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## Contents

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#### **Regular Papers**

SEVIER

### Ingrid K. Böhmer, Helmut G. Alt

J. Organomet. Chem. 694 (2009) 1001

Influence of triphenylphosphine on the activity of heterogeneous iridium, rhodium and platinum containing catalysts for the dehydrogenation of saturated hydrocarbons

Various complexes of iridium, supported on silica, in combination with triphenylphosphine as additive, are good catalysts for the activation of alkanes. "Sacrificing olefins" are not necessary.



#### Martin Bröring, Carsten Milsmann, Silke Ruck, Silke Köhler

J. Organomet. Chem. 694 (2009) 1011

Bis-picket-fence corroles

Palladium-catalyzed amidation is the key to sterically hindered and chiral triarylcorrole ligands. The steric encumbrance found in these species does not interfere with metal insertion but seems sufficient to direct a potential substrate. Metal chelates of such ligands therefore show much promise as bioinorganic models and stereoselective catalysts.



### Zhiqiang Yang, Kenneth J. Klabunde

J. Organomet. Chem. 694 (2009) 1016

Synthesis of nearly monodisperse palladium (Pd) nanoparticles by using oleylamine and trioctylphosphine mixed ligands Different appearance of the as-synthesized samples. The molar ratios of trioctylphosphine to Pd(II) = 0, 0.4, 0.6, 1.0, 1.4, and 2.0 from left to right.



Shengli Guo, Ralf Hauptmann, Serena Losi, Piero Zanello, Jörg J. Schneider

J. Organomet. Chem. 694 (2009) 1022

1,1' Ferrocenylenediol as chelating ligand for cobalt in fivefold and sixfold coordination geometry: Synthesis, Electrochemistry and X-ray crystal structure of [{((1,1'  $O_2(\eta^5-C_5H_5)_2Fe)_2$ }Co(OEt\_2){( $\eta^5-Me_5C_5$ )Co}\_2] and [{((1,1'  $O_2(\eta^5-C_5H_5)_2Fe)_3$ }Co(( $\eta^5$ -EtMe\_4C\_5)-Co)\_2]

#### Shengli Guo, Ildiko Balog, Ralf Hauptmann, Mathias Nowotny, Jörg J. Schneider

J. Organomet. Chem. 694 (2009) 1027

Synthesis and structure of mono- and dinuclear cyclopentadienyl-indenyl complexes of iron(II) and further reactions to mixed tri- and tetranuclear iron-cobalt complexes Reaction of the triple decker complexes  $[\{(\eta^5-Me_5C_5)Co\}_2(\eta^6:\eta^6-toluene)]$  (1) and  $[\{(\eta^5-EtMe_4C_5)Co\}_2(\eta^6:\eta^6-toluene)]$  (2) with 1,1' ferrocenylenediol in different ratios in ether at room temperature leads to the title compounds 3A and 4, respectively, in good yields. In 3 and 4 the central Co atoms are coordinated in a rather rare square-pyramidal (3) and trigonal-prismatic coordination (4) geometry, respectively.

3A 4

A series of mixed multidecker compounds of cobalt and iron with bridging indenyl ligands (derived from 2,2-bis(indenyl)propane) is presented. The coordination of  $[(\eta^5-CpR)Co]$ ligand fragments is performed under mild conditions using the triple-decker [{( $\eta^5$ - $Me_5C_5)Co_{2}(\mu-\eta^{6}:\eta^{6}-toluene)$ as  $[(n^{5}-$ CpR)Co] transfer agent. The  $[(\eta^5-CpR)Co]$ fragments in the new multidecker complexes are bonded via the six-membered rings of the indenyl ligands in a  $\eta^4$ -fashion. The first examples of slipped triple-decker complexes which comprise indenyl ligands in a  $\mu$ - $\eta^5$ : $\eta^4$ coordination mode are thus given.



