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# Contents

## Special Issue: Organometallic Chemistry – The Next Generation

## **Regular papers**

#### Frédéric Blanc, Mathieu Chabanas, Christophe Copéret, Bernard Fenet, Eberhardt Herdweck

J. Organomet. Chem. 690 (2005) 5014

Reactivity differences between molecular and surface silanols in the preparation of homogeneous and heterogeneous olefin metathesis catalysts The reaction of  $Mo(\equiv N)(CH_2tBu)_3$  and  $SiO_{2(700)}$  generates directly (SiO)Mo(=NH)-(=CHtBu)(CH<sub>2</sub>tBu), a highly active catalyst in olefin metathesis, while its reaction with a molecular silanol derivative yields a very stable complex, (c-C<sub>3</sub>H<sub>9</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>SiO-Mo(=NH)(CH<sub>2</sub>tBu)<sub>3</sub>, which is inactive because it does not contain an alkylidene ligand.



# Susie Douglas, John P. Lowe, Mary F. Mahon, John E. Warren, Michael K. Whittlesey

J. Organomet. Chem. 690 (2005) 5027

Synthesis and structural characterisation of rhodium hydride complexes bearing N-heterocyclic carbene ligands

The rhodium phosphine hydride complexes  $[HRh(PPh_3)_4]$  or  $[HRh(CO)(PPh_3)_3]$  lose between one and three PPh<sub>3</sub> ligands upon reaction with aryl and alkyl substituted N-heterocyclic carbenes (NHCs) at mild temperatures. Several mono- and dinuclear products have been structurally characterised, including *trans*-[HRh(I'Pr\_2Me\_2)(PPh\_3)\_2] (I'Pr\_2-Me\_2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and *trans*-[HRh(CO)(IMes)\_2] (IMes = 1,3-dimesitylimidazol-2-ylidene).



#### Li Liu, Suk-Yue Poon, Wai-Yeung Wong

J. Organomet. Chem. 690 (2005) 5036

Evolution of lowest singlet and triplet excited states with transition metals in group 10–12 metallaynes containing biphenyl spacer

A series of metal di-ynes and poly-ynes of group 10–12 transition elements containing biphenyl spacer moiety are prepared and characterized. A discussion on the heavy-atom effect of Pt(II), Au(I) and Hg(II) ions in harvesting the organic triplet emissions in such phosphorescent metal-organic systems is made and the influence of the metal center on the spatial extent of lowest singlet and triplet excited states is characterized in detail.



## Contents

#### Zigang Li, Zhangjie Shi, Chuan He

J. Organomet. Chem. 690 (2005) 5049

Addition of heterocycles to electron deficient olefins and alkynes catalyzed by gold(III)

AuCl<sub>3</sub> works as an excellent catalyst to mediate C–C bond formation between various heterocycles and electron deficient olefins and alkynes under mild conditions. Functional groups such as aldehyde, carboxylic acid and nitrile can be tolerated in these reactions.



#### Tilmann J. Geldbach, Melanie R.H. Brown, Rosario Scopelliti, Paul J. Dyson

J. Organomet. Chem. 690 (2005) 5055

Ruthenium-benzocrownether complexes: Synthesis, structures, catalysis and immobilisation in ionic liquids

A facile route to dimeric benzocrownether complexes of the type  $[RuCl_2(\eta^6-benzocrow$  $nether)]_2$  is reported. These compounds are valuable precursors to catalysts and have been evaluated in the asymmetric transfer-hydrogenation of acetophenone by derivatisation with a chiral amino-alcohol ligand. The effect of complexed alkaline cations in the crownether has been investigated. In view of biphasic catalysis, the crown-moiety may also be utilised to tune the solubility properties of the resulting complexes.



