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Construction of carbon chains on ruthenium and osmium carbonyl clusters

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Dedicated to Professor F. Gordon A. Stone on the occasion of his 80th birthday, with the greatest respect and admiration

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Abstract

We have used the elimination of $AuX(PR_3)$ (X = halide, R = Ph, tol) that occurs in reactions of alkynylgold(I)–phosphine complexes with $M_3(\mu\text{-H})_3(\mu_3\text{-CBr})(CO)_9$ (M = Ru, Os) to prepare the complexes $M_3(\mu\text{-H})_3(\mu_3\text{-CC}{\equiv}\text{CR})(CO)_9$ [M = Ru, R = Ph **2**, $C{\equiv}CSiMe_3$ **3**, Fc **4**, $C{\equiv}CFc$ **6-Ru**, $C{\equiv}C[Ru(PPh_3)_2Cp]$ **8**; M = Os, R = $C{\equiv}CFc$ **6-Os**, $C{\equiv}CC{\equiv}CFc$ **7**], $Fc'\{(\mu_3\text{-}C{\equiv}CC)Ru_3(\mu\text{-H})_3(CO)_9\}_2$ **5**, and bis-cluster-capped carbon chain complexes $\{M_3(\mu\text{-H})_3(CO)_9\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_nC\}$ (M = Ru, n = 2 **9**, 3 **10-Ru**; M = Os, n = 3 **10-Os**) and $\{(L)(OC)_8(\mu\text{-H})_3M_3\}C(C{\equiv}C)_nC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (n = 1, M = Ru, L = CO **11**, PPh_3 **12-Ru/P**; n = 2, L = CO **12-Ru**, PPh_3 **13**; M = Os, L = CO **12-Os**) in good to excellent yields. X-ray structural determinations of **2**–**5**, **6-Ru**, **6-Os**, **7**, **9**, **11**, **12-Ru**, **12-Os** and **12-Ru/P** are reported.

Keywords: Carbon chains; Ruthenium; Osmium; Capped clusters; Gold elimination

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1. Introduction

Current interest in metal complexes which may be considered to be models of molecular wires includes a vigorous sub-set comprised of carbon chains end-capped by redox-active metal–ligand fragments [1]. Several groups have concentrated on derivatives containing mononuclear fragments, such as $MnX(dmpe)_2$ (X = I, $C{\equiv}CH$) [2], $Re(NO)(PPh_3)Cp*$ [3], $Fe(CO)_2Cp*$ [4], $Fe(dppe)Cp*$ [5], $Ru(L)_2Cp'$ (L = PPh_3, Cp′ = Cp, L_2 = dppe, Cp′ = Cp*) [6] and $Pt(C_6F_5)(PR_3)_2$ [7], or the binuclear $Ru_2(ap)_4$ (ap = 2-anilinopyridinate) system [8]. However, relatively few examples of analogous complexes containing metal cluster moieties have been described. Prominent among these are the Co_3C clusters studied by Robinson [9], Seyferth [10] and others.

In previous papers, we have described that reactions between aurated poly-ynes and halo-alkynes result in a facile elimination of $AuX(PR_3)$ (X = halide, R = Ph, tol) and formation of a new C–C bond [11]. We have used this reaction to make complexes containing long carbon chains (C_n, $n > 4$), including $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_7C\}$ [12]. The reactions are carried out in ether solvents (Et_2O, thf) at moderate temperatures in the presence of a Pd(0)/Cu(I) catalyst, and generally proceed in excellent yield. Other studies in our laboratory have shown that this reaction, which may be considered to be a variant of the well-known Sonogashira reaction [13], has wide applicability. The $AuX(PR_3)$ product may be recovered and re-used.

