

Some complexes containing carbon chains end-capped by $M(\text{CO})_2\text{Tp}'$ [$M = \text{Mo}, \text{W}; \text{Tp}' = \text{HB}(\text{pz})_3, \text{HB}(\text{dmpz})_3$] groups

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Abstract

Complexes $M(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}'$ ($\text{Tp}' = \text{Tp} [\text{HB}(\text{pz})_3]$, $M = \text{Mo}$ **2**, W **4**; $\text{Tp}' = \text{Tp}^* [\text{HB}(\text{dmpz})_3]$, $M = \text{Mo}$ **3**) are obtained from $M(\equiv\text{CC}=\text{CSiMe}_3)(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})$ (**1**) and $\text{K}[\text{Tp}']$. Reactions of **2** or **4** with $\text{AuCl}(\text{PPh}_3)/\text{K}_2\text{CO}_3$ in MeOH afforded $M\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}'$ ($M = \text{Mo}$ **5**, W **6**) containing C_3 chains linking the Group 6 metal and gold centres. In turn, the gold complexes react with $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ to give the C_4 -bridged $\{\text{Tp}(\text{OC})_2\text{M}\}\equiv\text{CC}=\text{CC}=\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$ ($M = \text{Mo}$ **7**, W **8**), while $\text{Mo}(\equiv\text{CBr})(\text{CO})_2\text{Tp}^*$ and $\text{Co}_3\{\mu_3\text{-C}(\text{C}=\text{C})_2\text{Au}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$ give $\{\text{Tp}^*(\text{OC})_2\text{Mo}\}\equiv\text{C}(\text{C}=\text{C})_2\text{C}=\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$ (**9**) via a phosphine-gold(I) halide elimination reaction. The C_3 complexes $\text{Tp}'(\text{OC})_2\text{M}\equiv\text{CC}=\text{CRu}(\text{dppe})\text{Cp}^*$ ($\text{Tp}' = \text{Tp}$, $M = \text{Mo}$ **10**, W **11**; $\text{Tp}' = \text{Tp}^*$, $M = \text{Mo}$ **12**) were obtained from **2–4** and $\text{RuCl}(\text{dppe})\text{Cp}^*$ via KF-induced metalla-desilylation reactions. Reactions between $\text{Mo}(\equiv\text{CBr})(\text{CO})_2\text{Tp}^*$ and $\text{Ru}\{\text{C}(\text{C}=\text{C})_n\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ ($n = 2, 3$) afforded $\{\text{Tp}^*(\text{OC})_2\text{Mo}\}\equiv\text{C}(\text{C}=\text{C})_n\text{-}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ ($n = 2$ **13**, 3 **14**), containing C_5 and C_7 chains, respectively. Single-crystal X-ray structure determinations of **1**, **2**, **7**, **8**, **9** and **12** are reported.

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Keywords: Carbon chain; X-ray structures; Molybdenum; Tungsten; Gold; Ruthenium; Cobalt; Cluster

1. Introduction

Recent papers describing complexes containing carbon chains end-capped by various metal–ligand combinations describe not only inherently interesting new molecules [1,2], but also relate to nano-scale devices, where these complexes may be considered to be models for molecular wires [3–6]. As has been reviewed recently [1], the majority of these compounds contain chains with an even number of carbon atoms, which is largely a result of the synthetic methods available, which use acetylenic (C_2) synthons.

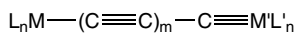
We and others have recently directed attention to the synthesis and properties of compounds containing chains

with an odd number of carbon atoms [7–10]. These compounds are of interest because their electronic structure requires at least one of the $\text{M}-\text{C}$ attachments to involve a multiple bond, i.e., structures **A** or **B** (Chart 1). In contrast, the even-numbered analogues may be represented by structures **C–E**, the vast majority having structure **C**, which contains two $\text{M}-\text{C}$ single bonds. The synthesis of **A** requires one precursor which contains the odd-numbered chain, onto which acetylenic units may be grafted; to our knowledge, the only synthesis (of a C_3 complex) using a carbene precursor is that of the Group 6 complexes $[\text{Tp}^*(\text{OC})_2\text{M}=\text{C}=\text{C}=\text{C}=\text{W}(\text{CO})_2\text{Tp}^*]$ and $\{\text{Tp}^*(\text{OC})_2\text{M}\}\equiv\text{CC}=\text{C}\{\text{M}'(\text{O})_2\text{Tp}^*\}$ ($M, M' = \text{Mo}, \text{W}; \text{Tp}^* = \text{BH}(\text{dmpz})_3$) [10].

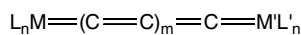
Consideration of possible precursors leads to the potential use of carbyne complexes, containing $\text{M}\equiv\text{C}$ triple bonds. Alternatively, carbynes attached to a bi- or

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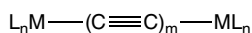
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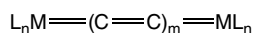
A



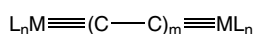
B



C



D



E

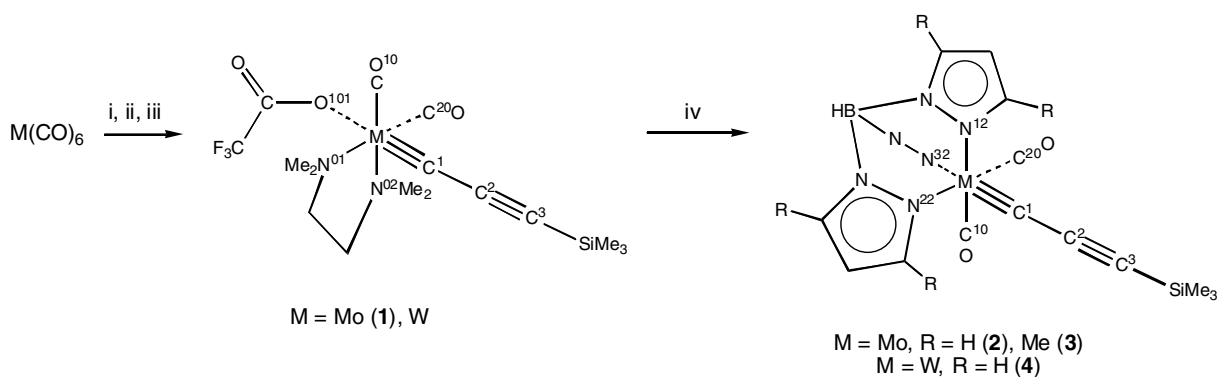
Chart 1.

2. Results and discussion

Earlier reports have described the synthesis of alkynylcarbyne–molybdenum complexes by treatment of $Mo(CO)_6$ with $LiC\equiv CBu^t$, followed by addition of $(CF_3CO)_2O$ and N,N,N',N' -tetramethyldiaminoethane (tmeda) to give $Mo(\equiv CC\equiv CBu^t)\{OC(O)CF_3\}(CO)_2$ (tmeda) [13]. We have made the $SiMe_3$ analogue **1** (Scheme 1) by this route, obtaining orange crystals, and have performed a single-crystal structure determination (Fig. 1). The Mo atom is octahedrally coordinated by the $CC\equiv CSiMe_3$ fragment, the CF_3CO_2 anion [$Mo-O$ 2.192(4) Å], two CO groups [$Mo-C(10,20)$ 2.009(9), 1.992(7) Å] and the chelating tmeda ligand [$Mo-N(01)$, $N(02)$ 2.281(6), 2.275(7) Å], with angles subtended at Mo by *cis* pairs of ligands ranging between 88.9° and 93.2(3)°, with the exception of the tmeda ligand which, with its small bite angle, subtends an angle of only 79.4(2)°; other $X-Mo-N(0n)$ angles are larger as a result, ranging from 87.9° to 109.3(5)°. In the context of the present work, the geometry of the alkynylcarbyne is of interest. The distances in the $Mo\equiv C-C\equiv C-Si$ fragment [1.82(1), 1.38(2), 1.21(2), 1.84(1) Å] confirm its formulation, with angles at C(1,2,3) of 174.2(12)°, 177.0(16)° and 178.3(13)°. This atom string is disordered, with an equal population in a rotamerically related second site, located with $C(1)-Mo-C(1')$ 18.0(8)° and essentially identical geometrical parameters. The spectroscopic properties are consistent with the solid state structure being retained in solution, with $\nu(CC)$ at 2046 cm^{-1} , $\nu(CO)$ at 2013 and 1934 cm^{-1} and the carboxylate $\nu(CO)$ at 1711 cm^{-1} . The NMR spectra contain resonances for the $SiMe_3$ group at δ_H 0.17 and δ_C 0.54, for the tmeda ligand at δ_H 3.02 (Me) and 2.80 (CH_2) and δ_C 50.85, 55.69 and 60.81, and the CF_3CO_2 group at δ_C 116.88 and 160.88 [quartets with $J(CF)$ 289 and 36 Hz, respectively]. One of the alkynyl carbons is found at δ_C 112.74 and the carbons attached to Mo are at δ_C 224.76 (CO) and 261.16 ($C\equiv Mo$).