#### Jun Pan, Jeff W. Kampf, Arthur J. Ashe III

J. Organomet. Chem. 694 (2009) 1036

The ligand properties of 2-vinyl-1,2azaboratabenzene The reaction of lithium 2-vinyl-1,2-azaboratabenzene **1b** with 1 equiv. of  $[Cp^*RuCl]_4$ gives a very labile sandwich complex **11**, while the reaction with 2 equiv gives a stable diruthenium complex **12**. The X-ray structure of **12** shows that the first Cp<sup>\*</sup>Ru moiety is  $\pi$ -bound to the 1,2-azaboratabenzene ring while the second is bound to Cl and to the nitrogen and the pendant Bvinyl of the 1,2-azaboratabenzene ring.



#### Konrad Kowalski, Rainer F. Winter

J. Organomet. Chem. 694 (2009) 1041

The synthesis and electrochemistry of 2,5dimethylazaferrocenes with heteroaryl bridges Heteroaryl bridged dinuclear 2,5-dimethylazaferrocene derivatives were prepared. Their radical cations have larger comproportionation constants  $K_c$  than the analogous ferrocenes.





#### Zhi-Ming Dai, Gerald Burgeth, Francesco Parrino, Horst Kisch

J. Organomet. Chem. 694 (2009) 1049

Visible light photocatalysis by a Titania-Rhodium(III) complex The Semiconductor Photocatalyst  ${[TiO_2]-O-RhCl_3\}^{-1}}$  contains titania as a complex ligand and catalyzes the mineralization of 4-chlorophenol with visible light.



#### Ulrich Siemeling, Dag Rother

J. Organomet. Chem. 694 (2009) 1055

Evaluation of heterocumulenic ferrocene derivatives for "click" chemistry type reactions

Azidoferrocene (1), 1,1'-diazidoferrocene (2) and 1,1'-diisothiocyanatoferrocene (3) were subjected to reactions from the repertoire of "click" chemistry, with a view to applications in the post-functionalisation of self-assembled monolayers. Nucleophilic additions of amines to 3 proved superior to copper-catalysed 1,3-dipolar cycloaddition reactions and Staudinger reactions performed with 1 and 2.



#### Paul Ransom, Andrew Ashley, Amber Thompson, Dermot O'Hare

J. Organomet. Chem. 694 (2009) 1059

Synthesis, structure and characterisation of *rac* and *meso-ansa*-bridged permethyl-indenyl cobalt complexes

*Rac-* and *meso-*ethylene-bis-hexamethylindenyl cobalt(II) (EBI\*Co) have been prepared. The *rac* and *meso* isomers can be separated by fractional crystallisation, the *rac-*isomer has been structurally characterised. Oxidation of the reaction mixture yields both *rac-* and *meso-*ethylene-bishexamethylindenyl cobalt(III) which have both been structurally characterised.



#### Engelbert Redel, Jérôme Krämer, Ralf Thomann, Christoph Janiak

J. Organomet. Chem. 694 (2009) 1069

Synthesis of Co, Rh and Ir nanoparticles from metal carbonyls in ionic liquids and their use as biphasic liquid–liquid hydrogenation nanocatalysts for cyclohexene Co, Rh and Ir nanoparticles from  $Co_2(CO)_8$ ,  $Rh_6(CO)_{16}$  and  $Ir_4(CO)_{12}$  in ionic liquids are synthesized and used as effective and recyclable catalysts in the hydrogenation of cyclohexene to cyclohexane with activities of up to 1900 mol<sub>product</sub>/(mol<sub>metal</sub> h) and quantitative conversion within 1 h at 4 bar H<sub>2</sub> pressure and 75 °C.



#### Miroslava Malenovska, Marco Litschauer, Marie-Alexandra Neouze, Ulrich Schubert, Anna Peled, Jean-Paul Lellouche

J. Organomet. Chem. 694 (2009) 1076

Multi-component hybrid inorganicorganic-inorganic particles with various metal oxide outer shells Inorganic–organic–inorganic hybrid particles were prepared by reacting the COOH groups of poly((*S*)-*N*-dicarbazolyl-lysine)covered silica particles with metal alkoxides, followed by sol–gel processing. With tetraethoxysilane, the silica core was growing rather than forming an external metal oxide shell, as observed for the other tested metal alkoxides.

