

MASTER'S THESIS

The chemistry of osmium and ruthenium carbonyl clusters with functionalized alkyne and phosphine ligands

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The Chemistry of Osmium and Ruthenium Carbonyl Clusters
with Functionalized Alkyne and Phosphine Ligands

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Abstract

Reactions of several diyne ligands $\text{HC}\equiv\text{CRC}\equiv\text{CH}$ ($\text{R} = 2,7\text{-fluorenediyl R}_1, 2,7\text{-fluoren-9-onediyl R}_2, 4,4'\text{-di(tert-butyl)-2,2'-bithiazole-5,5'-diyl R}_3$ or $2,2'\text{-bithiophene-5,5'-diyl R}_4$) with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ in CH_2Cl_2 at room temperature afforded the monomeric $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}\equiv\text{CH})]$ ($\text{R} = \text{R}_1$ **1a**, R_2 **2a**, R_3 **3a** or R_4 **4a**) and dimeric $[\{\text{Os}_3(\text{CO})_9(\mu\text{-CO})\}_2(\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}_2\text{H})]$ ($\text{R} = \text{R}_1$ **1b**, R_2 **2b**, R_3 **3b** or R_4 **4b**) complexes in moderate yields. New hexaruthenium carbonyl clusters $[\{\text{Ru}_3(\mu\text{-H})(\text{CO})_9\}_2\{\mu_3\text{-}\eta^2, \eta^2\text{-C}_2\text{RC}_2\}]$ **5** and $[\{\text{Ru}_3(\text{CO})_9(\mu\text{-CO})\}_2\{\mu_3\text{-}\eta^2\text{-HC}_2\text{RC}_2\text{H}\}]$ **6** ($\text{R} = \text{R}_2$) have been prepared by treatment of $\text{HC}\equiv\text{CRC}\equiv\text{H}$ with an equimolar amount of $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$, respectively, in refluxing THF. Reactions of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with platinum bis(alkynyl) complexes *cis*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{L})]$ ($\text{L} = \text{Me}_2\text{bipy}$, Bu^t_2bipy) at room temperature readily gave the novel, spiked-triangular heterometallic cluster complexes $[\text{Os}_3\text{Pt}(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\eta^1\text{-C}\equiv\text{CPh})(\text{L})]$ ($\text{L} = \text{Me}_2\text{bipy}$ **7** or Bu^t_2bipy **8**).

A novel phosphido-bridged complex $[\text{Ru}_2(\text{CO})_6\{\mu\text{-P}(\overline{\text{C}(\text{CH})_3\text{O}})_2\}(\mu\text{-}\eta^1, \eta^2\text{-}\overline{\text{C}(\text{CH})_3\text{O}})]$ **9** was produced in good yield by the thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with tri(2-furyl)phosphine. Complex **9** readily reacted with two equivalents of terminal alkynes $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, *p*- $\text{C}_6\text{H}_4\text{Me}$, *p*- $\text{C}_6\text{H}_4\text{NO}_2$, Fc , *p*- $\text{C}_6\text{H}_4\text{Fc}$, $(\text{C}_4\text{H}_2\text{S})\text{C}\equiv\text{CH}$ or

(C₄H₂S)₂C≡CH) by an interesting head-to-tail ynyl coupling with a furan group to form [Ru₂(CO)₄{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η¹,η²,η³-(R)CC(H)C(R)C(H) $\overline{C(CH)_3O}$ }] (R = Ph **10**, *p*-C₆H₄Me **11**, *p*-C₆H₄NO₂ **12**, Fc **13**, *p*-C₆H₄Fc **14**, (C₄H₂S)₂C≡CH **16** or (C₄H₂S)₂C≡CH **17**) containing a novel furyl-substituted C₄ hydrocarbyl chain. Reaction of **9** with a 1:1 mixture of ferrocenylacetylene and *p*-nitrophenylacetylene yielded an inseparable pair of isomers [Ru₂(CO)₄{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η¹,η²,η³-(R₁)CC(H)C(R₂)C(H) $\overline{C(CH)_3O}$ }] (R₁ = *p*-C₆H₄NO₂, R₂ = Fc **15a**, R₁ = Fc, R₂ = *p*-C₆H₄NO₂ **15b**), of which one isomer has been structurally characterized.