Reactions of **1** with KTp or KTp^* ($KTp = K[BH(pz)_3]$, $KTp^* = K[BH(dmpz)_3]$) overnight give $Mo(\equiv CC\equiv CSiMe_3)(CO)_2Tp'$ [$Tp' = Tp$ (**2**), 34%; Tp^* (**3**), 30%]

tri-nuclear cluster could be used, and we have shown the utility of the halocarbyne complexes $M_3(\mu_3-CX)L_9$ [$M = RuH, OsH, Co_3$; $X = Cl, Br, I$; $L_9 = (CO)_9, (CO)_7(dppm)$] in this regard [11]. Mononuclear complexes containing halocarbynes are also known, one of the first to be described being the Group 6 array $M(CX)(CO)_2Tp'$ ($M = Mo, W$; $X = Cl, Br$; $Tp' = Tp [BH(pz)_3]$, Tp^*) [12]. Several accounts of alkynylcarbyne complexes containing these Group 6 groups have appeared, commencing with the first preparation [13], and followed some years later by a modified synthesis directly from $M(CO)_6$ [14]. In independent studies, Hill and coworkers have recently described related complexes containing C_3 chains linking the Group 6 centre to various platinum metals [8], and these results prompt this account of our related results using these end-groups.



Scheme 1. Reagents: (i) $HC\equiv CSiMe_3/LiBu$; (ii) $(CF_3CO)_2O$; (iii) tmeda; (iv) KTp' ($Tp' = Tp, Tp^*$). In this and other schemes, the third pyrazolyl group is indicated by N–N.

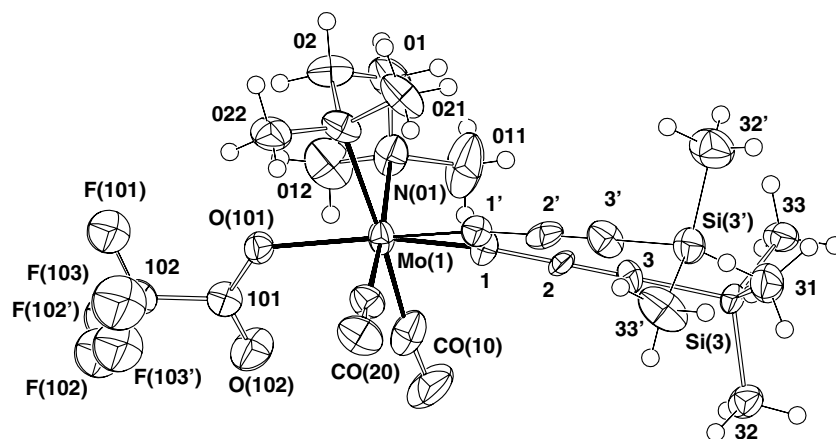


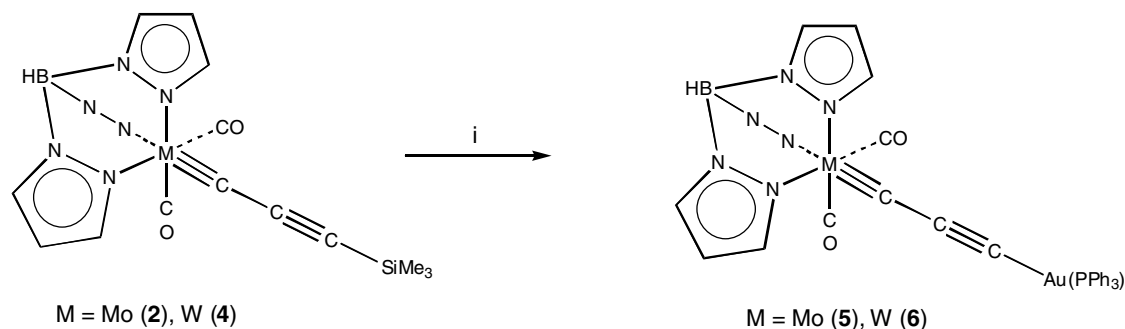
Fig. 1. Plot of a molecule of $\text{Mo}(\equiv\text{CC}\equiv\text{CSiMe}_3)\{\text{OC}(\text{O})\text{CF}_3\}_2(\text{CO})_2(\text{tmeda})$ (**1**).

(Scheme 1). The IR spectrum of **2** contains a $\nu(\text{BH})$ band at 2482 cm^{-1} , $\nu(\text{CC})$ at 2046 cm^{-1} , and terminal $\nu(\text{CO})$ bands at 2004 and 1925 cm^{-1} . As found for all complexes described herein, the Tp' ligands in **2** and **3** give rise to characteristic ^1H and ^{13}C resonances which generally have a 2/1 relative intensity as a result of the MoA_2B ligand coordination. These occur between δ_{C} 104.9 and 107.8, between 134.8 and 145.7 and between 143.1 and 152.1, being assigned to C^3 , C^4 and C^2 , respectively. For **3**, the latter two resonances are found ca. 8 ppm upfield from those in **2**. In a few cases, the two resonances overlap, as in **3**, where only one signal at δ_{C} 106.46 is observed. IR absorptions for the $\nu(\text{CC})$ and $\nu(\text{CO})$ vibrations are found in the usual regions, while the carbons of the $\text{Mo}\equiv\text{CC}\equiv\text{C}$ systems are now found at δ_{C} 259.41, 113.52 and 76.48 (for **2**) and at δ_{C} 255.41, 113.49 and 75.28 (for **3**). The analogous tungsten complex $\text{W}(\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Tp}$ (**4**) has been reported on an earlier occasion [14a].

Red crystalline $\text{Mo}\{\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (**5**) was obtained in 88% yield by reaction of **2** with $\text{AuCl}(\text{PPh}_3)$ in the presence of potassium carbonate (Scheme 2). The IR spectrum of this complex contains two strong $\nu(\text{CO})$ bands at 1982 and 1904, $\nu(\text{CC})$ at 2015 and $\nu(\text{BH})$ at 2483 cm^{-1} . In the ^1H NMR spectrum, the pz protons occur at δ 5.62, 5.72, 7.21, 7.26, 7.30 and 7.91, being differentiated by the asymmetry at the Mo centre. Carbons of the pz groups resonate at δ 106.22 and

106.27 (C^3), at 136.48 and 136.56 (C^4), and at 144.69 and 144.82 (C^2) in the ^{13}C NMR spectrum, with two of the $\text{C}(\text{sp})$ atoms found at δ 104.65 and 115.49. The $\text{Mo}-\text{CO}$ and $\text{Mo}\equiv\text{C}$ resonances are at δ 228.42 and 265.15, respectively. The ^{31}P NMR spectrum contains a singlet at δ 41.6 for the PPh_3 ligand. The electrospray (ES) mass spectrum contains various aggregate ions at m/z 1321 ($[\text{M} + \text{Au}(\text{PPh}_3)]^+$), 1125 ($[\text{M} + \text{HPPH}_3]^+$), 885 ($[\text{M} + \text{Na}]^+$) and 721 ($[\text{Au}(\text{PPh}_3)_2]^+$), these being commonly observed in the mass spectra of $\text{Au}(\text{PR}_3)$ complexes [15]. The analogous tungsten complex **6** was prepared in a similar fashion in 69% yield, and has similar spectroscopic properties, including $\nu(\text{BH})$ at 2483, $\nu(\text{CC})$ at 2020 and $\nu(\text{CO})$ at 1970 and 1886 cm^{-1} . In the ^{13}C NMR spectrum, the $\text{W}\equiv\text{C}$ and $\text{W}-\text{CO}$ resonances are at δ 258.25 and 226.73, but the other carbons of the C_3 were not resolved. Complex **6** was also reported by Hill and his group [16] during the preparation of this paper.

We have previously shown that the $\text{Pd}(0)/\text{Cu}(\text{I})$ -catalysed elimination of $\text{AuX}(\text{PR}_3)$ from reactions of compounds containing $\text{C}(\text{sp})-\text{X}$ [$\text{X} = \text{halide}$ and $\text{Au}(\text{PR}_3)$] groups is an efficient method of forming $\text{C}-\text{C}$ bonds which, in contrast to the well-known Sonogashira reaction, does not require the presence of a base (amine), which may attack the organometallic reactants and products [17]. In this work, we describe the reactions between **5** or **6** and $\text{Co}_3(\mu_3-\text{CBr})(\mu\text{-dppm})(\text{CO})_7$ [18], which proceed under mild conditions



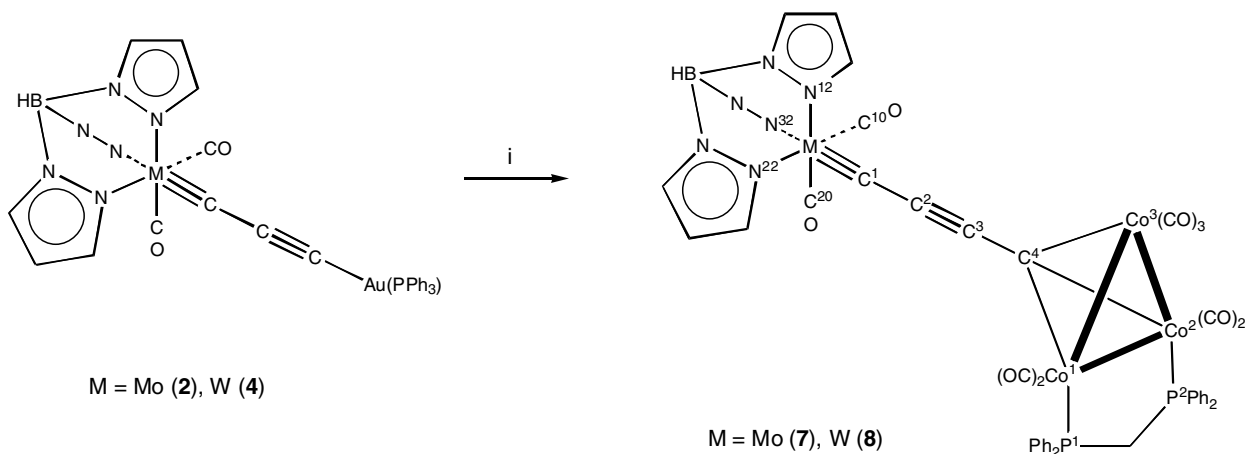
Scheme 2. Reagents: (i) $\text{AuCl}(\text{PPh}_3)/\text{K}_2\text{CO}_3$, MeOH .