#### Robin Haunschild, Sandor Tüllmann, Gernot Frenking, Max C. Holthausen

J. Organomet. Chem. 694 (2009) 1081

Ethylene addition to  $Ru(=CH_2)(=O)_3 - A$  theoretical study

Quantum chemical calculations on various reaction pathways for the addition of ethylene to  $RuO_3(CH_2)$  identify the  $[3+2]_{C,O}$  cycloaddition as the kinetically and thermodynamically preferred process. The  $[3+2]_{O,O}$  cycloaddition route is able to compete kinetically.



Si(OEt)

M(OnBu),

H<sub>2</sub>O

B

150 nm

50 nm

#### Stefan Erhardt, Gernot Frenking

J. Organomet. Chem. 694 (2009) 1091

Bonding situation and stability of  $\eta^1$ - and  $\eta^6$ -bonded heteroarene complexes  $M(\eta^1 - EC_5H_5)_6$  and  $M(\eta^6 - EC_5H_5)_2$  (M = Cr, Mo, W; E = N, P, As, Sb, Bi)

Quantum chemical calculations using DFT at the BP86 level make clear predictions about the relative stabilities of the title compounds  $M(\eta^1-EC_5H_5)_6$  and  $M(\eta^6-EC_5H_5)_2$  and they give a quantitative insight into the nature of the metal-ligand bonding in terms of electrostatic attraction, orbital interactions and Pauli repulsion.



#### Werner Uhl, Barun Jana

J. Organomet. Chem. 694 (2009) 1101

Reactions of  $\beta$ -diketiminatoaluminum hydrides with *tert*-butyl hydrogenperoxide – Facile formation of dialuminoxanes containing Al–O–Al groups The reactions of  $\beta$ -diketiminatoaluminum hydrides with *tert*-butyl hydrogenperoxide open the facile access to dialuminoxanes having almost linear Al–O–Al bridges.



#### Contents

### **Reinald Fischer. Helmar Görls.** Matthias Westerhausen

J. Organomet. Chem. 694 (2009) 1107

Reinvestigation of arylmanganese chemistry - Synthesis and molecular structures of  $[(thf)_4Mg(\mu-Cl)_2Mn(Br)Mes]$ ,  $[Mes(thf)Mn(\mu-Mes)]_2$ , and  $(MnPh_2)_{\infty}$  The synthesis of diarylmanganese proceeds from arylmagnesium bromide with manganese(II) chloride in THF via different intermediates. The first reaction step is an addition product shown in the picture (Mg blue, Mn violet, Cl green, Br blue, O red) with the aryl group already transferred to the manganese atom. Thereafter, the second Br atom can be substituted by another aryl ligand and magnesium(II) halide precipitates.

# Manfred Friedrich,

 $(Ph = C_6H_5; Mes = mesityl, 2,4,6-Me_3C_6H_2)$ 

#### Anne M. Wilson, Arnold L. Rheingold, Thomas E. Waldman, Michael Klein, Frederick G. West, Richard D. Ernst

*J. Organomet. Chem.* 694 (2009) 1112

Fused ring systems derived from reactions of half-open titanocenes with diynes: characterization. Syntheses. cage rearrangements, and structural studies

Half-open titanocenes,  $Ti(C_5H_5)$ (pentadienyl)(PR<sub>3</sub>), react with 1,5-hexadiyne, 1,6heptadiyne, and several heteroatom-substituted analogues, leading to couplings between the two diyne and two  $2,4-C_7H_{11}$ termini, generating nine-membered rings fused to four- or five-membered rings. The resulting 16 electron complexes can undergo subsequent cage rearrangements, via C–C bond activations.





#### Stéphanie Frantz, Monika Sieger, Ingo Hartenbach, Falk Lissner, Thomas Schleid, Jan Fiedler, Carole Duboc, Wolfgang Kaim

J. Organomet. Chem. 694 (2009) 1122

Structure, electrochemistry, spectroscopy, and magnetic resonance, including highfield EPR, of  $\{(\mu-abpy)|Re(CO)_3X|_2\}^{o/2}$ where abpy = 2,2'-azobispyridine and X = F, Cl, Br, I

Reduction to persistent radical anion complexes and further to labile dianions as well as the isomerization from isolated anti to syn forms is facilitated for the compounds  $(\mu-abpy)[Re(CO)_3X]_2$  on going from X = Ivia Br and Cl to F.



