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# Contents

# **Short Communications**

# Joseph M. O'Connor, Kevin D. Bunker

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Thermolysis of  $[(\eta^5-C_5H_5)Co(PPh_3)(\eta^2-DMAD)]$ , revisited: a solid state analysis reveals the true structure of the triphenylphosphine–alkyne coupling product

Thermolysis of the  $\eta^2$ -alkyne complex 1 leads to formation of the ortho-metalated vinyl-phosphonium derivative, as revealed by an X-ray crystallographic analysis.



# Yosuke Kosaka, Yuichi Shinozaki, Yoshihiro Tsutsumi, Yoshihiro Kaburagi, Yasuhiro Yamamoto, Yusuke Sunada, Kazuyuki Tatsumi

J. of Organomet. Chem. 671 (2003) 8

Stereochemistry of mono- and dinuclear complexes of rhodium, iridium and ruthenium bearing bis(diphenylphosphinomethyl)phenylphosphine  $[Cp*MCl_2]_2$  (M = Rh, Ir) or  $[(C_6Me_6)Ru-Cl_2]_2$  with bis(diphenylphosphinomethyl)phenylphosphine in the presence of KPF<sub>6</sub> gave mono- and dinuclear complexes that have four-membered ring coordinated by terminal and central P atoms.



# **Regular Papers**

# Clementina Reyes, Alfred Prock, Warren P. Giering

J. of Organomet. Chem. 671 (2003) 13

Analysis of the enantioselectivities and initial rates of the hydrosilylation of acetophenone catalyzed by [Rh(cod)Cl]<sub>2</sub>/(chiral diphosphine). The quantitative analysis of ligand effects

The effect of changing the size of the silanes in [Rh(cod)Cl]<sub>2</sub>/chiral diphosphine catalyzed hydrosilylation of acetophenone is non-linear. This is attributed to the turning on of steric effects at different values of  $\theta$  in the two stereo-differentiating transition states.



# Wai-Yeung Wong, Chun-Kin Wong, Guo-Liang Lu

J. of Organomet. Chem. 671 (2003) 27

 $\sigma\text{-}Acetylide \ complexes \ of \ ruthenium \ and \ osmium \ containing \ alkynylsilane \ ligands$ 

The use of diethynyldiphenylsilane and 1,3diethynyltetramethyldisiloxane in the formation of new Group 8 metal  $\sigma$ -acetylide mononuclear complexes is reported. The spectroscopic, redox and structural properties of these silicon-bridged metal alkynyls have been investigated.



### Ravi Shankar, Mukesh Kumar, Suraj P. Narula, Raj K. Chadha

J. of Organomet. Chem. 671 (2003) 35

Disproportionation reactions of (methoxy/ hydroxy)diorganotin(IV) methanesulfonates with carboxylic acids

Synthesis and structure of new diorganoti- n(IV) carboxylates

New diorganotin compounds,  $R_2Sn(O_2CR'-COOH)_2$  (R' = CHEt, CH=CH) and  $R_6Sn_3-(O_2CC_3H_4N-2)_3(OSO_2Me)_3$  have been synthesized by reacting  $R_2Sn(X)OSO_2Me$  (X = OMe or OH) with the corresponding carboxylic acid. Crystal structures of **3b**, **4b** and **5b**  $\cdot 2H_2O \cdot Et_2O$  are described.

been DSO<sub>2</sub>Me ponding of **3b**, **4b**  $\partial_{cs} \partial_{cs} \partial_{cr} \partial_{cr} \partial_{cr}$ 

Sandra Shotwell, Holly L. Ricks, Jason G.M. Morton, Matthew Laskoski, Jeff Fiscus, Mark D. Smith, Ken D. Shimizu, Hans-Conrad zur Loye, Uwe H.F. Bunz

J. of Organomet. Chem. 671 (2003) 43

*Trans*-spanning acetylenic bispyridine ligands: synthesis and structural characterization of novel organic and organometallic pseudodehydroannulenes A ferrocene containing enediyne pincer ligand is *trans*-spanning and analogous to 1,2-bis(2-pyridinylethynyl)-4,5-dimethoxybenzene. A series of *trans*-coordinated 1:1 or 2:1 complexes that form from the ligands and Cu(OTf)<sub>2</sub> or  $(CH_3CN)_2PdCl_2$  were obtained. All of the *trans*-spanning complexes were characterized by single crystal X-ray diffraction. Their molecular and solid-state structures are discussed.