(thf, r.t., 2 h) to give $\{\text{Tp}(\text{OC})_2\text{M}\}\equiv\text{CC}\equiv\text{CC}\equiv\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$ [$\text{M} = \text{Mo}$ (**7**) (39%), W (**8**) (37%)] as brown solids (Scheme 3). These complexes were characterised by elemental microanalysis and spectroscopically [IR: five terminal $\nu(\text{CO})$ bands between 2060 and 1885 cm^{-1} ; ^1H NMR; pz protons at δ 5.68, 5.77 (Mo), 5.60, 5.70 (W); ^{13}C NMR: pz carbons at δ 105.44/105.58, 135.47/135.65, 143.09/144.51 (Mo), 106.65/106.71, 135.44/135.76, 144.57/146.05 (W), $\text{C}\equiv\text{C}$ carbons at δ 87.79, 125.19 (Mo), Co–CO at δ 201.26, 209.90 (br) (Mo), 198.98, 202.00 (W), M–CO at δ 230.49 (Mo), 229.97 (W), $\text{M}\equiv\text{C}$ at δ 252.92 (Mo), 246.80 (W); ES-MS, $[\text{M} + \text{Na}]^+$ at m/z 1195 (Mo), $[\text{M} - \text{H}]^-$ at m/z 1257 (W)].

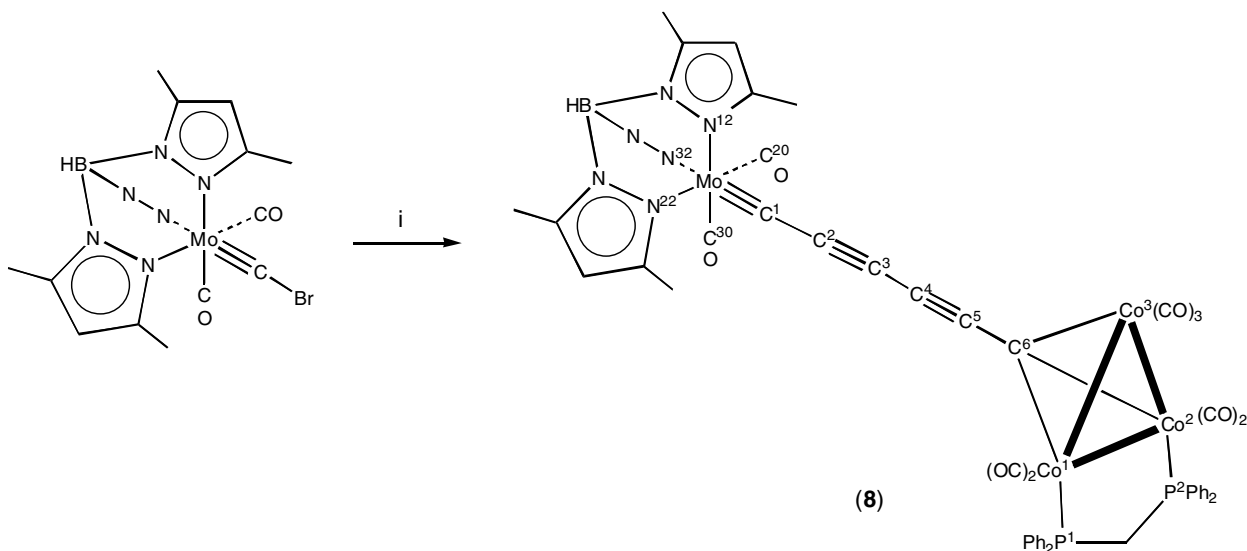
The reverse reaction, i.e., between $\text{Mo}(\equiv\text{CBr})(\text{CO})_2\text{Tp}^*$ and $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$, afforded the corresponding $\text{Tp}^*\text{Mo-C}_6$ derivative **9** in 72% yield (Scheme 4). The IR spectrum contains bands for $\nu(\text{C}\equiv\text{C})$ at 2109 cm^{-1} and $\nu(\text{CO})$ between 2060 and 1908 cm^{-1} . The ^1H NMR spectrum has two pairs of pyrazolyl-Me res-

onances at δ 2.32, 2.38 and 2.34, 2.61 and the two pyrazolyl protons at δ 5.71 and 5.88. In the ^{13}C NMR spectrum, the pyrazolyl-Me carbons are found at δ 12.68, 14.65, 15.93 while the ring carbons are at δ 106.34/106.36, 144.45/145.07 and 151.28, the Co–CO at δ 201.29, 209.49, the Mo–CO at δ 229.48 and the $\text{Mo}\equiv\text{C}$ at δ 261.02. We assign resonances at δ 52.55, 96.73, 100.92 and 107.95 to four of the six carbon chain nuclei; that attached to the Co_3 cluster is likely broadened by the ^{59}Co nuclear quadrupole [19,20]. The ES MS contains $[\text{M} + \text{Na}]^+$ at m/z 1302.

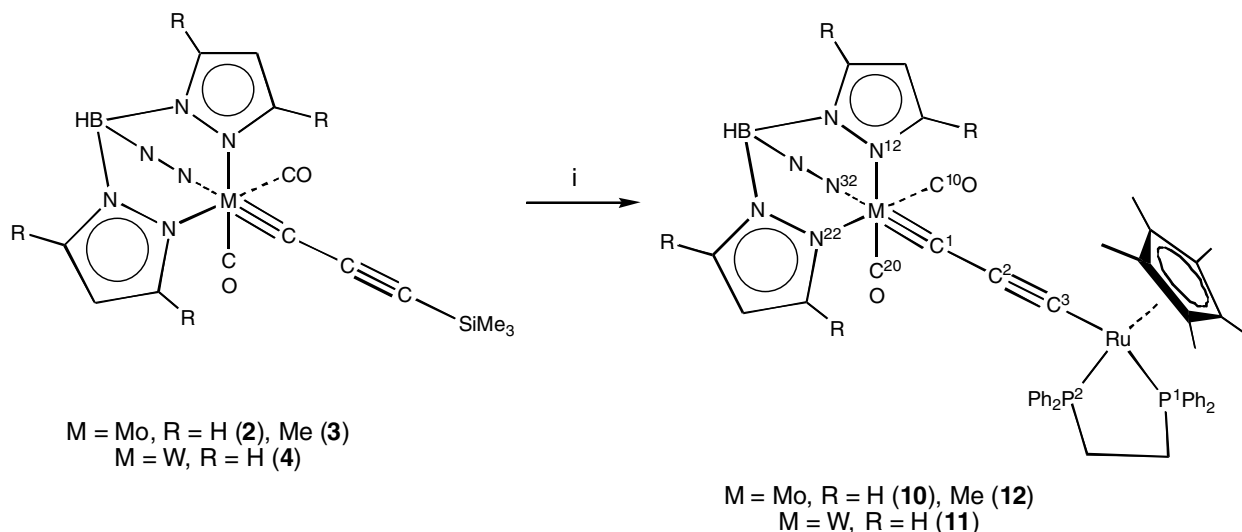
An alternative method of preparing M–C(sp) bonds is fluoride-induced metallo-desilylation, which we have shown to be particularly effective in reactions of trimethylsilyl-substituted alkynes with halides of electron-rich metal centres, such as $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ [21]. In the present study, the reaction of **2** with $\text{RuCl}(\text{dppe})\text{Cp}^*$ in the presence of KF in methanol afforded red $\{\text{Tp}(\text{OC})_2\text{Mo}\}\equiv\text{C}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**10**) in 60% yield (Scheme 5). The IR spectrum of this complex contains a $\nu(\text{CC})$ band at



Scheme 3. Reagents: (i) $\text{Co}_3(\mu\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$, $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$.



Scheme 4. Reagents: (i) $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$, $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$.

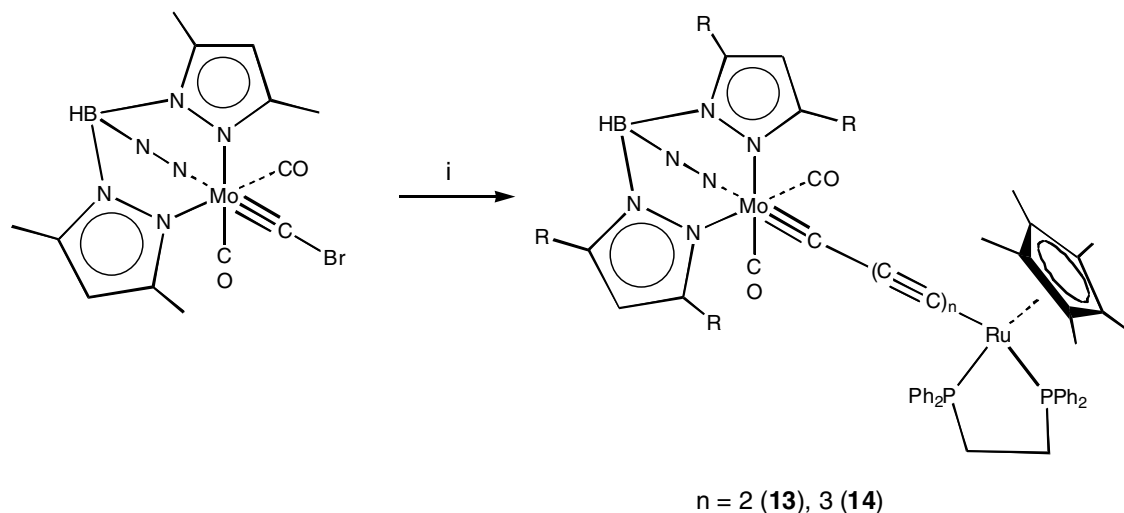
Scheme 5. Reagents: (i) $\text{RuCl}(\text{dppe})\text{Cp}^*$, KF , MeOH .

