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Special Issue: Metal-Carbon Multiple Bonds and Related Organometallics Dedicated to Professor E.O. Fischer on his 85th Birthday
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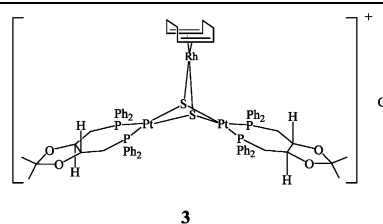
Regular Papers

**Henri Brunner, Matthias Weber,
Manfred Zabel**

J. Organomet. Chem. 684 (2003) 6

Enantioselective catalysis
Part 147. A Rh(cod) complex with the chiral
[Pt₂S₂{(–)diop}₂] ligand

The trinuclear complex [Pt₂Rh(μ₃-S)₂{(–)diop}₂(cod)]Cl (**3**) was synthesized starting from the chiral “ligand” [Pt₂(μ-S)₂{(–)diop}₂] (**2**) and [Rh(cod)Cl]₂, and characterized by X-ray crystallography. Compound **3** was used as a catalyst in the hydrosilylation of acetophenone with diphenylsilane and in the hydrogenation of ketopantolactone.

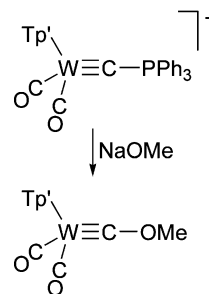


**Kenneth C. Stone, Peter S. White, Joseph L.
Templeton**

J. Organomet. Chem. 684 (2003) 13

Synthesis, protonation, and electrophilic reactions of Tp'(CO)₂W≡C–OMe, a tungsten methoxycarbyne complex

The synthesis and characterization of the terminal methoxycarbyne complex Tp'(CO)₂W≡C–OMe is described. Nucleophiles attack Tp'(CO)₂W≡C–OMe at the methyl group of the methoxide substituent. The carbyne complex undergoes reversible protonation at the carbyne carbon in the presence of [H(Et₂O)₂][BAR₄] to generate the α-agostic carbene complex [Tp'(CO)₂–W=C(H)OMe][BAR₄].

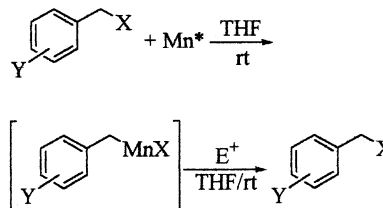


**YoungSung Suh, Jun-sik Lee,
Seoung-Hoi Kim, Reuben D. Rieke**

J. Organomet. Chem. 684 (2003) 20

Direct preparation of benzylic manganese reagents from benzyl halides, sulfonates, and phosphates and their reactions: applications in organic synthesis

The use of highly active manganese (Mn)*, prepared by the Rieke method, was investigated for the direct preparation of benzylic manganese reagents. The oxidative addition of the highly active manganese to benzylic halides was easily completed under mild conditions.



X = Br, Cl, OMs, OTs, OP(O)(OEt)₂
Y = H, Br, Cl, CF₃, F, OMe, CH₃CO₂

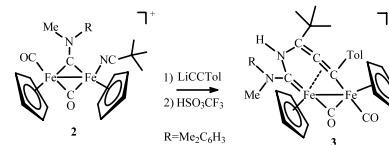
Vincenzo G. Albano, Silvia Bordoni, Luigi Busetto, Fabio Marchetti, Magda Monari, Valerio Zanotti

J. Organomet. Chem. 684 (2003) 37

C–N coupling between μ -aminocarbyne and nitrile ligands promoted by tolylacetylide addition to $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2][\text{SO}_3\text{CF}_3]$

Formation of a novel bridging $\eta^1:\eta^2$ allene-aminocarbene ligand

The reaction of μ -aminocarbyne complex **2** with tolylacetylide, followed by treatment with HSO_3CF_3 yields the complex **3** in which the novel bridging $\eta^1:\eta^2$ allene-aminocarbene ligand comes from acetylide addition at the nitrile and C–N coupling with the μ -carbyne. The addition intermediate is trapped as imine complex $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{Xyl}\}(\mu\text{-CO})(\text{CO})\{\text{NHC}(\text{C}\equiv\text{CTol})\text{CMe}_3\}(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**6**), by treatment with HSO_3CF_3 at an early stage of the reaction. The molecular structures of **3** and **6** have been elucidated by X-ray diffraction studies.

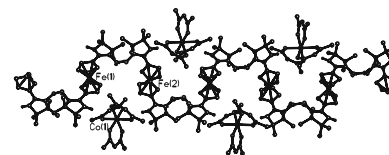


Christian Sporer, Klaus Wurst, Daniel Ruiz-Molina, Holger Kopacka, Jaime Veciana, Peter Jaitner

J. Organomet. Chem. 684 (2003) 44

Synthesis, X-ray structure and characterization of a novel $[\text{fc}(\text{IMH})_2\text{H}]^+[\text{Co}(\text{hfac})_3]^-$ salt with hydrogen bonded ferrocenyl bis(imino hydroxylamino) building blocks

The reaction of ferrocenyl bis(α -nitronyl nitroxide) diradical (**1**; $[\text{fc}(\text{NIT})_2]$) with $\text{Co}(\text{hfac})_2$ produces the reduction of the radical character of **1** with the formation of the diamagnetic ferrocenyl bis(α -imino nitroxide) cation, $[\text{fc}(\text{IMH})_2\text{H}]^+$, which forms with the $[\text{Co}(\text{II})\text{hfac}_3]^-$, as the counterion, the complex salt **4**.