# Debasis Hazra, Dilip K. Sinha-Mahapatra, Vedavati G. Puranik, Amitabha Sarkar

J. of Organomet. Chem. 671 (2003) 52

Synthesis and structure of novel, air-stable carbyne complexes of tungsten

New Fischer type carbyne complexes of tungsten,  $L(CO)_2W \equiv C-R/Ar$ , **1b**-7**b**, where  $R = CH_3$ , Ar = substituted phenyl, and  $LH = (2-hydroxyphenyl)-bis(3,5-dimethyl-pyrazolyl)methane, with <math>L^-$  being a tridentate, uninegative ligand, were synthesized from  $W(CO)_6$  via tetraethylammonium acylmetallate salt, as thermally stable and airstable solids. In another complex, **8b**, the aryl ring is complexed with tricarbonylchromium. Crystal structure of a representative complex was determined to confirm structural assignment.





### Karl Heinz Dötz, Normen Szesni, Martin Nieger, Kalle Nättinen

J. of Organomet. Chem. 671 (2003) 58

Reaction of complex ligands: Part 95. Chromium tricarbonyl complexes of polysubstituted naphthohydroquinones: regioselective synthesis via [3+2+1]-benzannulation and haptotropic rearrangement Naphthohydroquinoide chromium tricarbonyl complexes were prepared via [3+2+1]benzannulation of Fischer-type carbene complexes with alkynes. Their haptotropic  $\eta^6$ - $\eta^6$ -rearrangement was studied by in-situ NMR spectroscopy and revealed a significant effect of the substitution pattern on the kinetics and thermodynamics of the rearrangement with activation barriers for the metal migration ranging from 23 to 26 kcal mol<sup>-1</sup>.



# Uwe Böhme

J. of Organomet. Chem. 671 (2003) 75

Mechanism of metal-catalyzed CC-coupling reactions with titanocene vinylidene. A theoretical study

The mechanisms for the [2+2]-cycloaddition of titanocene vinylidene with different reagents (a) have been investigated at the B3LYP level of theory. Subsequently reactions of the titanacyclobutanes and -butenes have been investigated as well: Cycloreversion (b) occurs for titanacyclobutane, and with a substantial higher activation barrier for titanacyclobutene. Electrocyclic ring opening (c) is proposed for azatitanacyclobutene. Metathesis (d) are possible for titanaoxetanes.



# A.A. Pasynskii, I.V. Skabitski, Yu.V. Torubaev, N.I. Semenova, V.M. Novotortsev, O.G. Ellert, K.A. Lyssenko

J. of Organomet. Chem. 671 (2003) 91

Antiferromagnetic complexes with metalmetal bonds.

Part XXX. Synthesis and molecular structures of the antiferromagnetic adducts  $[Cp'Cr(\mu-SPh)]_2(\mu_3-Se)^{-}ML (Cp' = \eta^{-5}-CH_3-C_5H_4, ML = Fe_3(\mu_3-S)_2(CO)_8, Mn_2(CO)_9, Mn_2(CO)_8), paramagnetic complexes Cp'-Cr(\mu-SPh)_3Mn(CO)_3 and [Cp'Cr(\mu-SPh)]_2Te,$ 

# Sumit Bhaduri, Sami Mukhopadhyay, Sudhir A. Kulkarni

J. of Organomet. Chem. 671 (2003) 101

Origin of variation in polymerization activity for Ziegler–Natta catalyst with chloride and alkoxy ligands: a density functional study diamagnetic cluster  $Cp_2'Cr_2(\mu$ -SPh)( $\mu_3$ -S)( $\mu_3$ -Te)Co(CO)<sub>2</sub>

The chemical design and molecular structures of the mixed metal heteohalcogenige derivatives of  $[\pi-(CH_3C_5H_4)Cr(\mu-SPh)]_2(\mu-X)$  (X = Se, Te) are reported. Correlations between antiferromagnetic properties of clusters and electronic features of the chalcogenide bridge atom are discussed.



 $[TiCl_2CH_3]^+ \xrightarrow{C_2H_4} polyethylene$   $\xrightarrow{C_3H_6} polypropylene$   $[Ti(OR)_2CH_3]^+ \xrightarrow{C_2H_4} polyethylene$   $\xrightarrow{C_3H_6} No polymerization$ 

# Sandrine Langle, Franck David-Quillot, Alexia Balland, Mohamed Abarbri, Alain Duchêne

J. of Organomet. Chem. 671 (2003) 113

General access to para-substituted styrenes

A simple and efficient procedure has been developed for the synthesis of organogermanium compounds and styrenes *para*-substituted with groups containing an atom of the 14th group by one-pot reaction of halogenosilanes, germanes or stannanes, organic halides and magnesium using ultrasound methods.