#### Holger Braunschweig, Rainer Dörfler, Julian Mager, Krzysztof Radacki, **Fabian Seeler**

J. Organomet. Chem. 694 (2009) 1134

Structural characterization of the anionic [Li(TMEDA)<sub>2</sub>] halfsandwich complex  $[Mo(\eta^5-C_5H_5)(CO)_3]$  and its reactivity towards stannanes and distannanes

The crystal structure of the molybdenum half sandwich alkali salt [Li(TMEDA)<sub>2</sub>]  $[Mo(\eta^5-C_5H_5)(CO)_3]$  is reported and discussed. Reaction of Li[Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>] with <sup>t</sup>Bu<sub>2</sub>(Cl)Sn–Sn(Cl)'Bu<sub>2</sub> leads to the new molybdenum distannane complex [Mo- $(\eta^5 - C_5H_5)Sn^tBu_2 - Sn(Cl)^tBu_2(CO)_3]$ , which is fully characterized. Furthermore, the crystal structures of the long known organotin complexes  $[Mo(\eta^{5}-C_{5}H_{5})(SnMe_{3})(CO)_{3}],$  $[\{Mo(\eta^{5}\text{-}C_{5}H_{5})(CO)_{3}\}_{2}SnMe_{2}]$  and  $[Mo(\eta^{5}\text{-}$  $C_5H_5)(SnMeCl_2)(CO)_3]$  are presented.



#### Janet Petroski, Mei Chou, Carol Creutz

J. Organomet. Chem. 694 (2009) 1138

The coordination chemistry of gold surfaces: Formation and far-infrared spectra of alkanethiolate-capped gold nanoparticles Reaction of "naked gold" with thiols RS–H yields H<sub>2</sub>, establishing the fate of thiol H when RS-capped nanoparticles are formed. The far-infrared spectra of such nanoparticles exhibit  $v_{Au-S}$  very similar to values reported for 2D SAMs and for Au(I) complexes, consistent with recent structural models featuring a "staple" motif.



#### Ritu Ahuja, Munirathinam Nethaji, Ashoka G. Samuelson

J. Organomet. Chem. 694 (2009) 1144

Chelating and bridging diphosphinoamine (PPh<sub>2</sub>)<sub>2</sub>N(<sup>*i*</sup>Pr) complexes of copper(I)

Bis(diphenylphosphino)isopropylamine is quite flexible as a ligand and adopts either a chelating or bridging mode to facilitate the formation of a wide variety of complexes with copper(I).



#### Ritu Ahuja, Ashoka G. Samuelson

J. Organomet. Chem. 694 (2009) 1153

Catalytic cyclopropanation of olefins using copper(I) diphosphinoamines

Copper(I) diphosphinoamine complexes have been employed for catalytic cyclopropanation of olefins. The substituent on the nitrogen of the ligand influenced the rate of cyclopropanation and the reaction rates were found to be dependent on the copper:phosphine ratio. A tentative mechanism is proposed wherein a metalolefin complex is a common intermediate responsible for catalytic activity.



Piero Zanello, Rolfe H. Herber, Alexander R. Kudinov, Maddalena Corsini, Fabrizia Fabrizi de Biani, Israel Nowik, Dmitry A. Loginov, Mikhail M. Vinogradov, Lidia S. Shul'pina, Igor A. Ivanov, Anna V. Vologzhanina

### J. Organomet. Chem. 694 (2009) 1161

Synthesis, structure, electrochemistry, and Mössbauer effect studies of (ring)Fe complexes (ring = Cp, Cp<sup>\*</sup>, and C<sub>6</sub>H<sub>7</sub>). Photochemical replacement of benzene in the cyclohexadienyl complex  $[(\eta^5-C_6H_7)-Fe(\eta-C_6H_6)]^+$ 

A series of cyclohexadienyl complexes of general formula  $[(\eta^5-C_6H_7)FeL_3]^+$  [L = 'BuNC, P(OMe)\_3, P(OEt)\_3] has been prepared and their redox activity has been investigated by electrochemical techniques and compared with that of the related cyclopentadienyl complexes. DFT calculations of the redox potentials and the respective geometrical changes were performed. Variable temperature Mössbauer (ME) spectroscopy has elucidated the relationship between structure and formal oxidation state of the iron atom in these complexes.



