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Special Issue: Carbon-Rich Organometallic Compounds

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Reviews

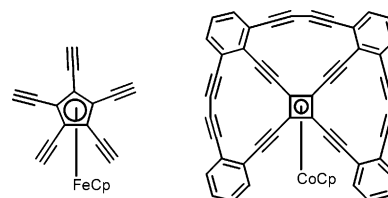
Uwe H.F. Bunz

J. Organomet. Chem. 683 (2003) 269

New carbon-rich organometallic architectures based on cyclobutadienecyclopentadienylcobalt and ferrocene modules

In this account the syntheses, structures and properties of highly alkynylated cyclobutadiene complexes and ferrocenes are discussed. Highly alkynylated cyclobutadiene complexes are excellent building blocks for the construction of new nanoscale carbon

rich organometallics. Butterfly, half wheel, and seco-wheel topologies have been made utilizing a step-by-step assembly process. The target structures have been characterized by crystal structure analysis that reveals an interesting out-of-plane distortion of the alkyne groups attached to the central cyclobutadiene complex. In addition, other carbon rich topologies containing dendrimeric and polymeric structure elements have been made and their chemistry/properties are discussed.

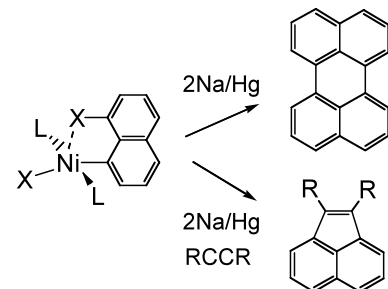


Paul R. Sharp

J. Organomet. Chem. 683 (2003) 288

Organometallic chemistry at the edge of polycyclic aromatic hydrocarbons

Results from this laboratory on the application of organometallic chemistry to the derivatization and synthesis of polycyclic aromatic carbon compounds is reviewed with an emphasis on zirconium and nickel bonded to two carbons at the edge of polycyclic aromatic carbon compounds.



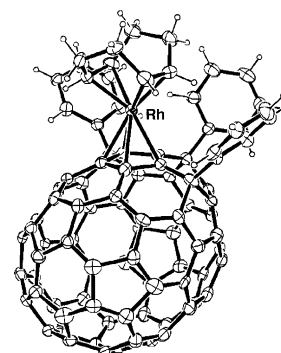
Regular Papers

Motoki Toganoh, Yutaka Matsuo, Eiichi Nakamura

J. Organomet. Chem. 683 (2003) 295

Synthesis and catalytic activity of rhodium diene complexes bearing indenyl-type fullerene η^5 -ligand

Rhodium η^5 -complexes bearing an indenyl-type fullerene ligand, $\text{Rh}[\text{C}_{60}(\text{PhCH}_2)_2\text{-Ph}](\text{cod})$ (**2**), $\text{Rh}[\text{C}_{60}(\text{PhCH}_2)_2\text{Ph}](\text{mbd})$ (**3**) and $\text{Rh}(\text{C}_{70}\text{Ph}_3)(\text{cod})$ (**4**), have been synthesized from the corresponding fullerene tri-adducts in 93–96% yields.

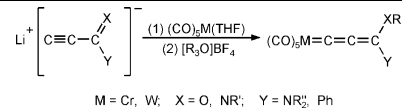


**Helmut Fischer, Normen Szesni,
Gerhard Roth, Nicolai Burzlaff,
Bernhard Weibert**

J. Organomet. Chem. 683 (2003) 301

A new method for the preparation of *N*-stabilized allenylidene complexes of chromium and tungsten

Sequential reaction of $\text{HC}\equiv\text{C}-\text{C}(=\text{X})\text{Y}$ ($\text{X} = \text{O}$; NR' ; $\text{Y} = \text{NR}_2''$, Ph) with BuLi, $[(\text{CO})_5\text{M}(\text{THF})]$ ($\text{M} = \text{Cr}$, W) and $[\text{R}_3\text{O}]\text{BF}_4$ ($\text{R} = \text{Me}$, Et) offers a convenient and versatile route to π -donor-substituted allenylidene complexes, $[(\text{CO})_5\text{M}=\text{C}=\text{C}=\text{C}(\text{XR})\text{Y}]$.