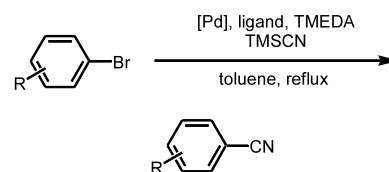


Mark Sundermeier, Sateesh Mutyala, Alexander Zapf, Anke Spannenberg, Matthias Beller

J. Organomet. Chem. 684 (2003) 50

A convenient and efficient procedure for the palladium-catalyzed cyanation of aryl halides using trimethylsilylcyanide

High yields of benzonitriles by slow dosage of trimethylsilylcyanide. An easy procedure for the palladium-catalyzed cyanation of aryl halides is presented.

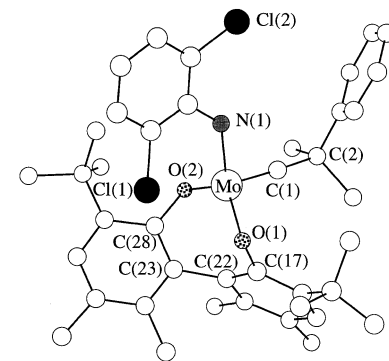


Richard R. Schrock, Jennifer Y. Jamieson, James P. Araujo, Peter J. Bonitatebus, Jr., Amritanshu Sinha, L. Pia H. Lopez

J. Organomet. Chem. 684 (2003) 56

Molybdenum alkylidyne complexes that contain a 3,3'-di-*t*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate ($[\text{Biphen}]^{2-}$) ligand

The reaction between $\text{K}_2[\text{Biphen}]$ ($[\text{Biphen}]^{2-} = 3,3'$ -Di-*t*-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate) and $\text{Mo}(\text{NAr}_{\text{Cl}})(\text{CH}-t\text{-Bu})(\text{OTf})_2(\text{dme})$ ($\text{Ar}_{\text{Cl}} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$) in the presence of ten equivalents of triethylamine gave $\text{Mo}(\text{N}(\text{HAr}_{\text{Cl}}))(\text{C}-t\text{-Bu})[\text{Biphen}]$ (**4a**) in 40–50% yield.

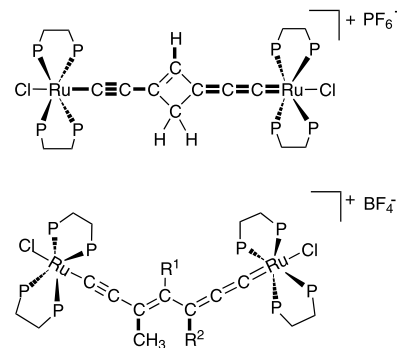


Stéphane Rigaut, Daniel Touchard, Pierre H. Dixneuf

J. Organomet. Chem. 684 (2003) 68

New coupling reactions for the construction of carbon-rich C₇ bridged di-ruthenium complexes

This microreview summarizes our work on new reactions to obtain ruthenium(II) binuclear species of type *trans*-[Cl(dppe)₂Ru-C≡C-C=CHC(CH₂)=C=C-Ru(dppe)₂Cl]PF₆ and *trans*-[Cl(dppe)₂Ru-C≡C-C(CH₃)=C(R¹)-C(R²)=C=C-Ru(dppe)₂Cl]BF₄ (R¹ = H, CH₃; R² = CH₃, Ph) with a charge highly delocalized over the seven conjugated carbon atoms between the remote metals. These complexes display attractive redox and optical properties.

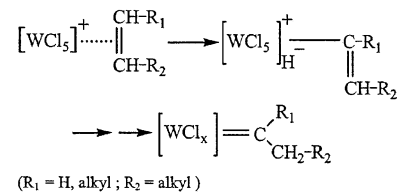


Bülent Düz, Kadir Pekmez, Yavuz İmamoğlu, Şefik Süzer, Attila Yıldız

J. Organomet. Chem. 684 (2003) 77

Electrochemically generated catalyst system with increased specificity and efficiency for olefin metathesis

A facile route for the electrochemical generation of an olefin metathesis catalyst from methylene chloride solution of WCl₆ was described.

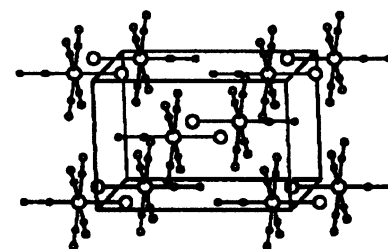


Nguyen Quy Dao

J. Organomet. Chem. 684 (2003) 82

Vibrational spectroscopic data of metallo-carbyne complexes

Vibrational spectroscopic data together with electron deformation density results on Fischer's carbyne complexes are briefly reviewed in this article. The nature of the metal-carbyne bonds and modifications in the molecular structures of some carbynes as a function of temperature are presented.

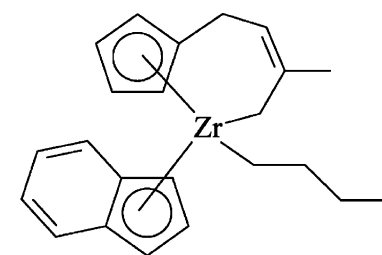


Andrea I. Licht, Helmut G. Alt

J. Organomet. Chem. 684 (2003) 91

CH-Aktivierungsreaktionen an substituierten Zirconocenkomplexen und deren Verwendung in der katalytischen Ethylenpolymerisation

Zirconocene dichloride complexes with alkyl or alkenyl substituents at the aromatic ligands react with two equivalents of *n*-BuLi to give metallacycles via aliphatic CH-activation reactions. In combination with methylalumoxane (MAO) these metallacycles are excellent catalysts for ethylene polymerization. The catalyst **25**/MAO is able to produce 2640 kg PE g⁻¹ Zr h (60 °C, pentane solution, 10 bar).



