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Journal of Organometallic Chemistry

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Contents

Special Issue: Recent Developments in Metal Alkynyl Organometallic Chemistry

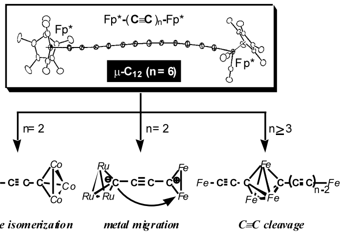
Review

Munetaka Akita, Aizoh Sakurai, Min-Chul Chung, Yoshihiko Moro-oka

J. of Organomet. Chem. 670 (2003) 2

Cluster compounds containing a linear carbon chain derived from polyynediyl and polyynyl complexes, Fp*–(C≡C)$_n$–X [X = Fp*, H; Fp* = Fe(η^5-C_5Me_5)(CO)$_2$]

Reaction of polyynyl [Fp*–(C≡C)$_n$–H] and polyynediyl complexes [Fp*–(C≡C)$_n$–Fp*; Fp* = FeCp*(CO)$_2$] with di- and trimetallic carbonyls results in not only formation of cluster compounds with alkynyl and cumulenic carbon chains but also unique cluster transformations such as valence isomerization of the conjugated carbon chain, metal migration along the carbon rod and C≡C cleavage reaction.



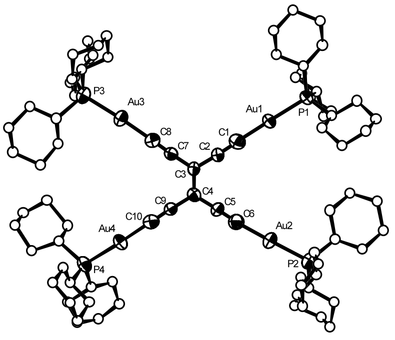
Regular Papers

Wei Lu, Nianyong Zhu, Chi-Ming Che

J. of Organomet. Chem. 670 (2003) 11

Luminescent properties of carbon-rich starburst gold(I) acetylide complexes. Crystal structure of [TEE][Au(PCy$_3$)]$_4$ ([TEE]H$_4$ = tetraethynylethene)

Carbon-rich starburst gold(I) acetylide complexes [TEE][Au(PCy$_3$)]$_4$ ([TEE]H$_4$ = tetraethynylethene) and [TEB][Au(PCy$_3$)]$_3$ ([TEB]H$_3$ = 1,3,5-triethynylbenzene) exhibit interesting luminescent properties in the solid state, in glassy and fluid solutions.

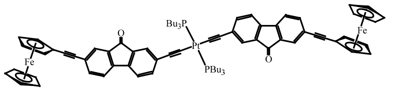


Wai-Yeung Wong, Ka-Yan Ho, Ka-Ho Choi

J. of Organomet. Chem. 670 (2003) 17

New ferrocenyl heterometallic complexes of 2,7-diethynylfluoren-9-one

The synthesis of a fluorenone-bridged ferrocenyl bis(alkynyl) complex and its use in the formation of novel heterometallic alkynyls are reported. The spectroscopic, redox and structural properties of these rigid-rod mixed-metal compounds have been investigated.



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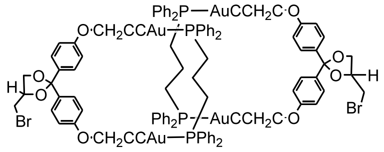
Fabian Mohr, Dana J. Eisler, Christopher P. McArdle, Khaled Atieh, Michael C. Jennings, Richard J. Puddephatt

J. of Organomet. Chem. 670 (2003) 27

Macrocyclic gold(I) complexes and [2]catenanes containing carbonyl functionalized diacetylide ligands

Macrocyclic gold(I) complexes of the type $[Au_2(\mu\text{-LL})(\mu\text{-PP})]$ are reported, where PP is a diphosphine ligand and LL is a diacetylide ligand derived from the diacetylene reagents $O{=}C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$, $RN{=}C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$ [$R = OH$, $NHC(O)NH_2$, $NHC_6H_3\text{-}2,4\text{-}(NO_2)_2$] or the 4-bromomethyl-1,3-dioxolane derivative $BrCH_2C_2H_3O_2C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$. The ability of these macrocyclic complexes to self-assemble to [2]catenanes has been studied, and the concept of a catenation trigger is developed.