#### Sanjukta Banerjee, Yanhui Shi, Changsheng Cao, Aaron L. Odom

J. Organomet. Chem. 690 (2005) 5066

Titanium-catalyzed iminohydrazination of alkynes

Titanium pyrrolyl complexes are effective catalysts for a new multicomponent coupling reaction between hydrazines, isonitriles, and alkynes. The products of the formal iminohydrazination reaction are 1,3-hydrazonylimines, and the regioselectivity of the reaction is quite sensitive to the catalyst structure. Studies concerning the mechanism of the reaction and some potential intermediates are discussed.



## Tarun K. Panda, Agustino Zulys, Michael T. Gamer, Peter W. Roesky

J. Organomet. Chem. 690 (2005) 5078

Bis(phosphinimino)methanides as ligands in divalent lanthanide and alkaline earth chemistry – synthesis, structure, and catalysis

The reaction of  $K \{CH(PPh_2NSiMe_3)_2\}$  with  $LnI_2 (Ln = Eu, Yb)$  and  $MI_2 (M = Ca, Sr, Ba)$  results in bis(phosphinimino)methanide metal iodidies. The lanthanide complexes were further reacted to give heteroleptic amides and were used as precatalyst for the the intramolecular hydroamination/cyclization reaction.



#### Christopher G. Andrews, Charles L.B. Macdonald

J. Organomet. Chem. 690 (2005) 5090

The unusual reactions of indium(I) trifluoromethanesulfonate with some first row metallocenes and the structure of "indium(II) cyclopentadienide"

Indium(I) trifluoromethanesulfonate, InOTf, does not react with ferrocene (Cp<sub>2</sub>Fe, Cp = C<sub>5</sub>H<sub>5</sub>) while cobaltocene reacts with InOTf to produce [Cp<sub>2</sub>Co]<sup>+</sup>[OTf]<sup>-</sup> and indium metal. The reaction of InOTf with manganocene results in the formation of the salt [In( $\mu^2$ , $\eta^5$ -Cp)In]<sup>+</sup>[Cp<sub>3</sub>In( $\mu^2$ , $\eta^1$ -Cp)InCp<sub>3</sub>]<sup>-</sup>: a crystalline form of "Cp<sub>2</sub>In". Similarly, the reaction of InOTf with [Cp<sub>2</sub>Fe]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> produces Cp<sub>2</sub>Fe and "In<sub>4</sub>OTf<sub>6</sub>" in addition to other products.



#### Hung A. Duong, Janis Louie

J. Organomet. Chem. 690 (2005) 5098

Regioselectivity in nickel(0)/phosphine catalyzed cycloadditions of alkynes and isocyanates The regioselectivity of Ni(0)-catalyzed cycloadditions of various isocyanates and asymmetrical alkynes to afford pyridones was explored. The use of  $PEt_3$  provided, in most cases, two of the four possible pyridone regioisomers in high overall yields. Mechanistic rationale for the product distribution is provided.



## Ayyamperumal Sakthivel, Jin Zhao, Gabriele Raudaschl-Sieber, Fritz E. Kühn

J. Organomet. Chem. 690 (2005) 5105

In situ grafting of cyclopentadienylmolybdenum complexes on mesoporous materials: The reaction of  $[\eta^5$ -CpMo-(CO)<sub>3</sub>]<sup>-</sup>Na<sup>+</sup> with surface fixed iodo-benzyl siloxane  $Na^{+}[\eta^{5}-CpMo(CO)_{3}]^{-}$  is grafted on aromatic silane (iodo-benzyl trimethoxy silane) modified surfaces of MCM-41 and MCM-48 molecular sieves. Molybdenum loadings of up to 8.3%are reached and the obtained materials are applicable as catalysts for olefin epoxidation.



## Gareth R. Owen, Hayley A. Burkill, Ramón Vilar, Andrew J.P. White, David J. Williams

J. Organomet. Chem. 690 (2005) 5113

Palladium complexes containing ligands with hydrogen-bonding functionalities. Reactivity and catalytic studies with CO and olefins The synthesis of a new palladium complex containing a pyridine-urea ligand is reported. The urea substituent on the ligand provides a weakly coordinating group (generating hemilability) and hydrogen bonding functionalities that could interact with incoming substrates. The reactivity of the complex towards CO and olefins has been studied. The complex has shown to be a good catalyst for CO/styrene copolymerization.