1975, and terminal $\nu(\text{CO})$ bands at 1902 and 1863 cm^{-1} . In the ^1H NMR spectrum, the pz protons are found at δ 5.65 and 5.85, with the Cp^* Me resonance at δ 1.50. Corresponding features are found in the ^{13}C NMR spectrum at δ 9.98 and 94.70 (Me and ring C of Cp^*), 104.91/105.10, 136.13/136.46, 143.46/144.32 (pz) and 230.65 (Mo–CO); the Mo \equiv C resonance was not found. Finally, the ES-MS contains $[\text{M} + \text{H}]^+$ at m/z 1036. The tungsten analogue $\{\text{Tp}(\text{OC})_2\text{W}\}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**11**) was obtained similarly from **4** in 36% yield and has comparable spectroscopic properties.

A reaction between **3** and $\text{RuCl}(\text{dppe})\text{Cp}^*$ gave the Tp^* analogue (**12**) as an orange solid in 36% yield. Spectral features are similar to those of **10**, with the dmpz Me groups resonating at δ_{H} 2.18, 2.24, 2.63 and 2.69 and the remaining pz H atoms at δ 5.46 and 5.65. In the ^{13}C NMR spectrum the Cp^* Me and ring carbons are at δ 10.67 and 95.07, respectively, with the pz Me groups at δ 13.30, 15.59 and

16.62; the ring carbons are found at δ 106.28/106.47, 143.51/143.86, 151.51/151.66, while the Mo-bonded CO and carbyne carbons resonate at δ 230.95 and 254.47, respectively.

Lengthening of the carbon chain was achieved by Pd(0)/Cu(I)-catalysed reactions between $\text{Mo}(\equiv\text{CBr})(\text{CO})_2\text{Tp}^*$ and $\text{Ru}\{(\text{C}\equiv\text{C})_n\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ ($n = 1, 2$) which afforded the red C_5 and C_7 complexes $\{\text{Tp}^*(\text{OC})_2\text{Mo}\}\equiv\text{C}(\text{C}\equiv\text{C})_n\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ ($n = 1$ **13**, **2** **14**) in 67 and 49% yield, respectively (Scheme 6). Elemental analyses and the ES mass spectra confirmed the formulations of these complexes, supported by the usual spectroscopic data. Thus, the IR spectra contain three $\nu(\text{CO})$ bands at 1971, 1899 and 1856 (for **13**) and 1990, 1916 and 1868 cm^{-1} (for **14**). Weak $\nu(\text{C}\equiv\text{C})$ bands were found at 2116, 2069 and 2010 cm^{-1} for **14**. In the ^1H NMR spectra, the usual resonances for the ligands are found, while in the ^{13}C NMR spectrum, characteristic resonances at δ 10.42

Scheme 6. Reagents: (i) $\text{Ru}\{(\text{C}\equiv\text{C})_n\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$, $\text{Pd}(\text{PPh}_3)_4/\text{CuI}$.

and 94.87 (for **13**) or 10.55, 95.30 (for **14**) (Cp* Me and ring carbons), between δ 13 and 17 (pz Me groups), and at δ 106.62/106.67, 143.80/144.38, 151.64/152.08 (**13**) and 107.81, 144.00/145.65, 151.77/152.03 (**14**) (pz ring carbons) are accompanied by signals at δ 53.66, 92.65 (carbon chain), 230.29 or 227.55 (M–CO) and 260.85 (Mo \equiv C).

2.1. Molecular structures

The molecular structures of **2**, **7**, **8**, **9** and **12** were confirmed by single-crystal X-ray studies. Individual molecules of each of the four complexes are illustrated in Figs. 2–5, with important bond parameters being collected in Table 1.

The common Mo(CO)₂Tp' fragments are similar to those found in many other derivatives which have been studied earlier, of which Mo(\equiv Ctol)(CO)₂Tp* (**15**) is perhaps the most closely related recent example [22]. In all complexes, the Mo atom is octahedrally coordinated, with the Tp' ligand occupying three facial positions. The Mo–N(12, 22) bonds [range 2.213(6)–2.235(9); 2.198(7), 2.231(6) Å for W–N in **8**] *trans* to CO are shorter than Mo–N(32) [Mo range 2.289(5)–2.328(7) Å; W–N(32) 2.296(6) Å] which is *trans* to the carbyne ligand, as a result of better back-bonding into the latter. The other three sites are occupied by the two CO ligands and the \equiv CC \equiv C group. The M \equiv C(1) bonds are considerably shorter, between 1.833(7)

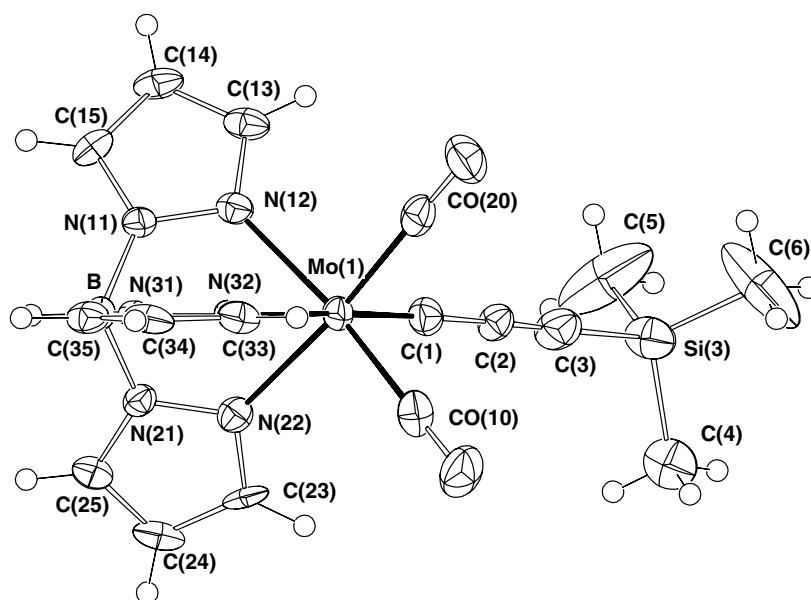


Fig. 2. Plot of a molecule of Mo(\equiv CC \equiv CSiMe₃)(CO)₂Tp (**2**).

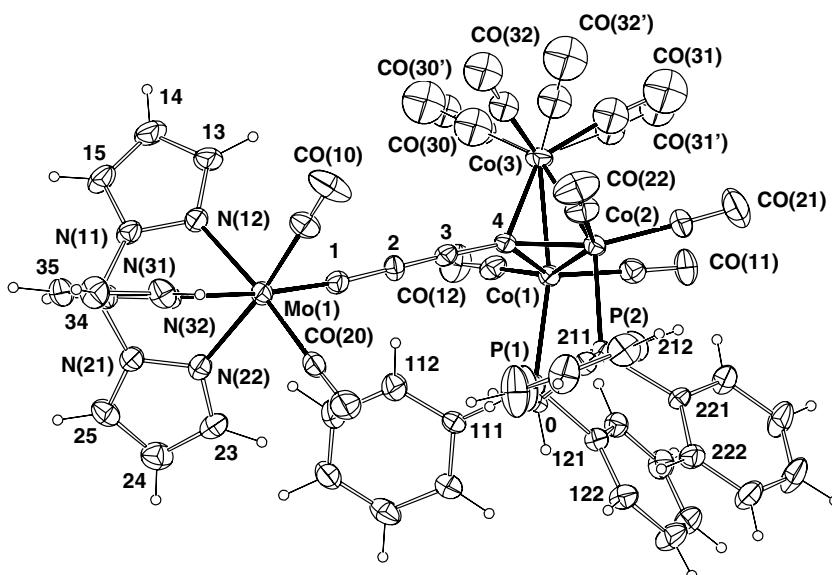


Fig. 3. Plot of a molecule of {Tp(OC)₂Mo} \equiv CC \equiv CC \equiv {Co₃(μ -dppm)(CO)₇} (**7**).

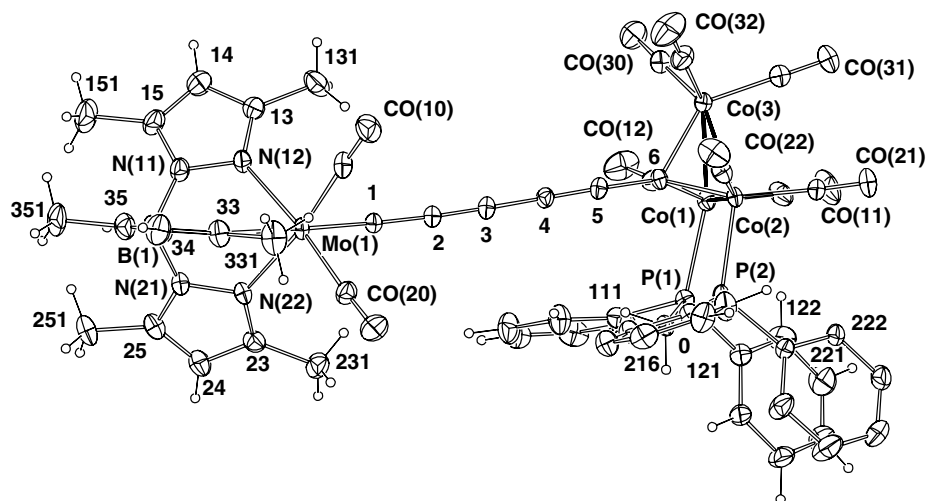


Fig. 4. Plot of a molecule of $\{\text{Tp}^*(\text{OC})_2\text{Mo}\}\equiv\text{C}(\text{C}\equiv\text{C})_2\text{C}\equiv\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$ (**9**).