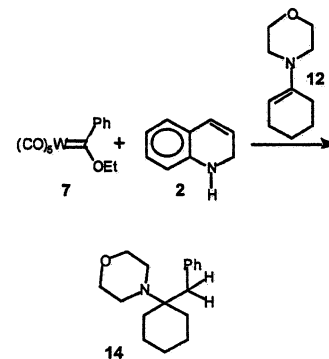
25

H. Rudler, C. Alvarez, B. Denise, A. Parlier, J. Vaissermann

J. Organomet. Chem. 684 (2003) 105

Reaction of alkoxy-carbene complexes of tungsten with 1,2-dihydroquinoline: single vs. double hydride transfers to the carbene-carbon: synthesis, X-ray structure and reactivity of a quinolinium ylide complex of tungsten pentacarbonyl

Carbene complex **7** $(\text{CO})_5\text{W}=\text{C}(\text{Ph})\text{OEt}$ reacts with dihydroquinoline **2** to give, upon a double hydride transfer to the carbene-carbon, with loss of EtO^- , the benzyltungstate $[(\text{CO})_5\text{WCH}_2\text{Ph}]^-$ which can be trapped with the enamine **12** to give the addition product **14**. In the case of complex **3**, $(\text{CO})_5\text{W}=\text{C}(\text{Me})\text{OEt}$, the same reaction leads to the quinolinium ylide complex **4**.

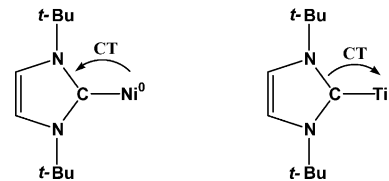


Horst Kunkely, Arnd Vogler

J. Organomet. Chem. 684 (2003) 113

Optical properties of transition metal complexes with *N*-heterocyclic carbenes as ligands. 1,3-di-*t*-Butylimidazol-2-ylidene as charge transfer donor and acceptor

The *N*-heterocyclic carbene 1,3-di-*t*-butylimidazol-2-ylidene (dbiy) can function as charge transfer (CT) donor and acceptor if it is coordinated to oxidizing and reducing metals, respectively. The complex $\text{Ti}^{\text{IV}}\text{Cl}_4(\text{dbiy})_2$ shows a LMCT absorption at 450 nm whereas $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ is characterized by a MLCT absorption at $\lambda_{\text{max}} = 365$ nm. While $\text{Ti}^{\text{IV}}\text{Cl}_4(\text{dbiy})_2$ is not luminescent, $\text{Ni}^0(\text{CO})_2(\text{dbiy})_2$ displays a room temperature emission at $\lambda_{\text{max}} = 510$ nm which is assumed to originate from the lowest-energy MLCT triplet.

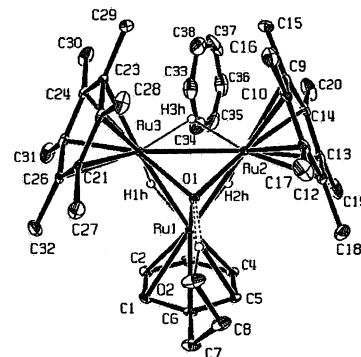


Ludovic Vieille-Petit, Bruno Therrien, Georg Süß-Fink, Thomas R. Ward

J. Organomet. Chem. 684 (2003) 117

Isolation and single-crystal X-ray structure analysis of the catalyst-substrate host-guest complexes $[\text{C}_6\text{H}_6 \subset \text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_n\text{OH}\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ ($n = 2, 3$)

The catalyst-substrate host-guest complexes, postulated as catalytic intermediates in the hydrogenation of benzene to give cyclohexane, catalysed under biphasic conditions by water-soluble trinuclear arene-ruthenium clusters, have been isolated and characterised by single-crystal X-ray structure analysis in the form of the two cationic derivatives $[\text{C}_6\text{H}_6 \subset \text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_n\text{OH}\}(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ ($n = 2, 3$), crystallised as the hexafluorophosphate or the tetrafluoroborate salts.

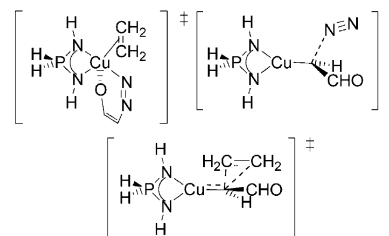


Bernd F. Straub, Irene Gruber, Frank Rominger, Peter Hofmann

J. Organomet. Chem. 684 (2003) 124

Mechanism of copper(I)-catalyzed cyclopropanation: a DFT study calibrated with copper(I) alkene complexes

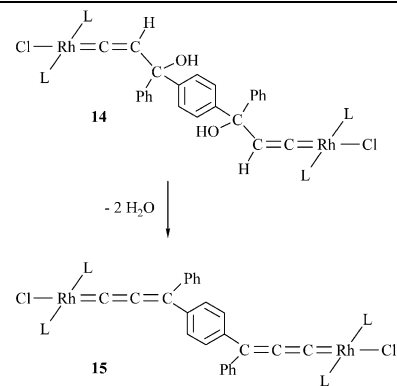
The complete cycle of copper-catalyzed cyclopropanation of alkenes and the electronic structure of the important intermediates has been studied by DFT calculations on models of the experimentally characterized uncharged copper iminophosphanamide system. A high accuracy of the computed relative energies was ensured by extensive comparison with experimental data on alkene ligand rotation barriers and relative ligation strengths.



