Methods for attaching metal-capped sp carbon chains to metal clusters: synthesis, structure and reactivity of rhenium–triosmium carbon complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CC)_nOs_3(CO)_{10}H]$

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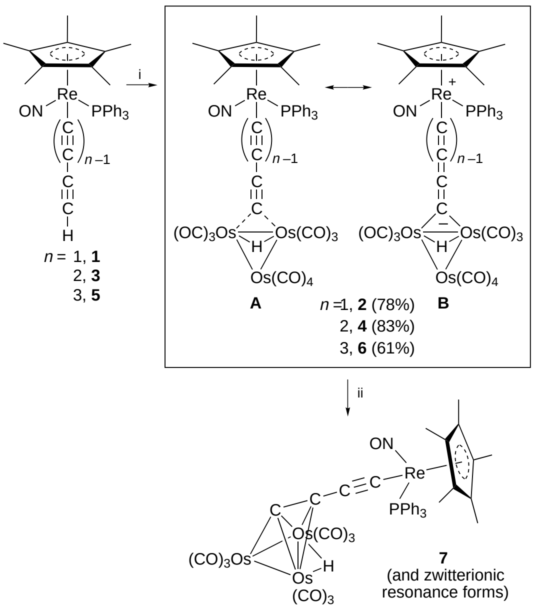
Reactions of $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)\{(C{\equiv}C)_nH\}]$ and $[Os_3(CO)_{10}(NCMe)_2]$ give the title $Re(CC)_nOs_3$ complexes (n = 1–3, 83–61%); a crystal structure (n = 1), and IR and NMR properties, indicate contributions by neutral Re–$(C{\equiv}C)_n$–(Os_3) and zwitterionic $^+Re{=}(C{=}C)_n{=}(Os_3)^-$ resonance forms.

There has been much recent interest in unsupported sp carbon chains that span two transition metals.[1–4] These wire-like assemblies offer intriguing possibilities for molecular-level devices.[5] To date, nearly all such compounds feature monometallic endgroups. However, polymetallic endgroups might confer special attributes, including enhanced electronic coupling or communication between the termini, or greater capacitance in the case of good electron reservoirs. Indeed, two-dimensional superlattices of alkynyl- and aryl-linked metal clusters are under active pursuit in other laboratories, with the ultimate aim of nanoelectronic digital circuits.[6]

We were attracted by the architectural versatility of trimetallic clusters, which allow three η^1 modes of carbon chain attachment: (*i*) a μ_1 link to one metal; (*ii*) an edge-bridging μ_2 link to two metals; (*iii*) a face-bridging μ_3 link to three metals. In the second and third modes, the ligating carbon does not necessarily remain sp hybridized. It should also be emphasized that there is extensive literature on metal cluster carbide complexes,[7] some of which provide models for surface-bound intermediates in heterogeneously catalysed commodity chemical processes. However, only a few contain sp carbon segments that span otherwise unconnected polymetallic termini.[3d,8–10]



Scheme 1 Syntheses of $Re(CC)_nOs_3$ complexes. *Reagents and conditions*: i, $Os_3(CO)_{10}(NCMe)_2$, CH_2Cl_2, 20 °C; ii, n = 2, hexane, reflux.

As shown in Scheme 1, the chiral, racemic rhenium ethynyl complex **1**[11] and triosmium complex $[Os_3(CO)_{10}(NCMe)_2]$ were reacted in CH_2Cl_2 at room temperature. After 3 h, chromatography gave an orange, air-stable product **2** (78%). The labelled complex $[^{13}C_2]$**2** was similarly prepared.† Spectroscopic data suggested the composition $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CC)Os_3(CO)_{10}H]$. In particular, a diagnostic hydride ligand ^1H NMR signal (δ −16.7), and ten terminal CO ^{13}C NMR signals (δ 184–171), were observed. However, the ReC ^{13}C signal was between those of **1** and the cationic vinylidene complex[12] $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}CH_2)]BF_4$ [δ 245.4 *vs.* 98.0 and 330.4, J_{CP} 8.8 *vs.* 15.8 and 9.5 Hz (CH_2Cl_2, C_6D_6, CH_2Cl_2]; ReC*C* at δ 124.2 *vs.* 116.0 and 116.1). The IR ν_{NO} value showed a similar relationship (1667 *vs.* 1637–1629 and 1728–1711 cm^{-1}).