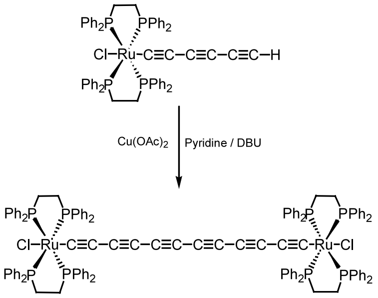


Stéphane Rigaut, Johann Perruchon, Luc Le Pichon, Daniel Touchard, Pierre H. Dixneuf

J. of Organomet. Chem. 670 (2003) 37

Synthesis of ruthenium acetylides: new building blocks for molecular electronics

Several ruthenium(II) mono(acetylides) *trans*-$[Cl(dppe)_2Ru{-}(C{\equiv}C)_n{-}R]$ ($n = 1$–4; $R = SiMe_3$, H) and bis(acetylide) *trans*-$[(dppe)_2Ru(-(C{\equiv}C)_2{-}R)_2]$ ($R = SiMe_3$, H) were selectively obtained. The potential of this new set of building blocks for rigid rod-like structure is illustrated with the synthesis of a ruthenium(II) binuclear complex with 12 carbons between the metals.

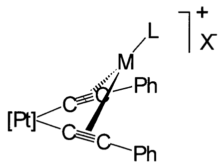


H. Lang, A. del Villar

J. of Organomet. Chem. 670 (2003) 45

Heterobimetallic platinum–copper and platinum–silver transition metal complexes based on *cis*-$[Pt](C{\equiv}CPh)_2$: an overview

The synthesis, reaction chemistry and structural aspects of alkynyl-bridged hetero(bi)-, tri-, tetra- or pentametallic transition metal complexes based on *cis*-$[Pt](C{\equiv}CPh)_2$ species is reported. The interconversion and mechanical aspects in the formation of such species are also discussed.



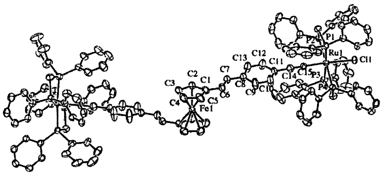
Stephanie K. Hurst, Mark G. Humphrey, Joseph P. Morrall, Marie P. Cifuentes, Marek Samoc, Barry Luther-Davies, Graham A. Heath, Anthony C. Willis

J. of Organomet. Chem. 670 (2003) 56

Organometallic complexes for nonlinear optics

Part 31. Cubic hyperpolarizabilities of ferrocenyl-linked gold and ruthenium complexes

$[Fe\{\eta\text{-}C_5H_4{-}(E){-}CH{=}CH{-}4\text{-}C_6H_4C{\equiv}CX\}_2]$ [$X = SiMe_3$ (**1**), H (**2**), $Au(Pcy_3)$ (**3**), $Au(PPh_3)$ (**4**), $Au(PMe_3)$ (**5**), $RuCl(dppm)_2$ (**8**)] and $[Fe\{\eta\text{-}C_5H_4{-}(E){-}CH{=}CH{-}4\text{-}C_6H_4CH{=}CRuCl(dppm)_2\}_2](PF_6)_2$ (**6**) were prepared and **1** and **7** structurally authenticated. Measurements of cubic nonlinearities by Z-scan at 800 nm for **6** and **7** reveal large negative γ_{real} and large γ_{imag} values, a factor of 4 difference in $|\gamma|$ and two-photon absorption cross-section σ_2 values suggesting that they have potential as protically switchable NLO materials.