Berta Callejas-Gaspar, Matthias Laubender, Helmut Werner
J. Organomet. Chem. 684 (2003) 144

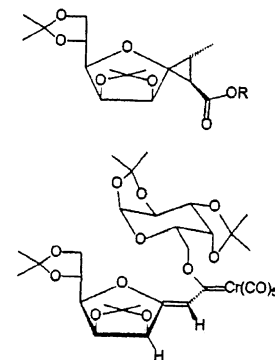
Synthesis and reactivity of dinuclear rhodium complexes with Rh=C=CHR and Rh=C=C=CRR' units as building blocks

A series of dinuclear bis(vinylidene)rhodium(I) complexes with either two Rh=C=CHR units or one Rh=C=CH=X=CH=C=Rh fragment have been prepared in a stepwise fashion from [Rh{κ²-O₂S(O)CF₃}{P^tPr₃}₂] as starting material. The functionalized derivative **14** affords by elimination of water the bis(allenylidene) complex **15**, being the first representative with a M=C=C=C(R)-X-C(R)=C=C=M framework.


Wilm-Christian Haase, Martin Nieger, Karl Heinz Dötz
J. Organomet. Chem. 684 (2003) 153

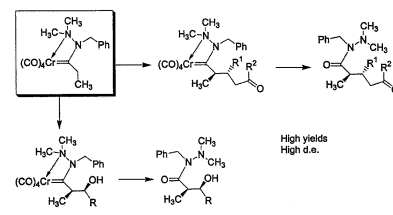
Organotransition metal-modified sugars Part 25. Spiro-C-glycosidation and C₂-homologization of carbohydrates via Fischer glycosylidene complexes: a strategy to novel organometallic disaccharides and a rare example of atropisomerism

Fischer-type glycosylidene complexes are shown to bear considerable potential for the synthesis of C-glycosidic compounds. Insertion of nucleophilic alkynes into the chromium glycosylidene bond as shown for mannosylidene complex **2** affords C₂-homologous carbohydrates still bearing the metal carbene functionality.


Emanuela Licandro, Dario Perdicchia, Stefano Maiorana, Clara Baldoli, Clelia Giannini, Claudia Graiff, Antonio Tiripicchio
J. Organomet. Chem. 684 (2003) 170

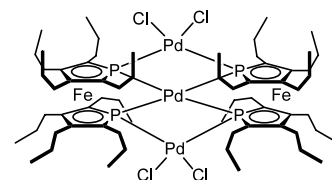
High diastereoselective Michael and aldol additions of Fischer-type alkyl(hydrazino)carbene complexes: synthesis of new hydrazides

The addition of the enolate, generated from the tetracarbonyl ethyl(hydrazino)carbene chromium complex **6**, to achiral enones and aldehydes gave the corresponding Michael and aldol adducts in very high chemical yield and d.e.. Some of the new δ-keto and β-hydroxy hydrazino carbene complexes have been oxidised to give the corresponding hydrazides in high yield.


Mohand Melaimi, Louis Ricard, François Mathey, Pascal Le Floch
J. Organomet. Chem. 684 (2003) 189

A mixed palladium(0) palladium(II) bis-diphosphaferrocene complex

The [(octa-*n*-ethyl-diphosphaferrocene)PdCl₂]₂ dimer complex reacts with [Pd(dba)₂] to afford a trimetallic complex featuring a central Pd(0). This edifice can also be prepared from the reaction of bis-(octa-*n*-ethyl-diphosphaferrocene)Pd(0) complex with two equivalents of [Pd(COD)Cl₂].

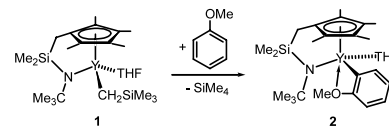


Thomas P. Spaniol, Jun Okuda, Masanori Kitamura, Tamotsu Takahashi

J. Organomet. Chem. 684 (2003) 194

ortho-Metalation of aromatic ethers by yttrium alkyl complexes that contain a linked amido-cyclopentadienyl ligand

The reaction of the alkyl complex $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (**1**) with anisole gives the *ortho*-metalation product $[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N^tBu)(2-C_6H_4OMe)(THF)]$ (**2**). Single-crystal X-ray structure analysis of **2** revealed a four-legged piano-stool configuration with the methoxy group coordinated *cis* to the amido function of the ancillary ligand.

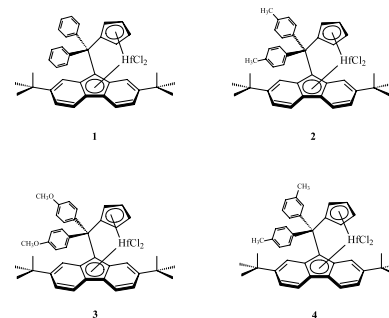


Walter Kaminsky, Andreas Hopf, Christian Piel

J. Organomet. Chem. 684 (2003) 200

C_3 -symmetric hafnocene complexes for synthesis of syndiotactic polypropene

Three new C_3 -symmetric *ansa*-hafnocene complexes such as dichloro[η^{10} -2,4-cyclopentadienyl-1-ylidenebis(4-methyldiphenylmethyl)-[2,7-bis(1,1-dimethylethyl)-9H-fluorene-9-ylidene]]hafnium (**2**) were synthesized which produce partially syndiotactic polypropylenes with very high molar weights. The influence of the methyl and methoxy substitution in the bridge was studied on the activity, tacticity, and molar mass.