#### Contents

#### Bela E. Bode, Jörn Plackmeyer, Michael Bolte, Thomas F. Prisner, Olav Schiemann

J. Organomet. Chem. 694 (2009) 1172

PELDOR on an exchange coupled nitroxide copper(II) spin pair

The synthesis and full characterization of an exchange coupled copper(II) porphyrin/ nitroxide model system is reported. It is possible to disentangle the dipolar through space interaction from the through bond exchange coupling contribution by pulsed electron–electron double resonance (PEL-DOR) experiments and simulations.



#### Sjoerd Harder, Christian Ruspic

J. Organomet. Chem. 694 (2009) 1180

Insight in cyclopentadienyl metal complexes with superbulky ligands: The crystal structure of  $[Cp^{BIG}K]_{\scriptscriptstyle \infty}$ 

The solvent-free supersandwich  $[Cp^{BIG}K]_{\infty}$   $(Cp^{BIG} = (4-nBu-C_6H_4)_5Cp)$  contains centro-symmetric as well as slightly bent  $(Cp^{BIG})_2K^-$  units. Remarkably short Cp–K contacts are explained by pairs of attractive interactions between the  $Cp^{BIG}$  ligands  $(C-H\cdots C(\pi)$  hydrogen bonding).



#### Annika Gross, Nils Metzler-Nolte

J. Organomet. Chem. 694 (2009) 1185

Synthesis and characterisation of a ruthenocenoyl bioconjugate with the cyclic octapeptide octreotate

The solid phase synthesis of the cyclic octapeptide octreotate with covalently attached ruthenocene is described. Conjugates of this kind have potential as targeted metal-based drugs.



### Karl-Christian Schwan, Ulf Vogel, Ariane Adolf, M. Zabel, Manfred Scheer

J. Organomet. Chem. 694 (2009) 1189

Halogenation of Lewis acid/base stabilised phosphanylboranes

The reaction of the Lewis acid/base stabilised phosphanylborane **1** with bromine and iodine results in a halogenation at the tungsten carbonyl moiety to give the products **2** and **3**. Compound **3** is very sensitive regarding the loss of CO and reacts with different donor molecules like  $[Et_4N][Br]$  or  $H_2PBH_2 \cdot NMe_3$  to form **5** or **6**, respectively. Without the presence of a donor, **3** dimerises under CO evolution to give  $[WBr_2(CO)_3(H_2PBH_2 \cdot NMe_3)]_2$  (**4**).



#### Yuri F. Oprunenko, Igor P. Gloriozov

J. Organomet. Chem. 694 (2009) 1195

Theoretical DFT studies of chromium tricarbonyl complexes with polycyclic aromatic ligands

This paper presents a theoretical analysis of the structures of tricarbonylchromium complexes of carbo- and heterocyclic polyaromatic ligands (PAL), the mechanism of the interring haptotropic rearrangement and some reactions (e.g. lithiathion) in such complexes performed using density functional theory (DFT) with the nonempirically constructed PBE functional and extended split basis sets.



#### Alex R. Petrov, Konstantin A. Rufanov, Klaus Harms, Jörg Sundermeyer

J. Organomet. Chem. 694 (2009) 1212

Re-investigation of *ortho*-metalated *N*,*N*dialkylbenzylamine complexes of rareearth metals. First structurally characterized arylates of neodymium and gadolinium Li[LnAr<sub>4</sub>] An improved protocol towards *tris*-aryl complexes of the type [Ln(dmba)<sub>3</sub>] (Ln = Y, Er and Yb, dmba = *ortho*-metal-lated dialkyl-benzylamine) has been developed. First structurally characterized homoleptic lithium ate-complexes of the type Li[Ln(dmba)<sub>4</sub>] (Ln = Gd, Nd) have been isolated using [GdCl<sub>3</sub>(dme)<sub>2</sub>] and [NdCl<sub>3</sub>(dme)] as precursors and THF-free reaction conditions. Factors influencing on possible degradation pathways of lanthanide *tris*-aryl complexes with dmba-type ligands are discussed.