Junes Ipaktschi, Katja Reimann, Michael Serafin, Ansgar Dülmer

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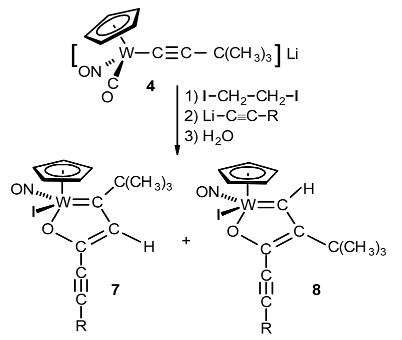
η^1-Alkynyl and vinylidene transition metal complexes
10. Reaction of the metal-acetylide $[(\eta^5\text{-}C_5H_5)(CO)(NO)W{-}C{\equiv}C{-}C(CH_3)_3]Li$ with 1,2-diiodoethane as electrophile and with various nucleophiles

Reaction of η^1-acetylide complex **4** with 1,2-diiodoethane in THF at −78 °C, followed by the addition of $Li{-}C{\equiv}C{-}R$ and protonation, afforded the oxametallacyclopentadienyl complexes **7** and **8**. The formation of these metallafuran derivatives is discussed. The reaction intermediate could be trapped with $CF_3SO_3CH_3$ and characterized by X-ray crystallography.



Victorio Cadierno, M. Pilar Gamasa, José Gimeno, Enrique Pérez-Carreño, Santiago García-Granda

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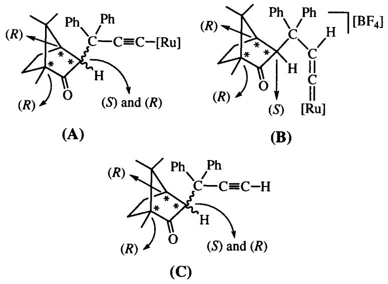
Synthesis of indenyl-ruthenium(II) σ-alkynyl complexes via nucleophilic addition of (1*R*)-(+)- and (1*S*)-(−)-camphor enolates on the allenylidene group of $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$: Efficient synthesis of novel optically pure vinylidene derivatives

The reactivity of the diphenylallenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ towards the lithium enolates derived from (1*R*)-(+)- and (1*S*)-(−)-camphor has been explored. Compounds **A**, **B** and **C**, and their corresponding enantiomers have been prepared (see figure).

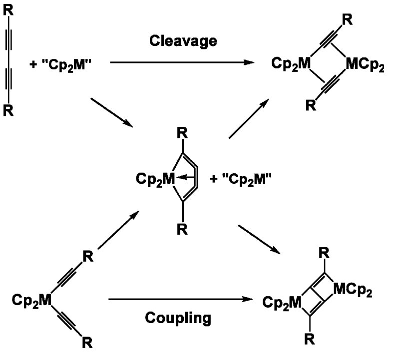


Uwe Rosenthal, Perdita Arndt, Wolfgang Baumann, Vladimir V. Burlakov, Anke Spannenberg

J. of Organomet. Chem. 670 (2003) 84

Titanocene and zirconocene σ-alkynyl complexes in C–C single bond coupling and cleavage reactions

Metallocene σ-alkynyl complexes $L_2M(\sigma\text{-}C{\equiv}CR)$ and $L_2M(\sigma\text{-}C{\equiv}CR)_2$ (M = Ti, Zr; L = Cp, Cp*) are important in the C–C single bond cleavage of 1,3-butadiynes $RC{\equiv}C{-}C{\equiv}CR$ to alkynyl groups and the opposite reaction of C–C single bond formation starting from alkynyl groups under the formation of 1,3-butadiynes. Five-membered metallacyclocumulenes $L_2M(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ are intermediates and depending on M and L either coupling or cleavage is favoured.

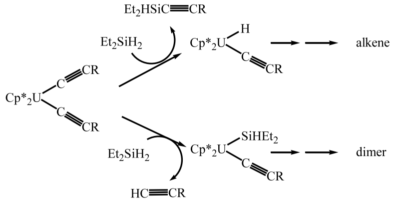


Ji Quan Wang, Moris S. Eisen

J. of Organomet. Chem. 670 (2003) 97

Et_2SiH_2 assisted the selective dimerization of terminal alkynes catalyzed by $Cp^*_2UMe_2$

The catalytic synthesis of regiospecific short oligomers of terminal alkynes has been achieved using the metallocene $Cp^*{}_2UMe_2$. This catalyst promoted the production of large number of various sizes oligomers however, the addition of Et_2SiH_2 diminished the extent of the reaction affording dimers and/or trimers, with the concomitant formation of the corresponding silylalkyne and alkene.