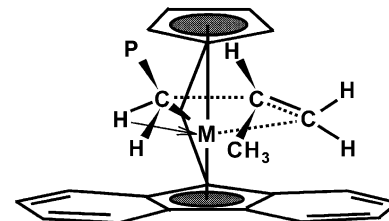


Abbas Razavi, Vincenzo Bellia, Yves De Brauwer, Kai Hortmann, Liliane Peters, Sabine Sirole, Stephan Van Belle, Vladimir Marin, Margarito Lopez

J. Organomet. Chem. 684 (2003) 206

Structural features of bridged cyclopentadienyl-fluorenyl based metallocene catalyst: origin of syndiospecificity

The mechanism of syndiospecific polymerization with $(\eta^5-C_5H_4-CMe_2-\eta^5-C_{13}H_8)MCl_2$; $M = Zr, Hf$ /MAO catalyst systems is discussed by taking into account the structural characteristics of the metallocene molecules and the chiral particularities of their cationic species within the framework of a chain migratory insertion mechanism.

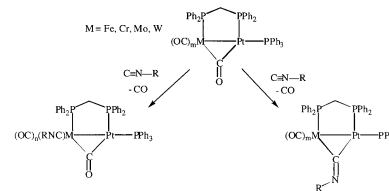


Michael Knorr, Isabelle Jourdain, Dieter Lentz, Stefan Willemsen, Carsten Strohmann

J. Organomet. Chem. 684 (2003) 216

Synthesis and reactivity of dinuclear iron–chromium–platinum, chromium–platinum, molybdenum–platinum and tungsten–platinum complexes with bridging carbonyl, isocyanide and aminocarbene ligands. An empirical study on the parameters decisive for the bonding mode of the isocyanide ligand

Heterobimetallic isocyanide complexes $[(OC)_n(RNC)M(\mu-CO)(\mu-dppm)Pt(PPh_3)]$ and $[(OC)_nM(\mu-CNR)(\mu-dppm)Pt(PPh_3)]$ have been prepared by the reaction of the μ -carbonyl complexes $[(OC)_mM(\mu-CO)(\mu-dppm)Pt(PPh_3)]$ with CNR. The bonding mode of the isocyanide ligand (bridging vs. terminal) is electronically controlled by the π -accepting propensity of CNR.

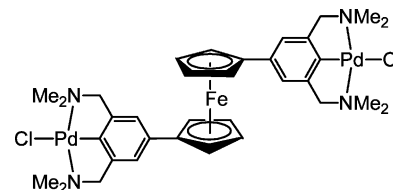


**Stefan Köcher, Gerard P.M. van Klink,
Gerard van Koten, Heinrich Lang**

J. Organomet. Chem. 684 (2003) 230

Ferrocene-bridged Pd–NCN pincer complexes

Reaction of $\text{Fe}[\eta^5\text{-C}_5\text{H}_4(\text{NCNH})]_2$ [$\text{NCNH} = 1\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-3,5}$] with $t\text{-BuLi}$ and $(\text{Me}_2\text{S})_2\text{PdCl}_2$ leads to the formation of trimetallic $\text{Fe}[\eta^5\text{-C}_5\text{H}_4(\text{NCN-4-PdCl})]_2$ $\{\text{NCN} = 1\text{-C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_{2-3,5}\}$ along with heterobimetallic $\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{-}(\text{NCNH})][\eta^5\text{-C}_5\text{H}_4(\text{NCN-4-PdCl})]$.

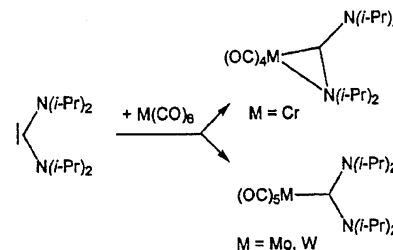


**Wolfgang A. Herrmann, Karl Öfele, Denise
v. Preysing, Eberhardt Herdtweck**

J. Organomet. Chem. 684 (2003) 235

Metal complexes of acyclic diaminocarbenes: links between *N*-heterocyclic carbene (NHC)- and Fischer-carbene complexes

The reactions of several free diaminocarbenes, for the first time isolated by R. Alder, with metal carbonyls of group 16 lead to different types of complexes, depending on the metal and the structure of the carbene (acyclic/cyclic). The yielding metal carbene complexes are compared with analogous NHC complexes and Fischer-carbene complexes.

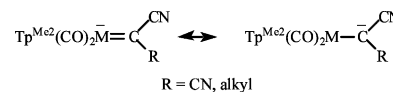


Fergus J. Lalor, S.A. O'Neill

J. Organomet. Chem. 684 (2003) 249

Synthesis and reactivity of air-stable isolable anionic Group 6 molybdenum and tungsten carbene complexes with a metal-centred negative charge

The first examples of air-stable carbene complexes with a metal-centred negative charge have been characterised and, in contrast to normal Fischer-type carbene complexes, the carbene ligand is nucleophilic. For $\text{R} = \text{alkyl}$, reaction with CH_3I yields 4-e donor alkyne complexes via a double alkylation at cyano nitrogen.