#### Contents

## Paul D. Knight, Guy Clarkson, Max L. Hammond, Brian S. Kimberley, Peter Scott

J. Organomet. Chem. 690 (2005) 5125

Radical and migratory insertion reaction mechanisms in Schiff base zirconium alkyls

Steric blocking of migratory insertion in the title complexes opens up a new radical pathway. Detailed kinetic studies lead to the synthesis of a stable alkyl and a long-lived catalyst for ethene polymerisation. Studies on unbridged iminophenolate catalysts indicate that 1,2-migratory insertion is probably not responsible for their high temperature instability.



#### Mani Ganesan, François P. Gabbaï

J. Organomet. Chem. 690 (2005) 5145

Synthesis, structure and catalytic properties of  $[Cp^*Cr(C_6F_5)(Bn)(THF)]$  toward ethylene in the presence of  $AlEt_3$ 

 $[Cp^*Cr(C_6F_5)(Bn)(THF)]$  (1) catalyzes the Aufbaureaktion in toluene at room temperature and under 1.1 atm of ethylene. The molecular weight distribution of the resulting ethylene oligomers is satisfactorily accounted for by the Poisson distribution formula, which is indicative of a living polymerization system.



#### Hongyu Xu, Nathalie LeGall, Li Jia, William W. Brennessel, Benjamin E. Kucera

J. Organomet. Chem. 690 (2005) 5150

The role of phosphine in cobalt-catalyzed carbonylative polymerization of *N*-alkyl-aziridine

A series of CH<sub>3</sub>COCo(CO)<sub>3</sub>L complexes bearing various phosphine ligands were synthesized and studied as precatalyst for the title polymerization. The effect of the electron-donating ability of phosphine ligands on the polymerization rate and the formation of  $\beta$ -lactam byproduct are discussed. The production of the  $\beta$ -lactam byproduct is proposed to have been caused by catalyst decomposition.



#### Hua Jiang, Wenbin Lin

J. Organomet. Chem. 690 (2005) 5159

Chiral molecular polygons based on the Ptalkynyl linkage: Self-assembly, characterization, and functionalization Treatment of 2,2'-diacetoxy-1,1'-binaphthyl-6,6'-bis(ethyne) with one equiv of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> led to a mixture of different sizes of chiral metallocycles [*trans*-(PEt<sub>3</sub>)<sub>2</sub>Pt(L)]<sub>n</sub> (n = 3-8, 1–6). The acetyl groups of 2 were readily deprotected under mild conditions to generate 2a which possesses exposed chiral dihydroxy functional groups. The dihydroxy groups were functionalized with *n*-octadecyl chains or Fréchet-type dendrons to generate dendritic molecules built on a chiral molecular square core.



#### Contents

## Gerhard Hilt, Wilfried Hess, Thomas Vogler, Christoph Hengst

J. Organomet. Chem. 690 (2005) 5170

Ligand and solvent effects on cobalt(I)catalysed reactions: Alkyne dimerisation versus [2+2+2]-cyclotrimerisation versus Diels– Alder reaction versus [4+2+2]-cycloaddition The cobalt catalysed conversion of phenyl acetylene led to linear enyne dimerisation products when CoBr<sub>2</sub>(dppe) was activated with magnesium in the absence of a Lewis acid. In contrast, in the presence of a Lewis acid the cyclotrimerisation process is favoured.



#### Daniela V. Vitanova, Frank Hampel, Kai C. Hultzsch

J. Organomet. Chem. 690 (2005) 5182

Rare earth metal complexes based on  $\beta$ -diketiminato and novel linked bis( $\beta$ -diketiminato) ligands: Synthesis, structural characterization and catalytic application in epoxide/CO<sub>2</sub>-copolymerization

The first homogeneous rare earth metal based catalysts for the copolymerization of cyclohexene oxide and  $CO_2$  are reported. A series of  $\beta$ -diketiminato and novel ethylene- and cyclohexyl-linked bis( $\beta$ -diketiminato) yttrium and lanthanum complexes were prepared via facile amine elimination.