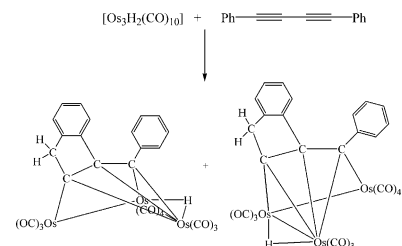


**Lionel P. Clarke, John E. Davies,
Dmitrii V. Krupenya, Paul R. Raithby,
Gregory P. Shields, Galina L. Starova,
Sergey P. Tunik**

J. Organomet. Chem. 683 (2003) 313

Molecular rearrangements of diynes coordinated to triosmium carbonyl clusters: the synthesis and structural characterisation of $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-Ph}(\text{C}_9\text{H}_6)\}]$, $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-Ph}(\text{C}_9\text{H}_6)\}]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_8(\text{MeCN})\{\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-Ph}(\text{C}_9\text{H}_6)\}]$

Reaction of the unsaturated cluster $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ with 1,4-diphenylbuta-1,3-diyne gives two isomeric products with 'open' triangular metal frameworks that show ring closure of the diyne on the cluster triangle. Decarbonylation of these clusters gives a single trinuclear product with a 'closed' triangular osmium core.

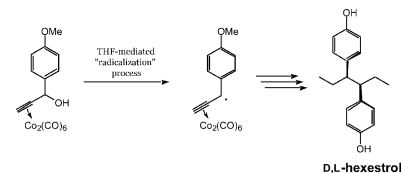


**Gagik G. Melikyan, Steve Sepanian,
Bobby Riahi, Ferdinand Villena,
John Jerome, Brian Ahrens,
Randolph McClain, John Matchett,
Stephanie Scanlon, Edwin Abrenica,
Kevin Paulsen, Kenneth I. Hardcastle**

J. Organomet. Chem. 683 (2003) 324

Tetrahydrofuran-mediated radical processes: stereoselective synthesis of D,L-hexestrol

The highly stereoselective synthesis of D,L-hexestrol, an inhibitor of microtubule assembly, has been developed based on novel stereoselective tetrahydrofuran-induced dimerization of cobalt-complexed propargyl alcohols and cations.

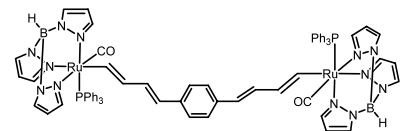


**Sheng Hua Liu, Haiping Xia,
Kam Lok Wan, Richard C.Y. Yeung,
Quan Yuan Hu, Guochen Jia**

J. Organomet. Chem. 683 (2003) 331

Synthesis of $[\text{TpRu}(\text{CO})(\text{PPh}_3)_2](\mu\text{-CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}=\text{CH})$ from Wittig reactions

Treatment of $[\text{TpRu}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)]\text{BPh}_4$ with $\text{NaN}(\text{SiMe}_3)_2$ and terephthalaldehyde produced the bimetallic complex $[\text{TpRu}(\text{CO})(\text{PPh}_3)_2](\mu\text{-CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}=\text{CH})$.

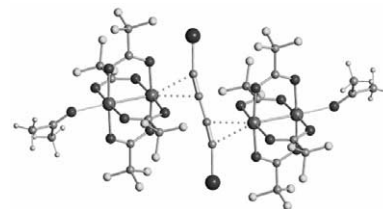


**Evgeny V. Dikarev, Nancy S. Goroff,
Marina A. Petrukhina**

J. Organomet. Chem. 683 (2003) 337

Expanding the scope of solvent-free synthesis: entrapment of thermally unstable species

This work has demonstrated the donor ability of the ambidentate 1,4-diiodo-1,3-butadiyne ligand and expanded the temperature limits of the deposition strategy for potential study of thermally sensitive species. A new mixed-ligand organometallic compound, $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (\text{OCMe}_2)_2 \cdot (\text{C}_4\text{I}_2)]$, has been isolated in crystalline form and has been found by X-ray study to have an $\eta^2(1,2):\eta^2(3,4)$ -bridging mode of diyne.

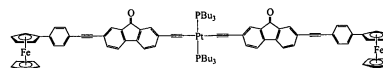


**Wai-Yeung Wong, Ka-Yan Ho,
Sze-Ling Ho, Zhenyang Lin**

J. Organomet. Chem. 683 (2003) 341

Carbon-rich organometallic materials derived from 4-ethynylphenylferrocene

A series of carbon-rich heterometallic alkynyl complexes based on 4-ethynylphenylferrocene building block were synthesized. The spectroscopic, photophysical, electrochemical and structural properties as well as theoretical calculations of these alkynylferrocenyl compounds have been studied.