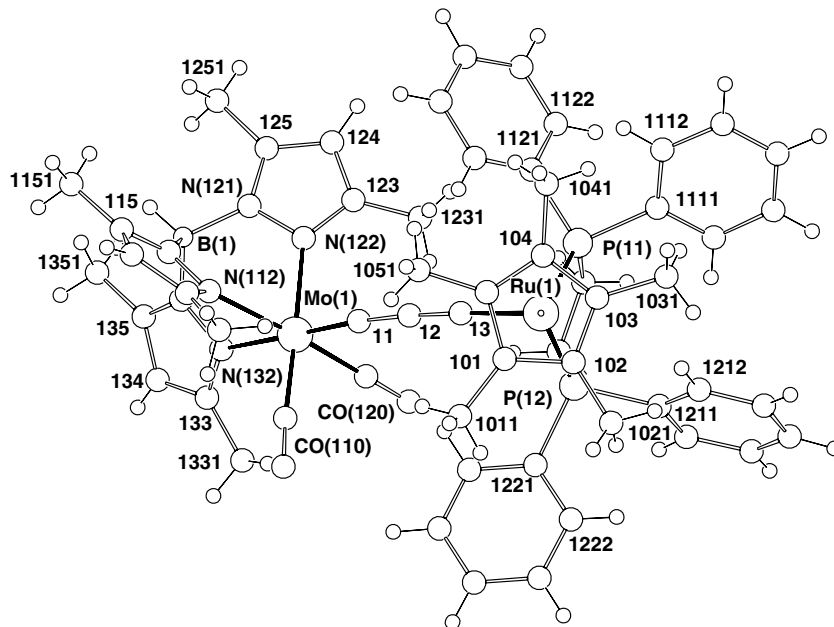


Fig. 5. Plot of a molecule of $\{\text{Tp}^*(\text{OC})_2\text{Mo}\}\equiv\text{C}\text{C}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**12**).

and 1.868(9) Å (Mo), 1.857(7) Å (W), than the two M–CO bonds [range 1.96(1)–2.010(8) Å; W–CO 1.961(9), 2.010(9) Å], as expected from its multiple-bond character, but longer than that in **15** [1.804(4) Å]. In the complex $\text{Mo}(\equiv\text{Ctol})(\text{CO})_2\text{Tp}^*$, corresponding values are: Mo–N(12,22) 2.218, 2.212(3), Mo–N(32) 2.306(3), Mo–CO 1.987(4), Mo≡C 1.804(4) Å [22].

Along the Mo/W–C(1)–C(2)–C(3)–X chain, C(1)–C(2) is between 1.34(1) and 1.399(10) Å, while C(2)–C(3) is between 1.24(1) and 1.258(11) Å, somewhat longer than expected for a normal C(sp)≡C(sp) triple bond. In the longer chain in **9**, alternation with C(sp)–C(sp) single bonds of 1.332(6) and 1.371(6) Å and the second C≡C triple bond of 1.231(6) Å, for example, shows that there is a small amount of electron delocalisation occurring. The car-

bon chain is essentially linear, angles at C(1,2,3) being 176.8(8)°, 178.9(7)° and 179.3(6)° (Mo), and 176.9(6)°, 175.0(7)°, 175.8(7)° for W, respectively. The C(3)–Si separation in **2** [1.846(9) Å] is not exceptional.

In **7**, **8** and **9**, the $\text{Co}_3(\mu\text{-dppm})(\text{CO})_7$ clusters are similar to those found in many related examples that we have reported recently, with the dppm ligand occupying equatorial coordination sites bridging the Co(1)–Co(2) bond [7,11,18]. The other bond parameters are unexceptional, with Co–Co distances between 2.475 and 2.502(1) Å, Co–P bonds of 2.198–2.219(3) Å, and Co–C(4 or 6) being in the range 1.880–1.953(8) Å.

In **12**, the Ru(dppe)Cp* fragment has the expected geometry, with Ru–P 2.269–2.297(3) Å and Ru–C(Cp*) 2.223–2/279(9) (av. 2.25₈ Å). The Ru–C(3) distance is

Table 1
Selected bond distances (Å) and angles (°)

	Complex 2	Complex 7	Complex 8 ^a	Complex 9	Complex 12 ^b
<i>Bond distances (Å)</i>					
Mo–C(10,20)	2.010(8), 2.007(8)	1.99(2), 1.993(9)	2.010(9), 1.961(10)	2.004(7), 1.983(7)	1.97, 1.97(1) <i>1.96, 1.97(1)</i>
Mo–N(12,22)	2.234(6), 2.222(6)	2.213(6), 2.231(9)	2.198(7), 2.231(6)	2.223(5), 2.216(5)	2.23(1), 2.235(9) <i>2.23, 2.25(1)</i>
Mo–N(32)	2.308(5)	2.313(6)	2.296(6)	2.289(5)	2.328(7), 2.324(8)
Mo–C(1)	1.833(7)	1.838(7)	1.857(7)	1.842(5)	1.868(9), 1.849(9)
C(1)–C(2)	1.399(10)	1.35(1)	1.35(1)	1.355(6)	1.34(1), 1.36(1)
C(2)–C(3)	1.258(11)	1.25(1)	1.24(1)	1.246(6)	1.24(2), 1.25(2)
C(3)–X [X]	1.846(9) [Si]	1.40(1) [C(4)]	1.38(1)	1.332(6) [C(4)]	1.97(1), 1.95(1) [Ru]
Co(1)–Co(2,3)		2.501, 2.485(2)	2.475, 2.491(1)	2.490, 2.483(1)	
Co(2)–Co(3)		2.502(1)	2.477(1)	2.472(1)	
Co(<i>n</i>)–P(<i>n</i>) (<i>n</i> = 1,2)		2.216, 2.215(3)	2.219, 2.211(2)	2.214, 2.198(2)	
Co(1,2,3)–C(<i>n</i>) [C(<i>n</i>)]		1.880, 1.916, 1.953(8) [C(4)]	1.909, 1.905, 1.950(7) [C(4)]	1.904, 1.910, 1.950(5) [C(6)]	
<i>Bond angles (°)</i>					
C(1)–Mo–N(12,22)	101.6(3), 98.4(3)	97.5(3), 103.2(4)	103.1, 96.2(3)	102.1, 105.9(2)	102.5(4), 95.8(4) <i>100.0(4), 95.6(4)</i>
C(1)–Mo–N(32)	176.9(3)	174.7(4)	174.9(3)	169.6(2)	175.6(5) 176.9(4)
C(1)–Mo–C(10,20)	86.5(4), 87.8(3)	85.0(4), 86.3(3)	88.4, 86.7(4)	81.5, 83.5(2)	83.9(5), 83.1(4) <i>85.7(4), 84.6(5)</i>
Mo–C(1)–C(2)	176.8(8)	172.9(9)	176.9(6)	166.2(4)	172.8(10), 174.5(9)
C(1)–C(2)–C(3)	178.9(7)	177.4(9)	175.0(7)	176.7(6)	172.2(10), 174.7(12)
C(2)–C(3)–X [X]	179.3(6) [Si]	177.1(7) [C(4)]	175.8(7)	177.8(6) [C(4)]	177.8(10), 176.7(10) [Ru]
C(5)–C(6)–Co(1,2,3)		138.4(8), 126.0(5), 128.6(6) [C(3,4)]	132.1(5), 135.2(6), 127.9(5) [C(3,4)]	131.6, 134.4, 129.2(4)	

For **9**: C(4)–C(5) 1.231(6), C(5)–C(6) 1.371(6) Å; C(3)–C(4)–C(5) 179.9(6), C(4)–C(5)–C(6) 178.7(7)°. For **12**: Ru–P(1,2) 2.272(3), 2.276(2); 2.269(3), 2.297(3); Ru–C(cp*) 2.223–2.279(9), 2.234–2.277(11); Ru–C(cp*) (av.) 2.26(2), 2.25(2) Å; P(1)–Ru–P(2) 81.7(1), 82.3(1); P(1,2)–Ru–C(3) 86.3(3), 84.6(3); 86.6(3), 85.4(3)°.

^a For Mo, read W.

^b Italicised values refer to molecule 2.

1.95(1) Å, somewhat shorter than that found in Ru(C≡CC≡CSiMe₃)(dppe)Cp* [1.983(2) Å], for example [23].

2.2. Electrochemistry

Most of these complexes are obtained in relatively low yields, one reason for this being their pronounced instability in normal organic solvents, perhaps as a result of ready oxidation. To some extent this is confirmed by electrochemical studies. Table 2 contains potentials measured from CVs obtained under anaerobic conditions. The Tp–Mo/W complexes **2** and **4** show one oxidation event at $E_1 = +0.89$ and $+0.82$ V (versus SCE), respectively, while the bromo-carbyne complex is similar, at $+0.83$ V. None of these complexes contains any other redox-active centre, so it may be reasonably assumed that the events involve the metal centres.

Complexes **7** and **9**, which also contain the Co₃ cluster as a second redox centre, each show a reduction wave between -1.07 and -1.02 V, which by comparison with Co₃(μ₃-CC≡CSiMe₃)(μ-dppm)(CO)₇ ($E_1 = -1.16$, $E_2 = +0.79$ V) may confidently be assigned to processes centred on the Co₃ cluster. Oxidation events are found between $+0.66$ and $+0.76$ V, but these cannot be assigned defini-

tively to either end-cap. Processes giving rise to the oxidations occur at higher potentials ($+1.16$ V for **7**, $+0.92$ and $+1.14$ V for **9**) and may arise from the carbon chains or from further chemical transformation of these complexes after oxidation.