#### Hélène Lebel, Chehla Ladjel

J. Organomet. Chem. 690 (2005) 5198

Rhodium-catalyzed cascade reactions: A methylenation-hydroboration homologative process

A very efficient rhodium-catalyzed cascade process allowing the transformation of aldehydes and ketones into their corresponding one or two-carbon homologated alcohol products through a methylenation-hydroboration sequence is reported. Wilkinson's complex is used to catalyze both reactions in a one-pot procedure that does not require the isolation of the alkene intermediate.



#### John E. McGrady, José Gracia

J. Organomet. Chem. 690 (2005) 5206

Catalytic hydrogenolysis of alkyl halides by sulfido-bridged molybdenum clusters: A density functional study Density functional theory has been used to explore the cleavage of H<sub>2</sub> at a molybdenum cluster, CpMo( $\mu$ -SH)( $\mu$ -S)( $\mu$ -S<sub>2</sub>CH<sub>2</sub>)MoCp. The addition occurs across a single Mo–S bond, and strong Mo–S  $\pi$  bonding in the ground state leads to a very high barrier ( $\Delta E^{\ddagger} = +43$  kcal mol<sup>-1</sup>). Once formed, hydride migration over the cluster is a facile process ( $\Delta E^{\ddagger} = +13$  kcal mol<sup>-1</sup>).



#### Klaus Ruhland, Eberhardt Herdtweck

J. Organomet. Chem. 690 (2005) 5215

Mechanistic investigation of the thermal decomposition of Biphen(OPi-Pr)PtEt<sub>2</sub>: An entrance into C–C single bond activation?

The [1]Pt(Ethene) complex illustrated was synthesized via thermolysis of the [1]PtEt<sub>2</sub>. Mechanistic investigations show that the ethene in [1]Pt(Ethene) is temporarily dissociated. We investigated whether by dissociation of the ethene the bridging C–C single bond of the biphenyl fragment can be activated.



# Hervé Clavier, Ludovic Coutable, Loïc Toupet, Jean-Claude Guillemin, Marc Mauduit

J. Organomet. Chem. 690 (2005) 5237

Design and synthesis of new bidentate alkoxy-NHC ligands for enantioselective coppercatalyzed conjugate addition A new class of chiral alkoxy-NHC ligands readily accessible in a five-step procedure from  $\beta$ -aminoalcohols is described. A small library of these chelating NHCs has been achieved by a modular synthesis allowing the design of the structure backbone. High reactivity and enantioselectivity were obtained at room temperature in the copper-conjugate addition of dialkylzinc to cyclic enones.



#### Jörg Teichgräber, Sebastian Dechert, Franc Meyer

J. Organomet. Chem. 690 (2005) 5255

Dicopper(I) oxalate complexes as molecular precursors for the deposition of copper compounds

A series of dinuclear complexes  $(RNC)_4Cu_2-(C_2O_4)$  has been prepared and structurally characterized. These rare examples of copper(I) oxalato complexes undergo well-behaved thermal decomposition to yield different copper compounds, with the decomposition pathway depending on the respective RNC capping ligand.



## Philip W. Dyer, John Fawcett, Martin J. Hanton

J. Organomet. Chem. 690 (2005) 5264

Diphenylphosphino(phenyl pyridin-2-yl methylene)amine palladium(II) complexes: Chemoselective alkene hydrocarboxylation initiators The P–N ligand diphenylphosphino(phenyl pyridin-2-yl methylene)amine has been synthesised via a simple 'one-pot' procedure, and been shown to form chelate complexes with a range of group 9 and 10 metal-containing fragments. In methanol, a combination of this ligand with sources of Pd(II) generates, exclusively, 4-oxo-hexanoic acid methyl ester from CO/ethene (38 bar, 90 °C).