Many reactions of terminal alkynes and triosmium complexes $[Os_3(CO)_{10}L(L')]$ (L/L′ = CO or NCMe) have been reported.[13] However, to our knowledge no adducts analogous to **2** have previously been isolated. Thus, a crystal structure was determined.‡ The molecular structure, and key metrical parameters, are given in Fig. 1. The hydride and ReCC terminus symmetrically bridge the same two osmiums, with the Os_3 and $ReOs_2$ planes roughly orthogonal (105°). The rhenium–carbon bond [1.964(9) Å] is shorter than in complexes of formula $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CX)]$ [2.079(9), 2.037(5), 2.032(7) Å],[2a,c,d] but longer than in analogous cationic species with $Re{=}C({=}C)_n$ linkages [1.909(7), 1.91(1), 1.916(7) Å].[2d,4a] Also, the carbon–carbon bond is longer than those in disubstituted organic alkynes and alkynyl complexes [1.252(12) Å *vs.* mean values of 1.192(12) and 1.210(13) Å].[14]

To help clarify these bonding issues, the IR spectra of **2** and $[^{13}C_2]$ **2** were compared. A 1705 cm^{-1} band shifted to 1632 cm^{-1} (calc for $\nu_{^{13}C^{13}C}$, 1637 cm^{-1}). Other absorptions in the 2100–1600 cm^{-1} region were unaffected. These ν_{CC} values confirm that the C_2 bridge has appreciable double bond character. Hence, **2** is best described as a hybrid of the neutral and zwitterionic resonance forms **A** and **B** in Scheme 1. Also,

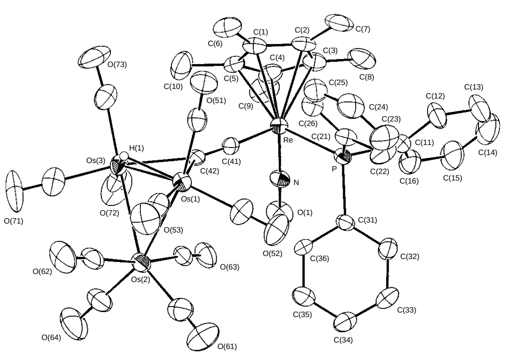


Fig. 1 Molecular structure of $\mathbf{2}\cdot0.5C_6H_{14}$. Selected bond distances (Å) and angles (°): Re–P 2.395(2), Re–N 1.757(7), Re–C(41) 1.965(9), Os(1)–Os(3) 2.7933(7), Os(1)–H(1) 1.79(9), Os(3)–H(1) 1.82(9), Os(1)–C(42) 2.150(9), Os(3)–C(42) 2.164(9), C(41)–C(42) 1.252(12); N–Re–P 90.5(2), N–Re–C(41) 97.5(3), C(41)–Re–P 94.4(2), C(42)–C(41)–Re 174.2(7), C(42)–C(41)–Os(1) 139.3(7), C(42)–C(41)–Os(3) 140.0(7).

the P–Re–C(41) and C(42)–Os(1)–Os(3) units were nearly coplanar [angle 14.5(5)°], consistent with a frontier-orbital-derived conformational minimum as commonly observed for $^{+}$Re=C adducts such as **B**.[2d]

The extension of this simple procedure to higher carbon chains was investigated (Scheme 1). A similar reaction of the butadiynyl complex **3**[2a] and $[Os_3(CO)_{10}(NCMe)_2]$ gave the ReC_4Os_3 species **4** (83%) as a red–orange powder.† A low-temperature reaction of the hexatriynyl complex **5**[2b] afforded the corresponding ReC_6Os_3 species **6** (62%) as a thermally labile red–brown powder. However, the analogous octatetraynyl complex[2b] gave a multitude of products. Mass spectra of **4** and **6** showed intense molecular ions, and many NMR and IR properties were close to those of **2** (NMR: OsH δ −13.10, −15.90; ReC δ 242.9, 204.9; PPh_3 δ 21.6, 22.3 *vs.* 21.0; IR ν_{NO} 1662, 1663 cm^{-1}). Low-temperature ^{13}C NMR spectra were complicated by decoalescence phenomena, and practical routes to labelled $^{13}C_4$ or $^{13}C_6$ derivatives are unavailable. Thus, most C_x NMR signals could only be provisionally assigned.