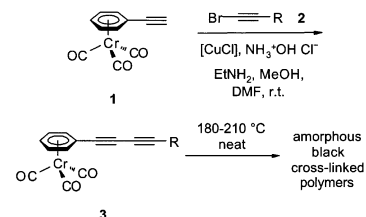


Thomas J. J. Müller, Janet Blümel

J. Organomet. Chem. 683 (2003) 354

Synthesis, structure, electronic properties and thermal behavior of butadiynyl substituted phenylCr(CO)₃-complexes

Butadiynyl-substituted η^6 -benzeneCr(CO)₃ complexes **3** are very efficiently prepared by a copper catalyzed coupling of the phenylacetylene complex **1** and bromo alkynes **2**. Electronic effects are transmitted through the butadiynyl bridge by resonance. Most interestingly, however, is an unusual thermal behavior that leads to intractable paramagnetic polymers of unknown structure.

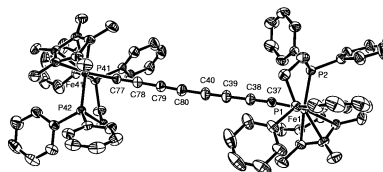


**Françoise Coat, Frederic Paul,
Claude Lapinte, Loic Toupet,
Karine Costuas, Jean-François Halet**

J. Organomet. Chem. 683 (2003) 368

Chemistry of the 1,3,5,7-octatetraynediyl carbon rod end-capped by two electron-rich (η^5 -C₅Me₅)(η^2 -dppe)Fe groups

The synthesis of the organoiron complex $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{Fe}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Fe}(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)]$ (**2**, dppe = 1,2-bis(diphenylphosphino)ethane) is reported with its full spectroscopic characterizations (¹H-, ³¹P-, and ¹³C-NMR, IR, Raman, UV-vis and ⁵⁷Fe Mössbauer). The X-ray analysis of **2** shows that the molecule adopts a geometry very close to the *anti* conformation in the solid state.

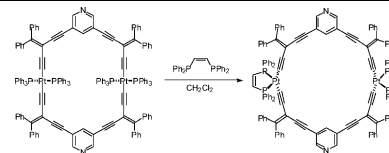


**Katie Campbell, Robert McDonald,
Michael J. Ferguson, Rik R. Tykwinski**

J. Organomet. Chem. 683 (2003) 379

Using ligand exchange reactions to control the coordination environment of Pt(II) acetylide complexes: applications to conjugated metallacyclines

Ligand exchange of *cis*-bis(diphenylphosphino)ethylene (dppee) with *trans*-(Ph₃P)₂Pt(C≡CR)₂ generates *cis*-complexes (dppee)Pt(C≡CR)₂. This strategy has been tested with simple molecular systems and applied to the generation of two pyridine-containing macrocycles. The solid state characteristics of the *trans*- and *cis*-complexes are compared via an analysis of their X-ray crystal structures.

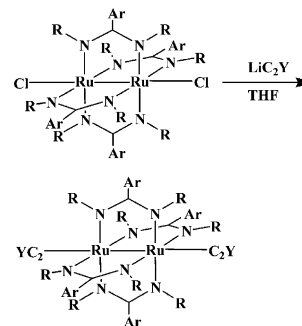


**Guo-Lin Xu, Conrad G. Jablonski,
Tong Ren**

J. Organomet. Chem. 683 (2003) 388

Further studies of tetrakis(*N,N'*-dialkylbenzamidinato)diruthenium(III) chloro and alkynyl compounds: molecular engineering of metallayne monomers

Three types of bis-alkynyl adducts Ru₂(L)₄(C₂Y)₂ (L: *m*MeODMBA, Di-MeODMBA, DEBA) were obtained through the metathesis of Ru₂(L)₄Cl₂ with excess of LiC₂Y.

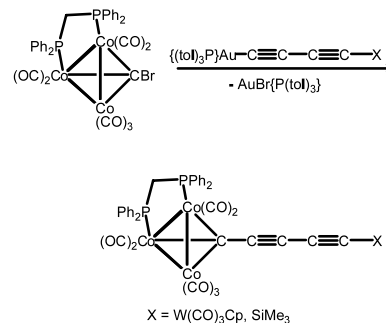


**Michael I. Bruce, Brian W. Skelton,
Allan H. White, Natasha N. Zaitseva**

J. Organomet. Chem. 683 (2003) 398

Preparation and molecular structures of some complexes containing C₅ chains

Reactions between Co₃(μ₃-CBr)(μ-dppm)(CO)₇ and X-C≡CC≡C-Au{P(tol)₃} give {(OC)₇(μ-dppm)Co₃}≡CC≡CC≡C-X [X = W(CO)₃Cp, SiMe₃] in which a five-carbon chain, formally a diynylcarbyne, links the Co₃ cluster with the X fragment. A related multi-step sequence was used to make the analogous ferrocenyl derivative.