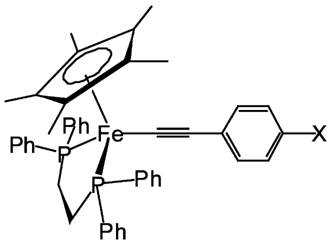


James Courmarcel, Gildas Le Gland, Loic Toupet, Frédéric Paul, Claude Lapinte

J. of Organomet. Chem. 670 (2003) 108

Versatile reactions of a *para*-bromophenylacetylide iron(II) derivative and X-ray structure of the fluoro analogue.
Synthesis of new redox-active organoiron(II) synthons

The reactivity of organoiron(II) bromophenylacetylides toward catalytic coupling or halogen exchange is investigated. Efficient synthetic ways to access the redox-active organoiron(II) acetylides featuring C≡C–H and SnR_3 substituents in *para*-position on the aryl ring are reported. The full characterisation of these promising building blocks and of some relevant analogues is presented.



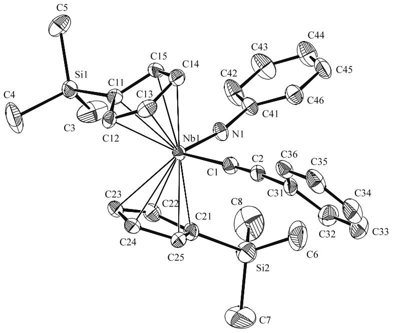
(X = Br, C≡C-H, SnR_3)

Antonio Antiñolo, Cristina García-Yebra, Mariano Fajardo, Isabel del Hierro, Carmen López-Mardomingo, Isabel López-Solera, Antonio Otero, Yolanda Pérez, Sanjiv Prashar

J. of Organomet. Chem. 670 (2003) 123

Synthesis and reactivity of alkynyl niobocene complexes

Alkynyl containing niobocene complexes with differing auxiliary ligands have been prepared and characterized. The reactivity of the alkynyl compounds towards oxidation and protonation is described.

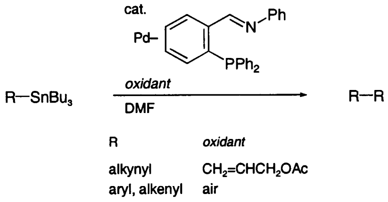


Eiji Shirakawa, Yoshiaki Nakao, Yasubumi Murota, Tamejiro Hiyama

J. of Organomet. Chem. 670 (2003) 132

Palladium–iminophosphine-catalyzed homocoupling of alkynylstannanes and other organostannanes using allyl acetate or air as an oxidant

A palladium–iminophosphine complex was demonstrated to be an efficient catalyst for the homocoupling of organostannanes. Allyl acetate works effectively as an oxidant in the reaction of alkynylstannanes to give conjugated diynes, whereas biaryls and dienes are readily obtained through the homocoupling of aryl- and alkenylstannanes in an open air.

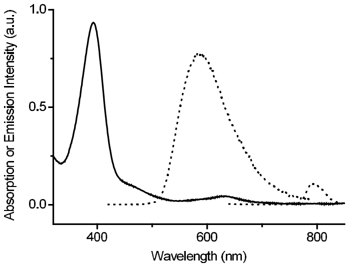


Joris van Slageren, Rainer F. Winter, Axel Klein, Stephan Hartmann

J. of Organomet. Chem. 670 (2003) 137

Long-lived higher excited state luminescence from new ruthenium(II)–allenylidene complexes

Ruthenium aminoallenylidene complexes *trans*-$[Cl(dppm)_2Ru{=}C{=}C{=}C(NR_2)R']^+$ are luminescent at 77 K. Our studies show that the emissions are rather long-lived ($\tau = 50–175$ µs) and originate from an excited ^{3}MLCT state. Some of the complexes also display an additional lower energy emission from the triplet ground state. The MLCT character for the underlying absorption bands has been authenticated by resonance Raman spectroscopy.