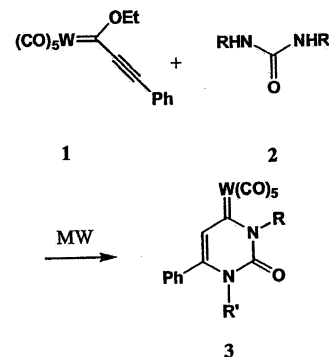


**Aldo Spinella, Tonino Caruso, Umberto
Pastore, Susagna Ricart**

J. Organomet. Chem. 684 (2003) 266

Improving methodology for the preparation of uracil derivatives from fischer carbene complexes. Microwave activation

The effect of the microwave irradiation on the reaction of alkynyl alkoxy carbene complexes with mono and disubstituted ureas is studied and uracil type complexes were obtained. Using microwave dielectric heating very slow reactions that take up to several hours or days (in conventional conditions) can be performed efficiently in good yields within minutes. Furthermore, the use of large amounts of solvents could be drastically reduced or even avoided. The results showed that the use of a microwave activation could represent an alternative to the reactions in conventional conditions for the metal carbene complex chemistry.

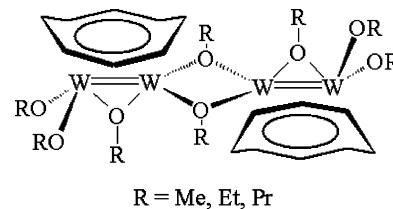


**Malcolm H. Chisholm, Judith C. Gallucci,
Carl B. Hollandsworth**

J. Organomet. Chem. 684 (2003) 269

Tetranuclear tungsten cyclooctatetraenyl alkoxides $[\text{W}_2\text{COT}(\text{OR})_4]_2$, where R = Me, Et and Pr

Two equivalents of $\text{W}_2\text{COT}(\text{NMe}_2)_4$ react with eight equivalents of methanol, ethanol, or *n*-propanol to form the corresponding alkoxide clusters: $[\text{W}_2\text{COT}(\text{OR})_4]_2$ where R = Me, Et or Pr. The tetranuclear compounds are characterized in the solid state and solution.



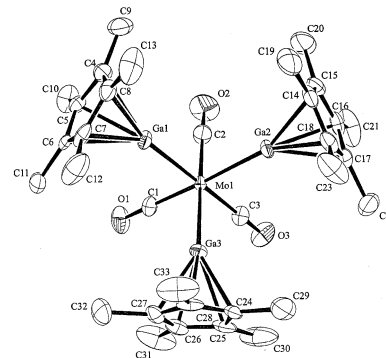
Mirza Cokoja, Tobias Steinke, Christian Gemel, Thea Welzel, Manuela Winter, Klaus Merz, Roland A. Fischer

J. Organomet. Chem. 684 (2003) 277

Ligand properties of Cp^*Ga : new examples of Mo–Ga and W–Ga complexes

The first transition complexes with three terminal GaCp^* ligands are presented. The complexes $[\text{fac}-(\text{Cp}^*\text{Ga})_3\text{M}(\text{CO})_3]$ (**1a**, M = Mo; **1b**, M = W) are accessible via substitution of alkylnitrile ligands of $[\text{fac}-(\text{RCN})_3\text{M}(\text{CO})_3]$ (R = Me, Et) by GaCp^* .

The compounds **1–3** were fully characterized including single crystal X-ray diffraction studies. Compound **1a** serves as a building block for the synthesis of the dinuclear cluster $[\text{Mo}_2(\text{CO})_6(\mu-\text{GaCp}^*)]_3$ (**2**), obtained by reaction of **1a** with $[\text{fac}-(\text{MeCN})_3\text{Mo}(\text{CO})_3]$. Furthermore, the addition of GaCp^* to unsaturated triply bonded metal centres in $[\text{CpM}(\text{CO})_2]$ (M = Mo, W) gives $[(\text{OC})_2(\text{Cp})\text{M}(\eta^1-\text{GaCp}^*)]_2$ (**3a**: M = Mo, **3b**: M = W), revealing a yet unknown reactivity pattern of GaCp^* .

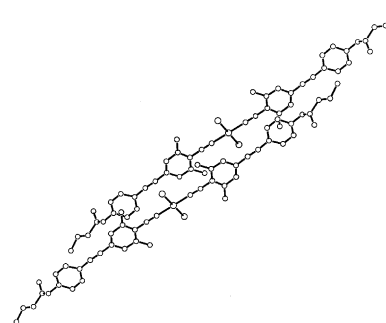


Andreas Mayr, Shuangxi Wang, Kung-Kai Cheung, Maochun Hong

J. Organomet. Chem. 684 (2003) 287

Synthesis, structure, and liquid crystal properties of a series of platinum(II) complexes containing chiral 4-(4-alkoxyphenylethynyl)phenylisocyanide ligands

Several platinum(II) isocyanide complexes of the type $\text{PtI}_2(\text{CNC}_6\text{H}_2-2,6-\text{R}_2-4\text{-CC}(\text{C}_6\text{H}_2-3,5-\text{R}'_2-4(\text{R} \text{ or } \text{S})\text{-OCHMeC}_{n-1}(\text{H}_{2(n-1)}\text{CH}_3)_2)$ have been prepared. The influence of methyl substituents in the positions R and R' on the mesomorphic properties has been evaluated.