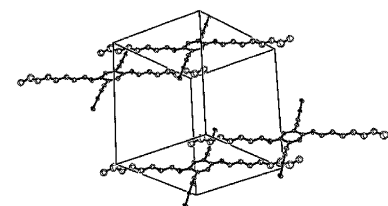


**Alessandra La Groia, Antonella Ricci,
Mauro Bassetti, Dante Masi,
Claudio Bianchini, Claudio Lo Sterzo**

J. Organomet. Chem. 683 (2003) 406

Preparation of models and oligomers of metal alkynyls
NMR, GPC and X-ray structural characterization of building blocks for the construction of molecular devices

By combination of the Pd-based Extended One Pot (EOP) synthetic protocol and uncatalyzed M-Cl and Bu₃Sn-C≡C- coupling (M = Pt, Pd), oligomers of general formula [-C≡C-Ar-C≡C-M(L)_m]_n have been prepared. Combination of ³¹P-NMR and GPC techniques have allowed properly estimation of polymer chain lengths. Single crystal X-ray determination has demonstrated the role of substituents to control the supramolecular order.



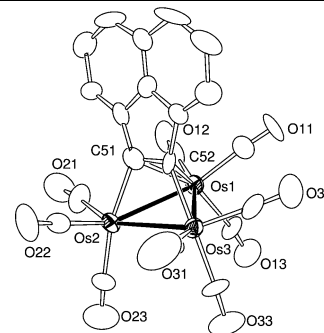
**Richard D. Adams, Burjor Captain,
Jack L. Smith, Jr.**

J. Organomet. Chem. 683 (2003) 421

The activation and transformations of acenaphthylene by osmium carbonyl cluster complexes

$\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (**1**) reacts with acenaphthylene to yield the complexes $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\eta^2\text{-C}_{12}\text{H}_7)$ (**2**) and $\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-C}_{12}\text{H}_6)$ (**3**) by a series of two CH bond cleavages on the five membered ring. Compound **3** contains a tri-

ply bridging acenaphthylene ligand. Compound **3** reacts with acenaphthylene at 160 °C to yield the cluster complexes: $\text{Os}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-}\eta^2\text{-C}_{12}\text{H}_6)$ (**4**); $\text{Os}_2(\text{CO})_6(\mu\text{-}\eta^4\text{-C}_{24}\text{H}_{12})$ (**5**); $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-}\eta^4\text{-C}_{24}\text{H}_{13})$ (**6**); and $\text{Os}_2(\text{CO})_5(\mu\text{-}\eta^4\text{-C}_{24}\text{H}_{12})(\eta^2\text{-C}_{12}\text{H}_8)$ (**7**). Compounds **5** and **7** are dinuclear osmium clusters containing metallacycles formed by the coupling of two acenaphthylene groups. Compound **6** contains an acenaphthylene ligand coupled to an acenaphthyl group by a C–C single bond.



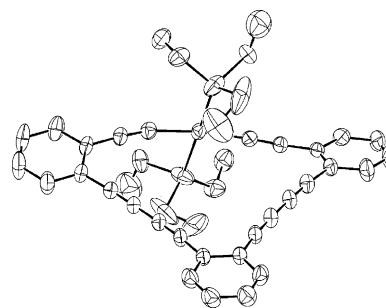
Note

**Joshua J. Pak, Ossama S. Darwish,
Timothy J.R. Weakley, Michael M. Haley**

J. Organomet. Chem. 683 (2003) 430

Synthesis and crystallographic characterization of a ‘palladadehydrobenzo[19]annulene’

The *trans*-bis(σ -acetylide) complex $(\text{Et}_3\text{P})_2\text{Pd}(\text{C}_{30}\text{H}_{12})$ (**2**) was synthesized in very good yield via three-step process. The X-ray crystal structure of **2** shows a strained and warped annulenic core upon insertion of the organometallic fragment. UV–vis data of the molecule suggest limited electronic delocalization throughout the metallacycle.



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