#### Stefan Roggan, Christian Limberg, Marcus Brandt, Burkhard Ziemer

J. Organomet. Chem. 690 (2005) 5282

Organometallic Mo-O-Bi complexes

Covalent Mo–O–Bi moities are found in the novel organometallic complex depicted, while structural analysis in combination with DFT calculations proved the interactions between molybdate anions and a bimuth(V) centre in a published compound to be of an electrostatic nature. Such complexes are interesting as molecular models for bismuthmolybdate catalysts.



#### Martin Bröring, Esther Cónsul Tejero

J. Organomet. Chem. 690 (2005) 5290

Conformational behaviour of dinuclear Rh(I) complexes of the open-chain tetrapyrrolic ligand 2,2'-bidipyrrin (H<sub>2</sub>BDP)

The treatment of [{Rh(Co)<sub>2</sub>}<sub>2</sub>BDP] complexes (BDP = dianion of 2,2'-bidipyrrin) with different alkyl and aryl phosphanes results in the regioselective exchange of one CO per metal ion and is accompanied by a large conformational change of the tetrapyrrole from a *syn* to an *anti* conformation. This conformational change was resolved by a combination of NMR spectroscopy and X-ray diffraction studies.



#### Michinori Suginome, Akihiko Yamamoto, Masahiro Murakami

J. Organomet. Chem. 690 (2005) 5300

Intramolecular cyanoboration of alkynes via activation of boron–cyanide bonds by transition metal catalysts Cyano(dialkylamino)boryl ethers of homopropargylic alcohols undergo intramolecular addition of a B–CN bond across their carbon–carbon triple bonds (cyanoboration) in the presence of palladium and nickel catalysts, furnishing five-membered cyclic boryl ethers regioselectively in good yields via 5exo cyclization.



# Bin Li, Baiquan Wang, Shansheng Xu, Xiuzhong Zhou

J. Organomet. Chem. 690 (2005) 5309

Synthesis and structures of dinuclear iron, molybdenum and tungsten complexes derived from (PhCHCHPh)-coupled bis(cyclopentadiene) Reaction of ligand CpPhCHCHPhCp (1) with  $Fe(CO)_5$  in refluxing xylene, or the lithium salts of 1 with (MeCN)<sub>3</sub>M(CO)<sub>3</sub> (M = Mo, W) followed by oxidation, afforded (PhCH-CHPh)-coupled bis(cyclopentadienyl) dinuclear iron, molybdenum and tungsten complexes.



#### Masaaki Okazaki, Masato Takano, Ken-ichi Yoshimura

J. Organomet. Chem. 690 (2005) 5318

Synthesis and property of BrCCH- and BrCCBr-coordinated tetrairon clusters

Treatment of the acetylene-coordinated tetrairon cluster,  $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)_2]^+$ , with *N*-bromosuccinimide (NBS) led to stepwise bromination of two acetylene ligands to form  $[(\eta^5-C_5H_4Me)_4Fe_4(HCCBr)(HCCH)]^+$ ,  $[(\eta^5-C_5H_4Me)_4Fe_4(HCCBr)_2]^+$ ,  $[(\eta^5-C_5H_4Me)_4-Fe_4(BrCCBr)(HCCBr)_2]^+$ , and  $[(\eta^5-C_5H_4Me)_4-Fe_4(BrCCBr)_2]^+$ . The bromoacetylene part shows a novel reactivity toward nucleophiles such as water,  $ZnR_2$  (R = Me, Et), H– C=CMgBr, LiS<sup>*p*</sup>Tol, pyridine, and bipyridyl to give the corresponding adducts.



#### Hiroyuki Kawaguchi, Tsukasa Matsuo

J. Organomet. Chem. 690 (2005) 5333

Complexes of tantalum with triaryloxides: Ligand and solvent effects on formation of hydride derivatives This paper desribes the synthesis of triply hydride bridged ditamtalum(V) complex bearing the triarylooxide ligand. The choice of ligand substituent and solvent is crucial to their success synthesis.