The stabilities of **2**, **4** and **6** decreased with increasing chain length. We sought to probe the nature of these decomposition pathways. When **4** was refluxed in hexane, CO was evolved. Work-up gave the nonacarbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCCC)Os_3(CO)_9(H)]$ **7** in 57% yield. Although material suitable for a crystal structure could not be obtained, the formulation was supported by microanalysis, mass spectrometry, NMR [(OsH δ δ22.34; ReC 242.9 (d, J_{CP} 11.5 Hz)] and IR (ν_{NO} 1663 cm^{-1}).† A structure consistent with these data is given in Scheme 1. Analogous adducts of $Os_3(CO)_9H$ and other CCR ligands (R = H, Me_3, *etc.*) have been previously characterized.[13,15] All exhibit OsH NMR signals near δ −23, and IR ν_{CO} band patterns similar to **7**.

Additional properties of **2**, **4**, and **6** were compared. UV–VIS spectra showed progressive red shifts of the longest wavelength band [λ/nm, hexane (ε/dm^3 mol^{-1} cm^{-1}): **2**, 316 (20 000), 350 (21 000), 384 (18 000); **4**, 296 (20 000), 388 (7500), 500 (4900); **6**, 306 (18 000), 516 (3600)]. No absorptions were significantly solvatochromic (hexane, CH_2Cl_2, acetonitrile). Cyclic voltammograms (CH_2Cl_2–NBu_4BF_4, 100 mV s^{-1}) showed partially reversible oxidations with $E°$ values of 0.78, 0.43, and 0.44 V, respectively (ferrocene standard, $E°' = 0.46$ V). These have no counterparts in triosmium complexes $[Os_3(CO)_{10}L_2]$, and are much less favourable thermodynamically than oxidations of $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CX)]$ complexes.[2] This may be due to the zwitterionic character.

While this work was in progress, the reaction of the tungsten butadiynyl complex $[(\eta^5\text{-}C_5H_5)W(CO)_3(C{\equiv}CC{\equiv}CH)]$ and triruthenium complex $[Ru_3(CO)_{10}(NCMe)_2]$ was briefly described.[16] In contrast to Scheme 1, a π adduct of the C≡CH moiety formed. This rearranged in refluxing benzene to a $[WC_4Ru_3(CO)_9H]$ complex analogous to **7**. Tungsten alkynyl complexes $[(\eta^5\text{-}C_5R_5)W(CO)_3(C{\equiv}CR')]$ and $[Os_3(CO)_{10}(NCMe)_2]$ react in refluxing toluene to give tetranuclear products of formula $(\eta^5\text{-}C_5R_5)WOs_3(CO)_{11}(C{\equiv}CR')$].[17]

We have demonstrated that sp carbon chains with $Os_3(CO)_{10}$ endgroups are easily constructed. However, the η^1,μ_2 assemblies are labile. From some standpoints this is desirable, as other architecturally interesting carbon complexes can be readily accessed. However, from the perspective of long-lived molecular devices, this is undesirable. Hence, future efforts would be best directed at trimetallic systems with less dissociable spectator ligands, a more restricted set of binding modes, and higher kinetic barriers. Regardless, the new $Re(CC)_nOs_3$ complexes described above have numerous interesting properties, and further investigations are ongoing.

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Footnotes

† All new complexes were characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized (with crystallographic data) in supplementary material provided to the reviewers and available from the author. Solid samples showed a marked tendency to retain hexane, even after vacuum drying. Correct microanalyses could be obtained for solvates of **2**, **6** and **7**. *Representative data*: IR (cm^{-1}, hexane) 2091m, 2054s, 2039m, 2005vs, 1981m, (sh) 1969m, 1705m, 1667m. NMR (δ, CD_2Cl_2): ^1H 7.99, 7.40, 7.26 (m, 3 Ph), 1.74 (s, C_5Me_5), −16.70 (s, OsH); $^{13}C\{^1H\}$ {for $[^{13}C_2]$ **2**} 245.4 (dd, J_{CP} 8.8, J_{CC} 64.5 Hz ReC), 183.9, 183.8, 182.8, 181.9, 179.4, 178.4, 175.3, 172.8, 172.4, 170.7 (s, 10 CO), 135.6 (br d, *o*-Ph), 132.1 (br d, *ipso*-Ph), 129.3 (s, *p*-Ph), 128.5 (br d, *m*-Ph), 124.2 (d, J_{CC} 64.5 Hz, ReCC), 104.8 [s, $C_5(CH_3)_5$], 10.2 [s, $C_5(CH_3)_5$]; $^{31}P\{^1H\}$ 21.0s.

‡ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/373.

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