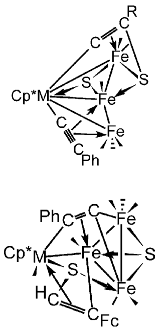


Pradeep Mathur, Anjan K. Bhunia, Chimalakonda Srinivasu, Shaikh M. Mobin

J. of Organomet. Chem. 670 (2003) 144

Reactivity of metal acetylides with chalcogen-bridged metal carbonyl cluster in presence of free alkyne molecule: synthesis and characterisation of $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{\mu_3\text{-}C(H){=}C(R)S\}(CO)_6(\mu_3\text{-}CCPh)]$ (R = Ph, *n*-Bu and M = W, Mo) and $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{\mu_3\text{-}C(Fc){=}C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (M = W, Mo)

Photolysis of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ with mononuclear acetylides in the presence of free acetylene yielded two types of metal clusters. Unusual flipping of the acetylide unit and formation of a carbon–sulfur bond were observed. Crystal structures were established by X-ray diffraction techniques.



Christine Tedeschi, Catherine Saccavini, Luc Maurette, Michèle Soleilhavoup, Remi Chauvin

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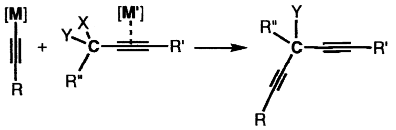
1,4-Diynes from alkynyl–propargyl coupling reactions

The state-of-the-art in propargylation of metal-alkynyls is reviewed according to the nature of the metal and to the sp^3 or sp^2 hybridization state of the electrophilic carbon. The allenic/propargylic regioselectivity being crucial, methods resorting to precomplexation of the propargylic moiety with transition-metals are specifically detailed. Alternative routes to skipped diynes are also discussed.



M = Li, Na, K, Mg, Cu, Zn, Al, Si, $-CMe_2OAl(OR)$

M' = Co, Mo, Ru

Michael I. Bruce, Mark E. Smith, Natasha N. Zaitseva, Brian W. Skelton, Allan H. White

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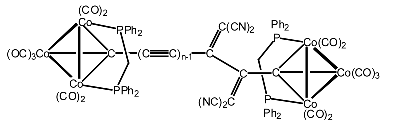
A new approach to the synthesis of carbon chains capped by metal clusters

Elimination of AuBr{P(tol)$_3$} in the reaction between $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ and $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ ($n = 2$–4) affords novel cluster-capped carbon chains $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_nC\}$, of which the X-ray structures of $n = 2$, 4 are reported. The reaction between $C_2(CN)_4$ and $n = 3$ gives $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\text{-}\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}$ (illustrated).

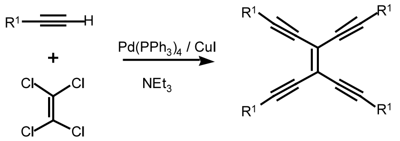


Olivia F. Koentjoro, Philipp Zuber, Horst Puschmann, Andres E. Goeta, Judith A.K. Howard, Paul J. Low

J. of Organomet. Chem. 670 (2003) 178

A simple synthesis of tetraethynylethenes and representative molecular structures of some dicobalt derivatives

A one-pot palladium–copper catalysed cross-coupling reaction between tetrachloroethene and terminal alkynes affords the corresponding tetraethynylethenes in good yield. Reaction of 1,6-bis(trimethylsilyl)-3-4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne with $Co_2(CO)_6(L_2)$ [$L_2 = (CO)_2$, (μ-dppm)] affords compounds in which one or two (*trans*) alkyne moieties are coordinated by the metal fragment.



$R^1 = SiMe_3$ (**2**), Ph (**3**), $C_6H_4CN\text{-}4$ (**4**)

Stephanie K. Hurst, Tong Ren

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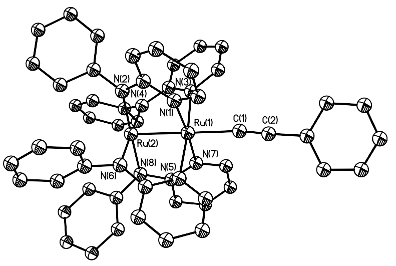
Homo-dinuclear σ-alkynyl complexes: past, present and opportunities

Diruthenium and dirhodium paddlewheel species readily form axial alkynyl adducts that are highly redox active. $M_2P_4(CCY)_4$ type of complexes with M as molybdenum and tungsten can be prepared from the reaction between $M_2P_4(Cl_4)_4$ and LiC_2Y. Singly bonded dinulear species (M = Mo, Mn, Re and Ru) form σ-alkynyl complexes, in which the alkynyl ligand also engages strong π-interaction with metal centers.