Two oxidation events are also found for the Mo–C_{*n*}–Ru complexes **10–14**. Replacement of Tp in **10** by Tp* in **12** has little observable effect on the potentials, while the W complex **11** is somewhat more difficult to oxidise than its Mo congener (by 90 mV). As the chain length increases from C₃ to C₅ to C₇, E_1 increase by 110 and 160 mV and E_2 by 20 and 90 mV per added C₂ unit, reflecting the increasing electron transfer from the metal centre(s) to the C_{*n*} chain. This feature has previously been observed in the series {Cp(OC)₃W}(C≡C)_{*n*}Fc where, for $n = 2–4$, E_1 increases by about 50 mV per added C≡C unit [24]. This is probably a result of the increasing localisation of the HOMO on the C_{*n*} chain as the latter increases in length. The related complex Ru(C≡CC≡CSiMe₃)(dppe)Cp* has $E_1 = +0.43$ V, suggesting that the first process may relate to oxidation at the Ru centre, being reduced by the electron donating power of the other end-cap for the shorter chains. For the C₇ complex **14**, there is essentially no difference between the two oxidation events and those for the individual end groups when attached to a non-redox-active group

Table 2
Selected electrochemical data

Complex	E_1	i_c/i_a	E_2	E_3	E_4
Mo(\equiv CBr)(CO) ₂ Tp*	+0.83	1.0			
2	+0.89	1.0			
4	+0.82	0.65			
7	-1.07	1.0	+0.66	+1.16 ^a	
9	-1.02	1.0	+0.71	+0.92 ^a	+1.14 ^a
Co ₃ (μ_3 -CC \equiv CSiMe ₃)(μ -dppm)(CO) ₇	-1.16		+0.79		
10	+0.23	0.7	+0.78 ^a		
11	+0.32	1.0	+0.76 ^a		
12	+0.20	0.8	+0.73 ^a		
13	+0.31	1.0	+0.75	+1.17 ^a	
14	+0.47	0.8	+0.84		

Conditions: 10⁻³ M complex, 0.1 M [NBu₄]PF₆ in CH₂Cl₂, scan rate 100 mV s⁻¹ at ambient temperature, referenced to FeCp₂/[FeCp₂]⁺ = +0.46 V. Three-electrode cell equipped with Pt disk working electrode, Pt gauze auxiliary electrode, Pt wire pseudo-reference electrode.

^a Irreversible.

(SiMe₃), suggesting that no electronic effect is being communicated between the end-groups.

3. Conclusions

The reactions described above have added significantly to the series of complexes containing the Tp'M(CO)₂ group (Tp' = Tp, Tp*; M = Mo, W) end-capping a carbon chain, examples containing three, four, five, six and seven carbons in the chain having been obtained. These compounds have been characterised by the usual spectroscopic methods, most distinctive being the ν (BH), ν (CO) and ν (CC) bands in the IR spectra, and the characteristic resonances of the Tp' and Cp* groups (if present) in the ¹H and ¹³C NMR spectra. Not all of the carbon atoms in the chains were found in the latter: the carbyne carbon attached to the Group 6 metal centre occurs at the expected downfield location (δ 253–265 for Mo \equiv C, 246.8 for W \equiv C in **9**), at higher frequencies than the M–CO resonances (δ 224–231).

Our synthetic approaches have employed either the AuX(PR₃)-elimination reaction between Au(C \equiv CR) (PPh₃) and halo-carbyne complexes [17] or the metalladesilylation reaction which occurs between trimethylsilyl-substituted alkyne and chlororuthenium precursors such as RuCl(dppe)Cp' [21]. Interesting cluster-capped carbon chains are present in **7–9**, formed by linking of the well-known carbon-tricobalt complex with the Group 6 precursors by means of the AuX(PR₃) elimination reaction. These compounds, in which the Co₃ cluster has been stabilised against possible fragmentation by incorporation of a bridging dppm ligand [17] have the expected spectroscopic properties.

Electrochemical measurements show the presence of reduction and oxidation waves, at ca. -1.1 V and ca. +0.7 V, respectively. Comparison with similar measurements carried out on the individual end-caps shows the former may be assigned to processes centred on the Co₃

clusters, while the oxidation can be associated with the Group 6 metal centres. In complexes containing an Ru(dppe)Cp* end-group, only oxidation processes are observed, with potentials somewhat reduced by the presence of the electron-releasing Group 8 fragment. As the chain length increases, a further pair of oxidation processes is found for the C₅ and C₇ complexes.

4. Experimental

4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in thf were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electrospray mass spectra (ES MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used [25]. Cyclic voltammograms were recorded using a PAR model 263 apparatus. Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

The complexes M(\equiv CBr)(CO)₂Tp [M = Mo, W; X = Cl, Br; Tp = HB(pz)₃] [12], Co₃(μ_3 -CBr)(μ -dppm)(CO)₇ [18] and RuCl(dppe)Cp' (Cp' = Cp, Cp*) [26] were prepared as described previously.

4.3.1. Mo(\equiv CC \equiv CSiMe₃){OC(O)CF₃}(CO)₂(tmeda) (**1**)

A mixture of HC \equiv CSiMe₃ (0.7 ml, 5 mmol) in diethyl ether (30 ml) was cooled to -30 °C and BuLi (2 ml, 5 mmol) added and stirred at -30 °C for 30 min before Mo(CO)₆ (1.32 g, 5 mmol) in thf (5 ml) was added. The resulting mixture was stirred at 20 °C for 1 h, cooled to -78 °C and (CF₃CO)₂O (0.7 ml, 5 mmol) added. At

–50 °C tmeda (0.75 ml, 5 mmol) was added and the reaction mixture slowly warmed to 20 °C. Pentane (60 ml) was then added and the resulting orange precipitate collected and washed with pentane followed by pentane/dichloromethane (3/1) to give $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)\{\text{O}-\text{C}(\text{O})\text{CF}_3\}(\text{CO})_2(\text{tmeda})$ (**1**) (980 mg, 40%). Single crystals suitable for the X-ray study were grown from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Anal. Calc. ($\text{C}_{16}\text{H}_{25}\text{F}_3\text{MoN}_2\text{O}_4\text{Si}$): C, 39.19; H, 5.24; N, 5.71. Found: C, 39.07; H, 5.24; N, 5.73. IR (thf, cm^{-1}): $\nu(\text{C}=\text{C})$ 2046w, $\nu(\text{CO})$ 2013s, 1934vs. ^1H NMR: δ 0.17 (s, 9H, SiMe_3) 3.02 (s, 6H, NMe), 2.80 (m, 4H, NCH_2), 2.60 (s, 6H, NCH_2). ^{13}C NMR: δ 0.54 (s, SiMe_3), 50.85, 55.69, 60.81 (3 \times s, tmeda), 73.33 (s, CCSiMe_3), 112.74 (s, $\text{C}=\text{C}$) 116.88 [q, $^1\text{J}(\text{CF})$ 289 Hz, CF_3], 160.88 [q, $^1\text{J}(\text{CF})$ 36 Hz, O_2CCF_3], 224.76 (s, CO), 261.16 (s, $\text{Mo}=\text{C}$). ES MS (m/z): 378, $[\text{M} - \text{O}_2\text{CCF}_3]^+$.

4.3.2. $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}$ (**2**)

A mixture of $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})$ (230 mg, 0.47 mmol) and $\text{K}[\text{Tp}]$ (150 mg, 0.60 mmol) in dichloromethane (5 ml) was stirred at r.t. for 16 h. The solvent was then removed, and the deep purple residue extracted into dichloromethane and chromatographed on a basic alumina column eluting with hexane/acetone (4/1). The purple band was collected to give $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}$ (**2**) (75.6 mg, 34%) as micro crystals. Single crystals suitable for X-ray were grown from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Anal. Calc. ($\text{C}_{17}\text{H}_{19}\text{BMoN}_6\text{O}_2\text{Si}$): C, 43.06; H, 4.04; N, 17.72; M, 476. Found: C, 43.09; H, 4.06; N, 17.61. IR (thf, cm^{-1}): $\nu(\text{BH})$ 2482w, $\nu(\text{C}=\text{C})$ 2046w, $\nu(\text{CO})$ 2004s, 1925vs. ^1H NMR (C_6D_6): δ 0.23 (s, 9H, SiMe_3), 6.14 (t, $^3\text{J}(\text{HH}) = 2.4$ Hz, 1H, pz- C_4H), 6.25 [t, $^3\text{J}(\text{HH}) = 2.4$ Hz, 2H, pz-CH], 7.54, 7.61 [2 \times d, $^3\text{J}(\text{HH}) = 2.1$ Hz, 2 \times 1H, 2 \times pz-CH], 7.68, 7.94 [2 \times d, $^3\text{J}(\text{HH}) = 2.4$ Hz, 2 \times 2H, 2 \times pz-CH]. ^{13}C NMR: δ 0.44 (s, SiMe_3), 76.48 (s, $\text{C}=\text{C}$), 106.05/106.20, 136.26/136.34, 143.43/144.79 (6 \times s, pz-ring C), 113.52 (s, $\text{C}=\text{C}$), 227.17 (s, CO), 259.41 (s, $\text{C}=\text{Mo}$). ES MS (positive ion, MeOH + NaOMe, m/z): 499, $[\text{M} + \text{Na}]^+$.