Contents



# Xavier Sava, Louis Ricard, F. Mathey, Pascal Le Floch

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Oxidation of the octa-(ethyl)diphosphaferrocene Oxidation of the octa-(ethyl)diphosphaferrocene with NOBF<sub>4</sub> yields a polymeric diphosphaferrocene [Fe(NO)<sub>2</sub>] complex and the 1-P-fluoro-2,3,4,5-tetraethylphosphole oxide. The stable octa-(ethyl)diphosphaferrocenium cation was obtained through reaction with iodine in dichloromethane. X-ray crystal structures of the two complexes were recorded.



# Christos Kaimakliotis, Haribabu Arthanari, Albert J. Fry

J. of Organomet. Chem. 671 (2003) 126

Synthesis, NMR spectroscopy, and conformational analysis of  $\alpha\text{-dimethylsilyl}$  esters

Treatment of esters successively with LiN(i-Pr)<sub>2</sub> and Me<sub>2</sub>SiHCl affords  $\alpha$ -dimethylsilyl esters in excellent yields. The conformational properties of esters explored by both molecular mechanics calculations and a variety of <sup>1</sup>H- and <sup>29</sup>Si-NMR spectroscopic experiments demonstrate that these esters exist as a mixture of conformations with low interconversion barriers.



# Karen Melis, Dirk De Vos, Pierre Jacobs, Francis Verpoort

J. of Organomet. Chem. 671 (2003) 131

Catalytic application of a Ru-alkylidene in the nucleophilic addition of several carboxylic acids on terminal alkynes and the homo-coupling of 1-alkynes Thermal treatment of Ru-alkylidene (4) bearing a triazol-5-ylidene (NHC) ligand at  $110 \,^{\circ}$ C and addition of a terminal alkyne generates a ruthenium vinylidene. The thermolysed Ru-alkylidene catalyses the vinylation and dimerisation of 1-alkynes.



### Giuliana Gervasio, Domenica Marabello, Philip J. King, Enrico Sappa, Andrea Secco

J. of Organomet. Chem. 671 (2003) 137

Formation of an allylic cluster in the reactions of  $[Ru_3(CO)_{12}]$  with diethylamino-propyne and trimethylsilyl propargyl alcohol. Crystal structure of  $[(\mu-H)Ru_3(CO)_9(\mu_3-\eta^3-C_3H_3)]$  The ( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^3$ -C<sub>3</sub>H<sub>3</sub>) has been obtained following two different reaction pathways. One is the deamination of diethylaminopropyne, HC=CCH<sub>2</sub>NEt<sub>2</sub> in the presence of Ru<sub>3</sub>(CO)<sub>12</sub> under thermal conditions; the other is the reaction of trimethylsilylpropargyl alcohol, (HO)H<sub>2</sub>C-C=C(SiMe<sub>3</sub>) with Ru<sub>3</sub>(CO)<sub>12</sub>. Other reaction products, formed by loss of alkyne fragments, have been isolated.



### Wen-Yann Yeh, Shie-Ming Peng, Gene-Hsiang Lee

J. of Organomet. Chem. 671 (2003) 145

Synthesis and reactivity of ditungsten helical complex  $W_2(CO)_6(\mu$ -Ph\_2PC=CPPh\_2)\_3

A triply-bridged complex  $W_2(CO)_6(\mu-Ph_2PC=CPPh_2)_3$  (1), containing a helical  $M_2L_3$  framework with an idealized  $D_3$  symmetry, and a vinylidene complex  $W_2(CO)_6-(\mu-Ph_2PC=CPPh_2)[\mu-C_4H(PPh_2)_3]$  (2) have been prepared and structurally characterized. The vinylidene group of **2** is not linear, with the W=C=C bond angle of 158.6(4)°.



TOHC + OHC

# Humberto J.V. Barros, Maria L. Ospina, Eduardo Arguello, William R. Rocha, Elena V. Gusevskaya, Eduardo N. dos Santos

J. of Organomet. Chem. 671 (2003) 150

Rhodium catalyzed hydroformylation of  $\beta$ pinene and camphene: effect of phosphorous ligands and reaction conditions on diastereoselectivity The diastereoselectivity of the rhodium catalyzed hydroformylation of  $\beta$ -pinene, differently from that of camphene, is largely influenced by the basicity of auxiliary ligands, however, no effect of their steric characteristics has been revealed. The systems with more basic ligands show higher diastereoselectivities for the *cis* aldehyde and usually higher chemoselectivities.

