically labelled metal hydrides in concentrated solution in toluene. Ionicities of 0.69–0.73 were obtained.  $[P_4]Fe \stackrel{R}{\downarrow}$ H Fe-H lonicity  $\approx 0.71$ 

# Anna M. Maj, Lionel Delaude, Albert Demonceau, Alfred F. Noels

J. Organomet. Chem. 692 (2007) 3048

Synthesis of *N*-heterocyclic carbene precursors bearing biphenyl units and their use in ruthenium-catalyzed ring-opening metathesis polymerization New *N*-heterocyclic carbene (NHC) precursors bearing biphenyl units on their nitrogen atoms were prepared and combined with [RuCl<sub>2</sub>(*p*cymene)]<sub>2</sub> and potassium *tert*-butoxide to generate the corresponding ruthenium–arene complexes [RuCl<sub>2</sub>(*p*-cymene)(NHC)] *in situ*. The catalytic activity of these species was investigated in the photoinduced ring-opening metathesis polymerization (ROMP) of cyclooctene.

Contents



# Santiago Gómez-Ruiz, Sanjiv Prashar, Mariano Fajardo, Antonio Antiñolo, Antonio Otero

J. Organomet. Chem. 692 (2007) 3057

Synthesis, structural characterization and reactivity of new tin bridged *ansa*-bis-(cyclopentadiene) compounds: X-ray crystal structures of  $Me_2Sn(C_5Me_4R-1)_2$  (R = H, SiMe<sub>3</sub>)

The preparation and characterization of tin bridged *ansa*-bis(cyclopentadiene) compounds are described. Their use as transmetalation reagents in the synthesis of group 4 and 5 metallocene complexes is also reported.



J. Organomet. Chem. 692 (2007) 3065

An efficient catalytic system for the hydrogenation of quinolines

A new catalyst system ( $[Ru(p-cymene)Cl_2]_2/I_2$ ) has been developed for the hydrogenation of quinoline derivatives with high reactivity. For the 2-methyl-quinoline, the hydrogenation reaction can proceed smoothly at an S/C of 20,000/1 with complete conversion. The iodine additive is important for full conversion.



# Joan Albert, Lucía D'Andrea, Jaume Granell, Raquel Tavera, Mercè Font-Bardia, Xavier Solans

J. Organomet. Chem. 692 (2007) 3070

Synthesis and reactivity towards carbon monoxide of an optically active *endo* five-membered *ortho*-cyclopalladated imine: X-ray molecular structure of *trans*-( $\mu$ -Cl)<sub>2</sub>[Pd( $\kappa^2$ -*C*,*N*-(*R*)-C<sub>6</sub>-H<sub>4</sub>-CH=N-CHMe-Ph)]<sub>2</sub> The synthesis, structure and reactivity towards carbon monoxide of an optically active *endo* cyclopalladated imine are described. The coligands of the palladium atom control the selectivity of the carbonylation reaction and permit the preparation of 3-methoxy-2-[(R)-1phenylethyl]isoindolin-1-one in 64% chemical yield and 20% diastereomeric excess.



## Sailer Santos dos Santos, Ernesto Schulz Lang, Gelson Manzoni de Oliveira

J. Organomet. Chem. 692 (2007) 3081

New versatile organyltellurium(IV) halides: Synthesis and X-ray structural features of the telluronium tellurolate salts  $[PhTe(CH_3)_2]_2$ - $[TeX_6]$  (X = Cl, Br) and  $[Ph_3Te][PhTeX_4]$ (X = Cl, Br, I) TeX<sub>4</sub> (X = Cl, Br) react in HCl/HBr with [Ph(CH<sub>3</sub>)<sub>2</sub>-Te]X (X = Cl, Br) to give [PhTe-(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[TeCl<sub>6</sub>] (1) and [PhTe(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[TeBr<sub>6</sub>] (2). The reactions of PhTeX<sub>3</sub> (X = Cl, Br, I) with [(Ph)<sub>3</sub>Te]X (X = Cl, Br, I) lead to [Ph<sub>3</sub>Te][PhTeCl<sub>4</sub>] (3), [Ph<sub>3</sub>Te][PhTeBr<sub>4</sub>] (4) and [Ph<sub>3</sub>Te]-[PhTeI<sub>4</sub>] (5). In the salts 1 and 2 octahedral TeX<sub>6</sub> dianions are linked by telluronium cations attaining bidimensional (1) and three-dimensional (2) assemblies. In 3, 4 and 5, anion–anion interactions form centrosymmetric dimers; telluronium–tellurolate interactions accomplish the centrosymmetric tectons of their supramolecular arrays, where phenyl C–H···halogen interactions also act as structure forming forces.



#### Notes

# Masaru Sato, Yuta Miyagawa, Shizuka Okada, Noboru Saito

J. Organomet. Chem. 692 (2007) 3089

Mono- and di-*t*-butyl substituted 2,2'-bis(1,3dithia[3]ferrocenophane-2-ylidene) derivatives: TTF-like ferrocene analogs Tetrathioethene-bridged dinuclear ferrocene derivatives substituted by mono- and di-*t*-butyl groups were prepared. Though the tetrathioethene-bridge is almost perpendicular to the  $\eta$ -C<sub>5</sub>H<sub>3</sub> ring plane, the  $\Delta E_{1/2}$  was similar to that of diferrocenylethyne.



# Daniel L. Reger, Russell P. Watson, Mark D. Smith

J. Organomet. Chem. 692 (2007) 3094

Synthesis of an anthracene-based bis(pyrazolyl)methane ligand and the structural characterization of its dinuclear tricarbonylrhenium(I) complex The new anthracene-based, bitopic bis(pyrazolyl)methane ligand 1,8-bis(4-[bis(1-pyrazolyl)methyl]phenyl)anthracene (1,8-[4-CH(pz)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub>) has been prepared by the cobaltcatalyzed reaction between thionyldipyrazole and 1,8-bis(4-formylphenyl)anthracene. The reaction between 1,8-[4-CH(pz)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub> and Re(CO)<sub>5</sub>Br yielded the dirhenium complex { $\mu$ -1,8-[4-CH(pz)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>C<sub>14</sub>H<sub>8</sub>}[Re(CO)<sub>3</sub>Br]<sub>2</sub>. The crystalline structure of this complex displays extensive noncovalent interactions, particularly CH– $\pi$  and  $\pi$ – $\pi$  interactions.



#### Konrad Kowalski, Sławomir Domagała

J. Organomet. Chem. 692 (2007) 3100

The synthesis and electrochemical behavior of 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne

The title compound (4) was prepared by oxidative homocoupling of 1'-ethynyl-2,5-dimethylazaferrocene. The cyclic voltammetry measurements of 4 were made within the scan rate range 0.1-2 V/s of two temperatures: -40 °C and 22 °C and indicate electronic communication between two iron centers.



# Aires da Conceição Silva, Andréa Luzia F. de Souza, O.A.C. Antunes

J. Organomet. Chem. 692 (2007) 3104

Phosphine-free Suzuki cross-coupling reactions under ultrasound

Suzuki cross-coupling reaction was carried out in ethylene glycol under phosphine-free condition to obtention of biaryls using ultrasonic irradiation. High yields were obtained using different palladium and bases sources. The catalyst was recycled up to three times with good to moderate activity.





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