#### Dirk Hollmann, Alan R. Kennedy, Mark D. Spicer, Taramatee Ramnial, Jason A.C. Clyburne, Colin D. Abernethy

#### J. Organomet. Chem. 690 (2005) 5346

Reactions of (imidazol-2-ylidene)silver(I) chlorides with group 4 metal containing Lewis acids

The reaction of the N-heterocyclic carbene silver(I) chloride complexes, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene silver(I) chloride ([Ag(IMes)Cl], 1) and 1,3-bis-(4-bromo-2,6-dimethylphenyl)imidazol-2-ylidene silver(I) chloride ([Ag(IMes<sup>Br</sup>)Cl], 2), with the Lewis acidic group 4 transition metal containing compounds, TiCl<sub>4</sub> and ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>, resulted in the formation of the salts [Ag-(IMes)<sub>2</sub>]<sup>+</sup>[(TiCl<sub>3</sub>)<sub>2</sub>( $\mu_{2}$ -Cl)<sub>3</sub>]<sup>-</sup> (3) and [Ag(I-Mes<sup>Br</sup>)<sub>2</sub>]<sup>+</sup>[( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>( $\mu_{2}$ -Cl)<sub>3</sub>]<sup>-</sup> (4).



## Ramel J. Rubio, Gurusamy Thangavelu Senthil Andavan, Eike B. Bauer, T. Keith Hollis, Joon Cho, Fook S. Tham, Bruno Donnadieu

J. Organomet. Chem. 690 (2005) 5353

Toward a general method for CCC *N*heterocyclic carbene pincer synthesis: Metallation and transmetallation strategies for concurrent activation of three C–H bonds A zirconium amido reagent has been successfully applied to deprotonate two imidazolium salts and activate and aryl C–H bond concurrently generating a CCC–NHC Zr pincer complex, which has been shown to efficiently transmetallate to Rh.



A series of ladder oligo(p-phenylenevinylene)s

(LOPVs) and related  $\pi$ -electron systems bearing silicon and carbon bridges has been

synthesized based on the newly developed intramolecular reductive cyclization. All the

J. Organomet. Chem. 690 (2005) 5365

Synthesis, structures, and photophysical properties of silicon and carbon-bridged ladder oligo(*p*-phenylenevinylene)s and related  $\pi$ -electron systems

#### Makoto Tokunaga, Yuki Shirogane, Hiroshi Aoyama, Yasushi Obora, Yasushi Tsuji

J. Organomet. Chem. 690 (2005) 5378

Copper-catalyzed oxidative cleavage of carbon-carbon double bond of enol ethers with molecular oxygen

#### Michito Yoshizawa, Muneki Nagao, Kazuhisa Kumazawa, Makoto Fujita

J. Organomet. Chem. 690 (2005) 5383

chain-directed complementary cis-Side coordination of two pyridines on Pd(II): Selective multicomponent assembly of square-, rectangular-, and trigonal prism-shaped molecules

## Shengming Ma, Bukuo Ni, Shaohui Lin, **Zhiqiang Liang**

J. Organomet. Chem. 690 (2005) 5389

Intramolecular double or triple Suzuki coupling reaction of substituted di- or tribromobenzenes. An easy synthesis of fused tri- or tetracycles with a benzene core

bond in the starting aryl halides and the intramolecular Suzuki coupling.

produced  $\pi$ -electron systems show intense fluorescence in the visible region.

Using CuCl<sub>2</sub> as catalyst, aromatic enol ethers were oxidatively cleaved to give ketones under O<sub>2</sub> atmosphere. On the other hand, the same substrates were hydrolyzed to give aldehydes under Ar atmosphere.

Complementary cis-coordination of two types

of pyridine-based ligands on Pd(II) ions by steric control leads to the selective assembly of

two- and three-dimensional polynuclear Pd(II)

complexes from multicomponents.

Double or triple intramolecular Suzuki coupling reaction has been developed for the efficient synthesis of tri- or tetracyclic products with a benzene core in good yields. The reaction was realized via a one-pot procedure combining the hydroboration of the C=C

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