#### Richard D. Adams, Burjor Captain, Wei Fu

J. of Organomet. Chem. 671 (2003) 158

Facile introduction of bridging MPh<sub>2</sub> groups (M=Ge, Sn, Pb) into platinum–pentaruthenium and hexaruthenium carbido carbonyl cluster complexes Reactions of  $PtRu_5(CO)_{16}(\mu_6-C)$  (1) with Ph<sub>3</sub>GeH and Ph<sub>3</sub>SnH afforded the trimetallic cluster complexes PtRu<sub>5</sub>(CO)<sub>15</sub>(µ- $GePh_2$ )( $\mu_6$ -C) (4) and PtRu<sub>5</sub>(CO)<sub>15</sub>(µ- $SnPh_2$ )( $\mu_6$ -C) (5), respectively. The lead compound  $PtRu_5(CO)_{15}(\mu-PbPh_2)(\mu_6-C)$  (6) was obtained from the reaction of 1 with Pb<sub>2</sub>Ph<sub>6</sub>. PtRu<sub>5</sub>(CO)<sub>14</sub>(µ-SnPh<sub>2</sub>)(PMe<sub>2</sub>Ph)- $(\mu_6-C)$  (7) and  $Ru_6(CO)_{13}(\mu-SnPh_2)(\eta^6 C_6H_6)(\mu_6-C)$  (8) were also prepared. All products were characterized crystallographically.



# Contents

### Mani Ganesan, Phillip E. Fanwick, Richard A. Walton

J. of Organomet. Chem. 671 (2003) 166

The synthesis of the triply bonded tetramethyl complex  $Re_2(CH_3)_4(\mu$ -dppm)<sub>2</sub> and its reaction with carbon monoxide to afford  $Re_2(\mu$ -CH<sub>2</sub>)\_2(CO)\_4(\mu-dppm)<sub>2</sub> The triply-bonded complex  $Re_2Cl_4(\mu-dppm)_2$  reacts with  $CH_3Li$  to afford the structurally similar compound  $Re_2(CH_3)_4(\mu-dppm)_2$  (1), which in turn undergoes a non-redox reaction with CO to form the edge-sharing bioctahedral di- $\mu$ -methylene dirhenium(II) complex  $Re_2(\mu-CH_2)_2(CO)_4(\mu-dppm)_3$  (2) in which a Re–Re single bond is present.



# Ana Belén Vázquez, Pascual Royo

J. of Organomet. Chem. 671 (2003) 172

Synthesis and characterization of  $\eta^5$ -tetramethylcyclopentadienyl-hydrido- and chloro-silyl- $\eta^1$ -amido zirconium complexes The tetramethylcyclopentadienyl silyl- $\eta^{1}$ -amido zirconium derivative [Zr( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>Si-MeH- $\eta^{1}$ -N'Bu)Cl<sub>2</sub>] was isolated by reaction of the dilithium salt Li<sub>2</sub>[C<sub>5</sub>Me<sub>4</sub>SiMeH(N'-Bu)] with ZrCl<sub>4</sub>(THF)<sub>2</sub>, and its chlorination with BCl<sub>3</sub> afforded the chlorosilyl compound [Zr( $\eta^{5}$ -C<sub>5</sub>Me<sub>4</sub>SiMeCl- $\eta^{1}$ -N'Bu)Cl<sub>2</sub>]. Alkylation and amidation of both zirconium complexes provided a series of monoand di-substituted derivatives which were characterized by NMR spectroscopy.



X = CI, Me, CH<sub>2</sub>Ph, C<sub>6</sub>F<sub>5</sub>, NMe<sub>2</sub>, N(SiMe<sub>3</sub>)<sub>2</sub>

#### Notes

# Takakazu Yamamoto, Isao Yamaguchi, Mahmut Abla

J. of Organomet. Chem. 671 (2003) 179

Reductive elimination of C–CN compounds from nickel complexes as a reverse reaction for oxidative addition of benzonitriles to nickel Reductive elimination of Ar-CN from Ni(CN)(aryl)(bpy) is promoted by acryloni-trile.



# Carol A. Quezada, Jered C. Garrison, Claire A. Tessier, Wiley J. Youngs

J. of Organomet. Chem. 671 (2003) 183

Synthesis and structural characterization of two bis(imidazol-2-ylidene) complexes of Pt(II)

The first synthesis of two Pt(II) complexes of a chelating N-heterocyclic carbene in wet solvent is described. These complexes are novel because not many Pt(II) complexes have been synthesized. Previous syntheses of Pt N-heterocyclic carbene complexes have involved using the free carbene, a lengthy and difficult route. Here we describe the synthesis in aerobic conditions using conventional solvent.



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