4.3.3. $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}^*$ (**3**)

A mixture of $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{tmeda})$ (180 mg, 0.37 mmol) and $\text{K}[\text{HB}(\text{dmpz}_3)]$ (124 mg, 0.37 mmol) in dichloromethane (20 ml) was stirred at r.t. for 72 h. The solvent was then removed and the deep purple residue extracted into dichloromethane and chromatographed on a basic alumina column, eluting with hexane/acetone (4/1). The purple band was collected to give $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}^*$ (**3**) (60 mg, 30%). Anal. Calc. ($\text{C}_{23}\text{H}_{31}\text{BMoN}_6\text{O}_2\text{Si}$): C, 49.47; H, 5.60; N, 15.05; M, 560. Found: C, 49.50; H, 5.62; N, 15.01. IR (thf, cm^{-1}): $\nu(\text{BH})$ 2549w, $\nu(\text{C}=\text{C})$ 2045w, $\nu(\text{CO})$ 1995s, 1915s. ^1H NMR (C_6D_6): δ 0.20 (s, 9H, SiMe_3), 2.32 (s, 3H, 5Me), 2.33 (s, 6H, 5Me), 2.37 (s, 3H, 3Me), 2.55 (s, 6H, 3Me). ^{13}C NMR: δ 0.04 (s, SiMe_3), 12.97, 14.84, 16.00 (3 \times s, pz-CMe), 75.28 (s, $\text{C}=\text{C}$), 106.46, 144.49/145.16, 151.25/151.52 (5 \times s, pz-ring C), 113.49 (s, $\text{C}=\text{C}$),

227.42 (s, CO), 255.41 (s, $\text{C}=\text{Mo}$). ES MS (positive ion, MeOH + NaOMe, m/z): 583, $[\text{M} + \text{Na}]^+$; 504, $[\text{M} - 2\text{CO}]^+$.

4.3.4. $\text{Mo}\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (**5**)

A mixture of $\text{Mo}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}$ (400 mg, 0.81 mmol), $\text{AuCl}(\text{PPh}_3)$ (400 mg, 0.81 mmol) and K_2CO_3 (112 mg, 0.81 mmol) in a 4:1 mixture of thf/MeOH (150 ml) was stirred at r.t. for 2 h. The solvent volume was then reduced (ca 15 ml), and the resulting precipitate collected to afford $\text{Mo}\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (**5**) (613 mg, 88%) as red micro crystals. Anal. Calc. ($\text{C}_{32}\text{H}_{25}\text{AuBMoN}_6\text{O}_2\text{P}$): C, 44.68; H, 2.93; N, 9.77; M, 862. Found: C, 44.61; H, 2.81; N, 9.66. IR (thf, cm^{-1}): $\nu(\text{BH})$ 2483w, $\nu(\text{C}=\text{C})$ 2015w, $\nu(\text{CO})$ 1982s, 1904s. ^1H NMR (C_6D_6): δ 5.62 [t, $^3\text{J}(\text{HH}) = 2.1$ Hz, 1H, pz- C^4H], 5.72 [t, $^3\text{J}_{\text{HH}} = 2.1$ Hz, 2H, pz- C^2H], 6.83–7.14 (m, 15H, Ph), 7.21, 7.26 [2 \times d, $^3\text{J}(\text{HH}) = 2.1$ Hz, 2 \times 1H, pz- C_5H and pz- C_3H], 7.30, 7.91 [2 \times d, $^3\text{J}(\text{HH}) = 2.1$ Hz, 2 \times 2H, pz- C_5H and pz- C_3H]. ^{31}P NMR (C_6D_6): δ 41.64 (s, 1P, PPh_3). ^{13}C NMR (d_6 -acetone): δ 104.65 (s, $\text{C}=\text{C}$), 106.22/106.27, 136.48/136.56, 144.69/144.82 (6 \times s, pz-ring C), 115.49 (s, $\text{C}=\text{C}$), 129.06–134.97 (m, Ph), 228.42 (s, CO), 265.15 (s, $\text{C}=\text{Mo}$). ES MS (positive ion, MeOH + NaOMe, m/z): 1322, $[\text{M} + \text{AuPPh}_3]^+$; 1126, $[\text{M} + \text{HPPPh}_3]^+$; 885, $[\text{M} + \text{Na}]^+$; 721, $[\text{Au}(\text{PPh}_3)_2]^+$.

4.3.5. $\text{W}\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (**6**)

A mixture of $\text{W}(\equiv\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}$ (500 mg, 0.9 mmol), $\text{AuCl}(\text{PPh}_3)$ (445 mg, 0.9 mmol) and K_2CO_3 (125 mg, 0.9 mmol) in a 4:1 mixture of THF/MeOH (150 ml) was stirred at r.t. for 3 h. After this time the solvent volume was reduced (ca 15 ml), and the resulting precipitate collected to afford $\text{W}\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (**6**) (580 mg, 69%) as red micro crystals. Anal. Calc. ($\text{C}_{32}\text{H}_{25}\text{AuBN}_6\text{O}_2\text{PW}$): C, 40.54; H, 2.66; N, 8.86; M, 948. Found: C, 40.57; H, 2.61; N, 8.76. IR (thf, cm^{-1}): $\nu(\text{BH})$ 2483w, $\nu(\text{C}=\text{C})$ 2020w, $\nu(\text{CO})$ 1970s, 1886s. ^1H NMR (C_6D_6): δ 5.55 [t, $^3\text{J}(\text{HH}) = 2.4$ Hz, 1H, pz- C_4H], 5.65 [t, $^3\text{J}(\text{HH}) = 2.4$ Hz, 2H, pz- C^4H], 6.87–6.92 (m, 15H, Ph), 7.11, 7.31 [2d, $^3\text{J}(\text{HH}) = 2.4$ Hz, 2 \times 1H, pz- C^2H], 7.21, 7.97 [2 \times d, $^3\text{J}(\text{HH}) = 2.4$ Hz, 2 \times 2H, pz- C^2H]. ^{31}P NMR (C_6D_6): δ 42.85 (s, 1P, PPh_3). ^{13}C NMR (d_6 -acetone/ C_6D_6): δ 106.12/106.17, 135.67/135.85, 144.05/145.23 (6 \times s, pz-ring C), 127.58–135.85 (m, Ph), 226.73 (s, CO), 258.25 (s, $\text{C}=\text{W}$). ES MS (m/z): 1406, $[\text{M} + \text{Au}(\text{PPh}_3) - \text{H}]^+$; 1351, $[\text{M} + \text{Au}(\text{PPh}_3) - 2\text{CO}]^+$; 1089, $[\text{M} + \text{Au}(\text{PPh}_3) - 2\text{CO}]^+$; 971, $[\text{M} + \text{Na}]^+$; 721, $[\text{Au}(\text{PPh}_3)_2]^+$; 500, $[\text{Au}(\text{MeCN})]^+$; 459, $[\text{Au}(\text{PPh}_3)]^+$.

4.3.6. $\{\text{Tp}(\text{OC})_2\text{Mo}\}\equiv\text{CC}=\text{CC}=\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$ (**7**)

A mixture of $\text{Mo}\{\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{CO})_2\text{Tp}$ (50 mg, 0.06 mmol), $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (98 mg, 0.06 mmol), $\text{Pd}(\text{PPh}_3)_4$ (15 mg, 0.013 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (15 ml) at r.t. for 2 h. The solvent was then removed and the resulting dark purple

residue purified by preparative TLC eluting with acetone/hexane (3/7) to obtain $\{Tp(OC)_2Mo\}\equiv CC\equiv CC\equiv \{Co_3(\mu-dppm)(CO)_7\}$ (**7**) as a yellow brown band (R_f 0.23) (48 mg, 39%). Anal. Calc. ($C_{47}H_{32}BCo_3MoN_6O_9P_2$): C, 48.24; H, 2.76; N, 7.18; M , 1172. Found: C, 48.16; H, 2.81; N, 7.02. IR (thf, cm^{-1}): $\nu(BH)$ 2482w, $\nu(CO)$ 2060s, 2011s, 1997 (sh), 1981m, 1904m. 1H NMR (C_6D_6): δ 3.10, 4.58 (2m, $2 \times 1H$, CH_2), 5.68, 5.77 ($2 \times s$, br, 2H, $2 \times pz-CH$), 6.69–7.74 (m, 26H, Ph). ^{31}P NMR: δ 41.64 (s, 2P, dppm). ^{13}C NMR: δ 40.35 (s, CH_2), 105.44/105.58, 135.47/135.65, 143.09/144.51 ($6 \times s$, pz-ring C), 87.79, 125.19 (s, $C\equiv C$), 128.54–135.65 (m, Ph), 201.26, 209.90 (2s, br, Co–CO), 230.49 (s, Mo–CO), 252.92 (s, $C\equiv Mo$). ES MS (positive ion, MeOH + NaOMe, m/z): 1195, $[M + Na]^+$; 1171, $[M - H]^+$; 1142, $[M - CO]^+$.