#### Cátia Ornelas, Jaime Ruiz, Didier Astruc

J. Organomet. Chem. 694 (2009) 1219

Visible-light photolysis of  $[FeCp(\eta^6-toluene)][PF_6]$  as a clean, convenient and general route to iron-vinylidene and iron-acetylide complexes

Iron-vinylidene (and subsequently ironacetylide) complexes are easily and quantitatively synthesized by photolysis of the sandwich complex [FeCp( $\eta^6$ -toluene)][PF<sub>6</sub>] using visible light in the presence of a terminal alkyne. The reaction is general and extended to the synthesis of bimetallic complexes.



#### Jürgen Panhans, Frank W. Heinemann, Ulrich Zenneck

J. Organomet. Chem. 694 (2009) 1223

Diphospholyl and triphospholyl zirconium  $\pi$ -complexes: Ziegler–Natta oligomerization catalysts and reactive intermediates in P–C cage formation by hydrolysis Zirconocene derivatives with P-heterocycles as  $\pi$ -ligands are potential Ziegler– Natta catalysts. They are accessible with 1,3-diphospholyl and 1,2,4-triphospholyl ligands, but presence of even traces of water changes the course of the reactions completely. Oligo- or polycyclic organophosphorus compounds are formed by highly diastereoselective dimerization of the homochiral intermediates only.



#### Contents

J. Organomet. Chem. 694 (2009) 1235

A vanadium(V) complex with a tetradentate [OSSO]-type bis(phenolato) ligand: Synthesis, structure, and ethylene polymerization activity

Reaction of VOCl<sub>3</sub> with racemic *trans*-1, 2-dithiacyclohexanediyl-2,2'-bis(6-*tert*-butyl-4-methylphenol) gave the chiral-atmetal vanadium(V) complex [V{( $C_6H_2O-6$ -*tert*-Bu-4-Me)\_2S\_2C\_6H\_{10}}OCl] (1). Upon activation with MAO, 1 was found to be a highly active catalyst for the polymerization of ethylene.



#### William J. Evans, Justin R. Walensky, Timothy M. Champagne, Joseph W. Ziller, Antonio G. DiPasquale, Arnold L. Rheingold

J. Organomet. Chem. 694 (2009) 1238

Displacement, reduction, and ligand redistribution reactivity of the cationic mono- $C_5Me_5$   $Ln^{2+}$  complexes ( $C_5Me_5$ )- $Ln(BPh_4)$  (Ln = Sm, Yb)

Both the metal and the  $(BPh_4)^{1-}$  ion are reactive in  $(C_5Me_5)Ln(BPh_4)$  complexes (Ln = Sm, Yb) generating a variety of product classes depending on the specific metal and substrate.



### Susanne Büschel, Thomas Bannenberg, Cristian G. Hrib, Andreas Glöckner, Peter G. Jones, Matthias Tamm

J. Organomet. Chem. 694 (2009) 1244

Adduct formation of  $[(\eta^7-C_7H_7)Hf(\eta^5-C_5H_5)]$  with isocyanides, phosphines and N-heterocyclic carbenes: An experimental and theoretical study

The reactivity of the sandwich compound  $[(\eta^7-C_7H_7)Hf(\eta^5-C_5H_5)]$  (trohafcene) towards the two-electron donor ligands *tert*-butyl isocyanide (*t*BuNC), 2,6-dimethylphenyl isocyanide (XyNC), 1,3,4,5-tetramethylimidazolin-2-ylidene (IMe) and trimethylphosphine (PMe<sub>3</sub>) has been studied, and the stabilities of the resulting 1:1 adducts were probed via spectroscopic and theoretical methods.





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