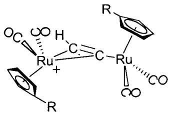


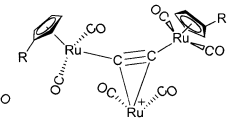
Christopher S. Griffith,
George A. Koutsantonis, Brian W. Skelton,
Allan H. White

J. of Organomet. Chem. 670 (2003) 198

Reactions of metalloalkynes VII. Protonation of ruthenium ethyne-1,2-diyl complexes

The acid–base chemistry of some ruthenium ethyne-1,2-diyl complexes, $[\{Ru\text{-}\{(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu_2\text{-}C{\equiv}C)]$ (R = H, Me) has been investigated.





Vivian Wing-Wah Yam,
Keith Man-Chung Wong,
Samuel Hung-Fai Chong,
Victor Chor-Yue Lau,
Sally Chan-Fung Lam, Lingjun Zhang,
Kung-Kai Cheung

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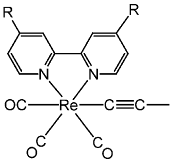
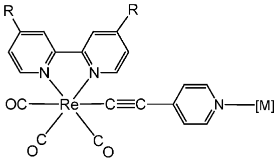
Synthesis, electrochemistry and structural characterization of luminescent rhenium(I) monoynyl complexes and their homo- and hetero-metallic binuclear complexes

A series of luminescent rhenium(I) monoynyl complexes, $[Re(N\text{–}N)(CO)_3(C{\equiv}C\text{–}R)]$ (N–N = bpy, $^tBu_2bpy$; R = C_6H_5, C_6H_4–Cl-4, C_6H_4–OCH_3-4, C_6H_4–C_8H_{17}-4, C_6H_4–C_6H_5, C_8H_{17}, C_4H_3S, C_4H_2S–C_4H_3S, C_5H_4N), together with their homo- and hetero-metallic binuclear complexes, $\{Re(N\text{–}N)(CO)_3(C{\equiv}C\text{–}C_5H_4N)[M]\}$ (N–N = bpy, $^tBu_2bpy$; [M] = $[Re\{(CF_3)_2\text{-}bpy\}\text{-}(CO)_3]ClO_4$, $[Re(NO_2\text{-}phen)(CO)_3]ClO_4$, $W(CO)_5$) have been synthesized and their electrochemical and photoluminescence behaviors determined.





Irene Ara, Jesús R. Berenguer,
Eduardo Eguizábal, Juan Forniés,
Julio Gómez, Elena Lalinde

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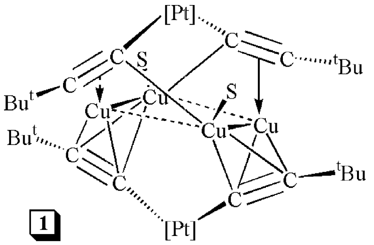
Synthesis, structures and photophysics of novel luminescent platinum–copper complexes

Novel hexanuclear platinum–copper solvate clusters $[Pt_2Cu_4(C_6F_5)_4(C{\equiv}CR)_4(acetone)_n]$ (R = ^tBu, $n = 2$ (**1**); R = Ph, $n = 4$ (**2**)·(acetone)$_4$) have been prepared starting from $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ and $[Cu(C{\equiv}CR)]_x$, and trinuclear complexes $[\{cis\text{-}Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2\}\{CuL_2\}_2]$ (L_2 = bipy, dppe) using **1** and **2** as precursors. The luminiscent behaviour of all of these compounds and a comparison with the photoluminiscent properties of related platinum–silver species are also presented.