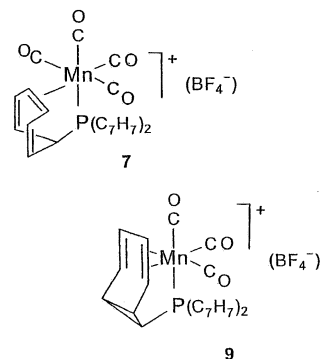


Max Herberhold, Andreas Pfeifer, Wolfgang Milius

J. Organomet. Chem. 684 (2003) 300

Cationic carbonylmanganese complexes of the olefinic ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, $\text{P}(\text{C}_7\text{H}_7)_3$

Carbonylmanganese cations may contain $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) either as conventional two-electron phosphane ligand or—under incorporation of a cyclic olefinic substituent—as four- and six-electron chelate ligand, thus occupying 2 or 3 ligand positions in the octahedral complex, as shown by X-ray studies **7** and **9**.

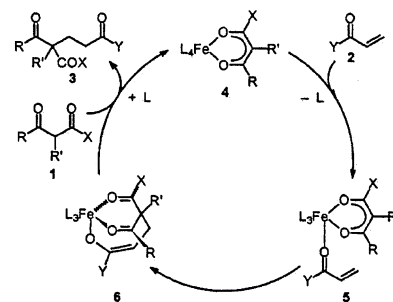


Silke Pelzer, Thomas Kauf, Christoph van Wüllen, Jens Christoffers

J. Organomet. Chem. 684 (2003) 308

Catalysis of the Michael reaction by iron(III): calculations, mechanistic insights and experimental consequences

The proposed mechanism for the Fe^{III} catalysed Michael reaction of β -oxo esters **1** with methyl vinyl ketone (**2a**) and methyl acrylate (**2b**) as acceptors to give addition products **3** is supported for the first time by ab initio calculations.

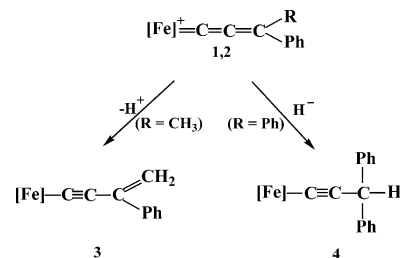


Ana I.F. Venâncio, Luísa M.D.R.S. Martins, Armando J.L. Pombeiro

J. Organomet. Chem. 684 (2003) 315

Allenyldene and derived alkynyl complexes of iron(II) with the $\{\text{FeBr}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2\}^+$ centre

Allenyldene complexes of iron(II), $[\text{Fe}]^+ = \text{C}=\text{C}=\text{C}(\text{R})\text{Ph}$ ($[\text{Fe}] = \text{trans-FeBr}(\text{depe})_2$; $\text{R} = \text{Me}$ **1**, Ph **2**) are obtained by reaction of $[\text{Fe}]-\text{Br}$ with the appropriate alkynol $\text{HC}\equiv\text{C}-\text{C}(\text{R})\text{Ph}(\text{OH})$. The methylallenyldene **1** undergoes reversible deprotonation to afford the enynyl $[\text{Fe}]-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Ph}$ **3**, whereas the diphenylallenyldene **2** undergoes hydride γ -addition to yield the alkynyl $[\text{Fe}]-\text{C}\equiv\text{C}-\text{C}(\text{H})\text{Ph}_2$ **4**.

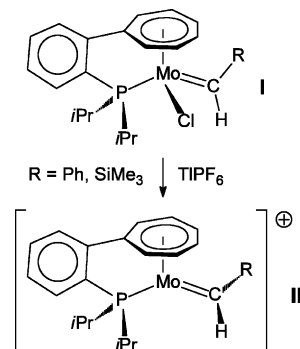


Matthias Tamm, Bernd Dreßel, Thomas Lügger

J. Organomet. Chem. 684 (2003) 322

Molybdenum alkylidene complexes with linked cycloheptatrienyl-phosphane ligands for potential use in olefin metathesis

Chiral-at-metal alkylidene complexes of type **I** containing the chelating $[(o\text{-}i\text{Pr}_2\text{P}-\text{C}_6\text{H}_4-\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{P-Mo})]$ moiety are reported. Preliminary results show that halide abstraction is possible to generate 16-electron carbenes of type **II**, which are potentially useful for applications in catalytic olefin metathesis.

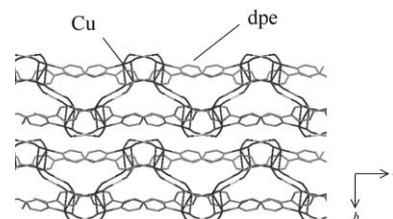


Hilka Hanika-Heidl, Safaa El-din H. Etaiw, Moustafa Sh. Ibrahim, Ahmed S. Bader El-din, R. Dieter Fischer

J. Organomet. Chem. 684 (2003) 329

New supramolecular organotin(IV)/-copper(I) cyanides containing the unique $\{\text{Cu}_2(\mu\text{-CN})_2\}$ building block

Reaction of $\text{Me}_3\text{SnCl}/\text{K}_3[\text{Cu}(\text{CN})_4]$ with the bipodal nitrogen bases ($\mu\text{-L}$): bis(4-pyridyl)-*trans*-ethene (bpe), bis(4-pyridyl)-1,2-ethane (bpeH₂), 4-cyanopyridine (cpy) and bis(4-pyridyl)-*trans*-1,4-divinylbenzene (pdvb) affords the new coordination polymers $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{bpe}]$ (**2**), $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{bpeH}_2]$ (**3**), $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot\text{cpy}]$ (**4**) and $[\text{CuCN}\cdot\text{pdvb}]$ (**5**).