Simple mono- and disubstitution products [Ru₂(CO)₅{P($\overline{C(CH)_3O}$)₃}{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η²- $\overline{C(CH)_3O}$ }] **19a** and [Ru₂(CO)₄{P($\overline{C(CH)_3O}$)₃}{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η²- $\overline{C(CH)_3O}$ }] **19b** were produced by the thermal reaction of **9** with tri(2-furyl)phosphine. Similar thermal substitution reactions also proceeded when **9** reacted with the diphosphines, namely bis(diphenylphosphido)methane (dppm), bis(diphenylphosphido)amine (dppa) or bis(diphenylphosphido)methylamine (dppma), affording [Ru₂(CO)₄{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η²- $\overline{C(CH)_3O}$ }(μ-L)] (L = dppm **20**, dppa **21** or dppma **22**) in good yields. Upon reaction with bis(diphenylphosphido)ferrocene (dppf), a mixture of [{Ru₂(CO)₅{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η²- $\overline{C(CH)_3O}$ }]₂(η¹,η¹-dppf)] **23a** and polymeric [Ru₂(CO)₄{μ-P($\overline{C(CH)_3O}$)₂}{μ-η¹,η²- $\overline{C(CH)_3O}$ }(η¹,η¹-dppf)]_n **23b** was obtained in which the dppf was found to bridge two identical μ-phosphido Ru₂ units.

When the reactions were carried out using bis(diphenylphosphido)ethane (dppe) or bis(diphenylphosphido)propane (dppp), compounds $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^1\text{-C}_6\text{H}_4\text{PPh}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 2$ **24** or 3 **25**) were isolated as the thermodynamic products, in which both P atoms chelate to one Ru centre to afford five- (for **24**) and six-membered (for **25**) ruthenacycles, accompanied by orthometallation reaction and reductive elimination of furan. As the length of the methylene segment between PPh₂ groups is increased for bis(diphenylphosphido)butane (dppb) and bis(diphenylphosphido)pentane (dpppe), cyclometallation is not favoured in either case. Instead, $[\{\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}\}_2(\eta^1,\eta^1\text{-L})]$ ($L = \text{dppb}$ **26a** or dpppe **27a**) and $[\text{Ru}_2(\text{CO})_4\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}(\eta^1,\eta^1\text{-L})]_n$ ($L = \text{dppb}$ **26b** or dpppe **27b**) were obtained with the product yield depending on the stoichiometry of the reactants. Another novel diruthenium complex $[\text{Ru}_2(\text{CO})_5\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^1,\eta^1,\eta^2\text{-C}_{14}\text{H}_8\text{PPh}_2\}]$ **28** was also obtained through the thermal treatment of **9** with (9-anthracenyl)diphenylphosphine.

Two phosphine-disubstituted isomers $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{10}\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2]$ **29a** and **29b**, a μ -phosphido tetraruthenium cluster $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_7(\mu\text{-CO})\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2\{\mu\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_2\}\{\mu\text{-}\eta^2\text{-}\overline{\text{C}(\text{CH}_3)_3\text{O}}\}]$ **30** and two μ_3 -phosphinidene tetraruthenium clusters $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}\{\mu_3\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})\}]$ **31** and $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{10}\{\text{P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})_3\}_2\{\mu_3\text{-P}(\overline{\text{C}(\text{CH}_3)_3\text{O}})\}]$ **32** have been synthesised by reaction of tri(2-furyl)phosphine with $[(\mu\text{-}$

$\text{H})_4\text{Ru}_4(\text{CO})_{12}]$ in THF under reflux. Reaction of (9-anthracenyl)diphenylphosphine with $[(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{12}]$ under similar conditions afforded the new compound $[\text{HRu}(\text{CO})_3(\text{PPh}_2\text{C}_{14}\text{H}_8)][(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{11}(\text{PPh}_2\text{C}_{14}\text{H}_9)]$ 33.

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