1

[Pt] = [*cis*-Pt(C_6F_5)$_2$]
S = acetone

Quan-Ming Wang, Guo-Cong Guo,
Thomas C.W. Mak

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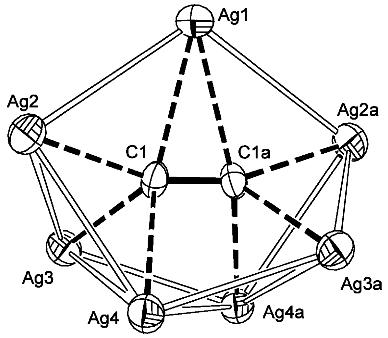
Structural varieties in double salts of silver acetylide containing ancillary anions and terminal ligands

$Ag_2C_2 \cdot 6AgO_2CCHF_2$ (**1**) has a three-dimensional structure containing basket-like silver cages. In $[HPyCH_2OH][Ag_9(C_2)(CF_3CO_2)_9(HPyCH_2OH)(H_2O)] \cdot 0.5H_2O$ ($PyCH_2OH$ = 4-(hydroxymethyl)pyridine) (**2**), centrosymmetric $(C_2)_2@Ag_{14}$ double cages are linked through additional silver atoms to generate an infinite chain, and one of the two independent 4-(hydroxymethyl)pyridinium ions acts in the *O*-ligating mode, which is observed for the first time. Both $Ag_2C_2 \cdot 5CF_3SO_3Ag \cdot 2MeCN \cdot 2H_2O$ (**3**) and $Ag_2C_2 \cdot 8CF_3SO_3Ag \cdot 2EtCN \cdot 3H_2O$ (**4**) have layer-type structures.



Qianyuan Hu, Man Fung Lo,
Ian D. Williams, Naoko Koda,
Yuko Uchimaru, Guochen Jia

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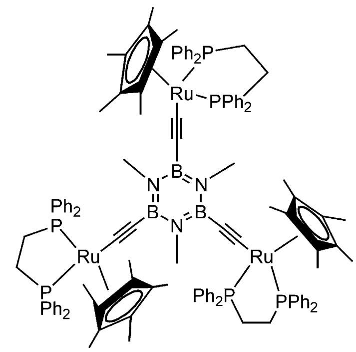
Synthesis and characterization of trimetallic complexes with a borazine core

Reaction of $[Cp^*Ru(dppe)]^+$ with B-triethynyl-*N*-trimethylborazine and piperidine produced the trimetallic complex $[Cp^*Ru(dppe)(C{\equiv}C)]_3B_3N_3Me_3$. Reaction of $RuHCl(CO)(PPh_3)_3$ with B-triethynyl-*N*-trimethylborazine gave the trimetallic complex $[RuCl(CO)(PPh_3)_2(CH{=}CH)]_3B_3N_3Me_3$.



Joseph P. Morrall, Clem E. Powell,
Robert Stranger, Marie P. Cifuentes,
Mark G. Humphrey, Graham A. Heath

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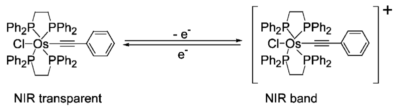
Organometallic complexes for nonlinear optics

Part 32. Synthesis, optical spectroscopy and theoretical studies of some osmium alkynyl complexes

Cyclic voltammetric studies of *trans*-$[Os(C{\equiv}CPh)Cl(dppe)_2]$ (**1**), *trans*-$[Os(4\text{-}C{\equiv}CC_6H_4\text{-}C{\equiv}CPh)Cl(dppe)_2]$ (**2**), and 1,3,5-$\{$*trans*-$[OsCl(dppe)_2(4\text{-}C{\equiv}CC_6H_4C{\equiv}C)]\}_3C_6H_3$ (**3**) reveal a quasi-reversible oxidation process for each complex at 0.36–0.39 V. The UV–vis-NIR spectra of the corresponding cationic complexes $\mathbf{1}^+$–$\mathbf{3}^+$ reveal a low-energy band in the near IR region (11 000–14 000 cm^{-1}) in each case, density functional theory (DFT) calculations suggesting that they can be assigned to transitions involving orbitals delocalized over the metal, chloro and alkynyl ligands.



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