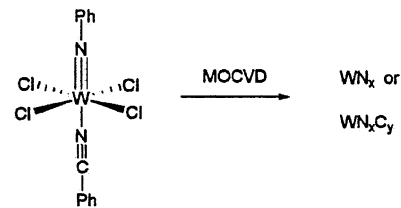


Omar J. Bchir, Kelly M. Green, Mark S. Hlad, Timothy J. Anderson, Benjamin C. Brooks, Corey B. Wilder, David H. Powell, Lisa McElwee-White

J. Organomet. Chem. 684 (2003) 338

$\text{Cl}_4(\text{PhCN})\text{W}(\text{NPh})$ as a single-source MOCVD precursor for deposition of tungsten nitride (WN_x) thin films

Tungsten nitride (WN_x) thin films were grown from the single-source precursor $\text{Cl}_4(\text{PhCN})\text{W}(\text{NPh})$ and compared to films from the related isopropylimido complex $\text{Cl}_4(\text{PhCN})\text{W}(\text{N}^i\text{Pr})$. Differences in growth rate and film properties are attributed to the higher C–N bond dissociation energy in the phenylimido ligand as compared to isopropylimido.

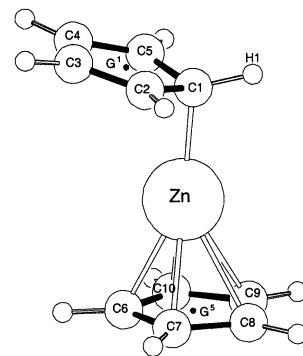


Arne Haaland, Svein Samdal, Natalya V. Tverdova, Georgii V. Girichev, Nina I. Giricheva, Sergej A. Shlykov, Oleg G. Garkusha, Boris V. Lokshin

J. Organomet. Chem. 684 (2003) 351

The molecular structure of dicyclopentadienylzinc (zincocene) determined by gas electron diffraction and density functional theory calculations: η^5, η^5 , η^3, η^3 or η^5, η^1 coordination of the ligand rings?

Density functional theory calculations and structure refinements to gas electron diffraction data show that dicyclopentadienylzinc, Cp_2Zn , has an η^5, η^1 slip sandwich structure in the gas phase.

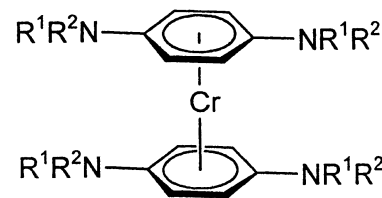


Christoph Elschenbroich, Mathias Pietras, Klaus Harms

J. Organomet. Chem. 684 (2003) 359

Metal π complexes of benzene derivatives Part 57. *p*-Phenylenediamine as a sandwich-complex ligand

Complexes **4** and **5**, prepared by means of metal-atom ligand-vapor cocondensation, have been studied by X-ray diffraction and by cyclic voltammetry. Coordination induced ligand distortion is sizeable for **5** but insignificant for **4**. The redox couple $5^{+/0}$ is the most cathodic one as yet reported for a bis(arene)chromium complex. EPR serves to identify paramagnetic species forming during exhaustive oxidation of **5**.



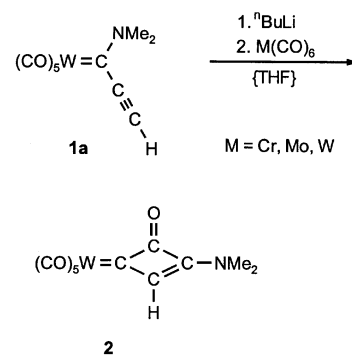
4 $\text{R}^1 = \text{H}, \text{R}^2 = \text{SiMe}_3$
5 $\text{R}^1 = \text{R}^2 = \text{Me}$

Bettina Fuß, Bernhard Weibert, Helmut Fischer

J. Organomet. Chem. 684 (2003) 368

Mono- and binuclear 3-amino cyclobuten-2-one complexes of tungsten—facile migration of pentacarbonylmetal fragments in carbene complexes

Reaction of the ethynylcarbene complex **1a** with *n*-BuLi and $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{W}, \text{Cr}, \text{Mo}$) in THF followed by chromatography on silica affords, independent of the metal in $[\text{M}(\text{CO})_6]$, the tungsten complex **2**. Sequential treatment of **1a** with *n*-BuLi, $[\text{W}(\text{CO})_6]$, and water in Et_2O –THF (5:1) produces a $(\text{CO})_9\text{W}_2$ complex with the cyclobuten-2-on-1-ylidene ligand of **2** in a bridging position.

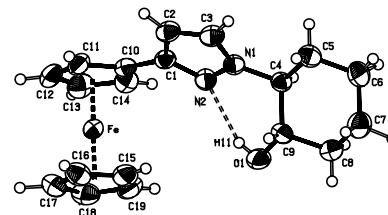


Holger Glas, Anna-Katharina Pleier,
Eberhardt Herdtweck, Werner R. Thiel

J. Organomet. Chem. 684 (2003) 376

2-(3-Ferrocenylpyrazol-1-yl)cyclohexanol: a
new building block for ferrocenyl ligands

Epoxycyclohexane reacts with 3(5)-ferrocenylpyrazole to give *trans*-2-(3-ferrocenylpyrazol-1-yl)cyclohexanol in high yields. This compound exhibits an intramolecular hydrogen bond between the OH group at the cyclohexane ring and a nitrogen atom the pyrazole moiety.



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