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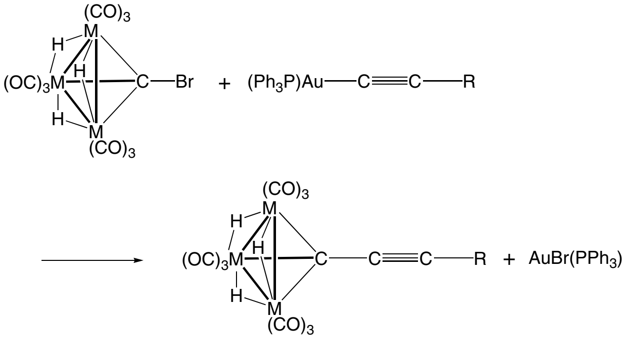
Part of our studies of molecules which contain a carbon chain linking two metal centres has been concerned with the electronic communication between the end-caps and we have been interested to examine compounds in which one or two metal cluster moieties cap the chain. Of these, some contain the metal cluster bonding via three metal atoms to a C(sp) atom, the C(1)–C(2) distance being of the same order as that expected for a CC triple bond. An example is $[M_3(\mu_3\text{-CCBu}^t)_2(\mu\text{-dppm})_3]^+$ (M = Cu, Ag) [14,15]. The clusters here usually contain Group 11 atoms (Cu, Ag). Other cluster carbyne systems are also known, in which the cluster-bonded carbon C(1) also interacts with three metal atoms, but is only singly bonded to C(2). Examples include the well-established $Co_3(\mu_3\text{-CX})(CO)_9$ [9,10] and related complexes of the Group 8 metals, $M_3(\mu\text{-H})_3(\mu_3\text{-CX})(CO)_9$ (M = Ru, Os) [16,17]. In principle, many other cluster cores can be obtained by conventional metal-exchange reactions. This paper describes some carbon-chain complexes in which one end-cap is the $M_3(\mu\text{-H})_3(CO)_9$ (M = Ru, Os) group which have been prepared by the general reaction shown in Eq. (1).



(1)

The electronic nature of carbon chains is of interest in connection with their possible use as molecular wires. For chains containing an even number of carbon atoms, three symmetrical electronic configurations are possible (neglecting radical species), as indicated by structures A–C in Chart 1 [1]. This type of complex is the most prevalent, because of the use of mono- or poly-yne precursors in their syntheses. For odd-numbered chains, only two representations are possible, namely D and E. The former is related to B, and both involve at least one M–C multiply-bonded linkage. Possible precursors of the odd (single) carbon atom, which might be linked to an even-numbered chain from another source, include metal carbyne complexes. These contain M≡C bonds, as in $W(\equiv CR)(CO)_2Tp^*$ [18], or a carbon μ_3-bonded to a trinuclear cluster, as in the $Co_3(\mu_3\text{-CR})(CO)_9$ complexes mentioned above. Several other systems are known and, in addition to some Co_3C systems, we have chosen to study the Group 8 clusters $M_3(\mu\text{-H})_3(\mu_3\text{-CX})(CO)_9$ (M = Ru, Os) as precursors.

$$L_nM{-}(C{\equiv}C)_m{-}ML_n$$

A

$$L_nM{=}(C{=}C)_m{=}ML_n$$

B

$$L_nM{\equiv}(C{-}C)_m{\equiv}ML_n$$

C

$$L_nM{=}(C{=}C)_m{=}C{=}M'L'_n$$

D

$$L_nM{-}(C{\equiv}C)_m{-}C{\equiv}M'L'_n$$

E

Chart 1.

2. Results

The halo-carbyne complexes $M_3(\mu\text{-H})_3(\mu_3\text{-CX})(CO)_9$ (M = Ru, Os, X = Cl, Br, I) were originally described by Shapley [17] and are readily available from the parent $M_3(CO)_{12}$ by sequential treatment with NEt_3 [or more recently, with $(MeNCH_2)_3$], MeOTf and then BX_3 [19,20]. Reactions of these complexes with aurated alkynes have given the 16 complexes to be described below in good to excellent yield. All have been characterized by satisfactory elemental analyses, appropriate spectroscopic properties and in 12 cases, by single-crystal X-ray structure determinations.

The reaction between equimolar amounts of $Ru_3(\mu\text{-H})_3(\mu_3\text{-CBr})(CO)_9$ (**1-Ru**) and $Au(C{\equiv}CPh)(PPh_3)$ was carried out in thf at r.t. with added $Pd(PPh_3)_4$ and CuI as catalyst and afforded yellow-orange crystals of $Ru_3(\mu\text{-H})_3(\mu_3\text{-CC{\equiv}CPh})(CO)_9$ (**2**) in 74% yield. Similar reactions were carried out with the copper and silver analogues of the gold alkynyl and gave **2** in 75% and 32% yields, respectively; unreacted **1-Ru** (42%) was recovered from the silver reaction. The IR spectrum of **2** contained a $\nu(C{\equiv}C)$ band at 2110 cm^{-1} and terminal $\nu(CO)$ bands between 2084 and 1991 cm^{-1}, the vs–vs–s–s pattern of which is characteristic of the $Ru_3(\mu\text{-H})_3(CO)_9$ fragment. The ^1H NMR spectrum contains two resonances at δ −17.64 (Ru–H) and between 7.20 and 7.39 (Ph), while the ^{13}C NMR spectrum contains, in addition to signals between δ 126.9 and 130.8 (Ph) and at δ 188.9 and 189.8 (CO), three singlets at δ 93.1, 110.1 and 156.4, which are assigned to the three carbons of the C_3 chain. In **1-Ru** and **1-Os**, the cluster-bonded carbons resonate