4.3.7. $\{Tp(OC)_2W\}\equiv CC\equiv CC\equiv \{Co_3(\mu-dppm)(CO)_7\}$ (**8**)

A mixture of $W(\equiv CC\equiv CAuPPh_3)(CO)_2Tp$ (57 mg, 0.06 mmol), $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ (98 mg, 0.06 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (10 ml) at r.t. for 2 h. The solvent was then removed and the resulting residue purified by preparative TLC eluting with acetone/hexane (3/7) to obtain $\{Tp(OC)_2W\}\equiv CC\equiv CC\equiv \{Co_3(\mu-dppm)(CO)_7\}$ (**8**) as a brown band (R_f 0.36) (28 mg, 37%). Anal. Calc. ($C_{47}H_{32}BCo_3N_6O_9P_2W$): C, 44.84; H, 2.56; N, 6.68; M , 1258. Found: C, 44.72; H, 2.58; N, 6.54. IR (thf, cm^{-1}): $\nu(CO)$ 2058s, 2010s, 1994 (sh), 1970m, 1885m. 1H NMR (C_6D_6): δ 3.11, 4.70 (2m, $2 \times 1H$, CH_2), 5.60, 5.70 [$2 \times t$, $^3J(HH) = 2.1$ Hz, 2H, $2 \times pz-CH$] 6.66–8.04 (m, 26H, Ph). ^{31}P NMR: δ 32.15 (s, 2P, dppm). ^{13}C NMR: δ 41.93 (s, CH_2), 106.65/106.71, 135.44/135.76, 144.57/146.05 ($6 \times s$, pz-ring C), 128.08–141.41 (m, Ph), 198.89, 202.00 ($2 \times s$, br, Co–CO), 229.97 (s, W–CO), 246.80 (s, $C\equiv W$). ES MS (m/z): 1257, $[M - H]^+$; 1229, $[M - H - CO]^+$.

4.3.8. $\{Tp^*(OC)_2Mo\}\equiv C(C\equiv C)_2C\equiv \{Co_3(\mu-dppm)(CO)_7\}$ (**9**)

A mixture of $Mo(\equiv CBr)(CO)_2Tp^*$ (28 mg, 0.047 mmol), $Co_3\{\mu_3-C(C\equiv C)_2Au(PPh_3)\}(\mu-dppm)(CO)_7$ (60 mg, 0.047 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (10 ml) at r.t. for 1 h. The solvent was then removed and the resulting residue purified by preparative TLC eluting with acetone/hexane (3/7) to obtain $\{Tp^*(OC)_2Mo\}\equiv C(C\equiv C)_2C\equiv \{Co_3(\mu-dppm)(CO)_7\}$ (**9**) as a brown band (R_f 0.34) (43 mg, 72%). An analytically pure sample was obtained through crystallisation from chloroform. Anal. Calc. ($C_{55}H_{44}BCo_3MoN_6O_9P_2.CHCl_3$): C, 48.07; H, 3.24; N, 6.01; M (unsolvated), 1279. Found: C, 48.60; H, 3.14; N, 5.45. IR (thf, cm^{-1}): $\nu(C\equiv C)$ 2109w, $\nu(CO)$ 2060s, 2012s, 1989m, 1973m, 1908m. 1H NMR ($CDCl_3$): δ 2.32, 2.34, ($2 \times s$, $2 \times 3H$, Me), 2.38, 2.61 ($2 \times s$, $2 \times 6H$, Me), 3.42, 4.26 ($2 \times m$, $2 \times 1H$, CH_2), 5.71 (s, 1H, H^3), 5.88 (s, 2H, H^3), 7.23–7.54 (m, 26H, Ph). ^{13}C NMR: δ 12.68, 14.65, 15.93 (3 s s, pz- C_3Me), 44.45 [t, $J(CP)$ 22 Hz, CP_2], 52.55,

96.73, 100.92, 107.95 ($4 \times s$, $C\equiv C$), 106.34/106.36, 144.45/145.07, 151.28 ($5 \times s$, pz-ring C), 128.57–135.06 (m, Ph), 201.29, 209.49 ($2 \times s$, br, Co–CO), 229.48 (s, Mo–CO), 261.02 (s, $C\equiv Mo$). ^{31}P NMR: δ 34.13 (s, 2P, dppm). ES MS (positive ion, MeOH + NaOMe, m/z): 1302, $[M + Na]^+$.

4.3.9. $\{Tp(OC)_2Mo\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**10**)

To a mixture of $RuCl(dppe)Cp^*$ (40 mg, 0.06 mmol) and KF (3.5 mg, 0.06 mmol) in methanol at 0 °C was added $Mo(\equiv CC\equiv CSiMe_3)(CO)_2Tp$ (22.5 mg, 0.06 mmol). The resulting mixture was allowed to warm to r.t. and stirred for 2 h. The precipitate which formed was then collected and washed with MeOH (10 ml) followed by hexane (20 ml) to obtain $\{Tp(CO)_2Mo\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**10**) as a red solid (37 mg, 60%). Anal. Calc. ($C_{50}H_{49}BMoN_6O_2P_2Ru$): C, 57.98; H, 4.77; N, 8.11; M , 1035. Found: C, 57.94; H, 4.69; N, 8.80. IR (thf, cm^{-1}): $\nu(BH)$ 2469w, $\nu(CO)$ 1975m, 1902s, 1863s. 1H NMR (C_6D_6): δ 1.50 (s, 15H, Cp^*), 1.79, 2.61 (2m, $2 \times 2H$, CH_2CH_2), 5.65 (s, br, 1H, pz- C^3H), 5.85 [t, $^3J_{HH} = 2.4$ Hz, 2H, pz-CH], 6.93–7.85 (m, 26H, Ph). ^{31}P NMR (C_6D_6): δ 79.38 (s, 2P, dppe). ^{13}C NMR (C_6D_6): δ 9.98 (s, C_5Me_5), 29.78 (m, CH_2CH_2), 94.70 (s, C_5Me_5), 104.91/105.10, 136.13/136.46, 143.46/144.32 ($6 \times s$, pz-ring C), 127.58–137.95 (m, Ph), 230.63 (s, CO). ES MS (m/z): 1036, $[M + H]^+$; 1058, $[M + Na]^+$.

4.3.10. $\{Tp(OC)_2W\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**11**)

Similarly, the reaction between $W(\equiv CC\equiv CSiMe_3)(CO)_2Tp$ (34 mg, 0.06 mmol) and $RuCl(dppe)Cp^*$ (40 mg, 0.06 mmol) and KF (3.5 mg, 0.06 mmol) in methanol at 0 °C gave $\{Tp(OC)_2W\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**11**), obtained as an orange solid (24 mg, 31%). Anal. Calc. ($C_{50}H_{49}BN_6O_2P_2RuW$): C, 53.37; H, 4.39; N, 7.47; M , 1124. Found: C, 53.23; H, 4.28; N, 7.31. IR (thf, cm^{-1}): $\nu(BH)$ 2478w, $\nu(CC)$ 1976m, $\nu(CO)$ 1900s, 1849s. 1H NMR (C_6D_6): δ 1.55 (s, 15H, Cp^*), 1.85, 2.73 (2m, $2 \times 2H$, CH_2CH_2), 5.60 (s, br, 1H, pz- C_4H), 5.82 (s, br, 2H, pz- C_4H), 6.90–7.92 (m, 26H, Ph). ^{31}P NMR (C_6D_6): δ 78.87 (s, 2P, dppe). ^{13}C NMR (C_6D_6): δ 10.41 (s, C_5Me_5), 30.79 (m, CH_2CH_2), 94.90 (s, C_5Me_5), 105.94/106.04, 134.84/135.15, 145.40/145.51 ($6 \times s$, pz-ring C), 129.95–141.03 (m, Ph), 228.46 (s, CO). ES MS (positive ion, MeOH + NaOMe, m/z): 1146, $[M - H + Na]^+$; 1124, $[M + H]^+$; 635, $[Ru(dppe)Cp^*]^+$.

4.3.11. $\{Tp^*(OC)_2Mo\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**12**)

Similarly, from $RuCl(dppe)Cp^*$ (36 mg, 0.05 mmol) and KF (3 mg, 0.05 mmol) was obtained $\{Tp^*(OC)_2Mo\}\equiv CC\equiv C\{Ru(dppe)Cp^*\}$ (**12**) as an orange solid (20 mg, 36%). Anal. Calc. ($C_{56}H_{61}BMoN_6O_2P_2Ru$): C, 60.06; H, 5.49; N, 7.50; M , 1120. Found: C, 58.98; H, 5.33; N, 7.44. IR (thf, cm^{-1}): $\nu(BH)$ 2524w, $\nu(CC)$ 1971w, $\nu(CO)$ 1899s, 1856s. 1H NMR (C_6D_6): δ 1.59 (s, 15H, Cp^*), 1.98, 2.81 (2m, $2 \times 2H$, CH_2CH_2), 2.18, 2.63 ($2 \times s$, $2 \times 3H$, Me), 2.24, 2.69 ($2 \times s$, $2 \times 6H$, Me), 5.46 (s, 1H, H^3), 5.65 (s, 2H, H^3), 6.93–7.87 (m, 20H, Ph). ^{31}P NMR

Table 3
Crystal data and refinement details

	Complex 1	Complex 2	Complex 7	Complex 8	Complex 9	Complex 12
Formula	C ₁₆ H ₂₅ F ₃ MoN ₂ O ₂ Si	C ₁₇ H ₁₉ BMoN ₆ O ₂ Si · 0.167CH ₂ Cl ₂	C ₄₇ H ₃₂ BCo ₃ MoN ₆ O ₉ P ₂ · 0.5CH ₂ Cl ₂	C ₄₇ H ₃₂ BCo ₃ N ₆ O ₉ P ₂ W	C ₅₅ H ₄₄ BCo ₃ MoN ₆ O ₉ P ₂ · 2CHCl ₃	C ₅₆ H ₆₁ BMoN ₆ O ₂ P ₂ Ru · 1.25C ₆ H ₆
<i>M</i> _w	490.46	488.41	1212.77	1258.21	1517.24	1217.56
<i>T</i> (K)	153	153	298	298	298	170
Crystal system	Monoclinic	Trigonal	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> $\bar{3}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	19.350(3)	38.253(4)	26.186(5)	14.792(1)	12.032(1)	17.491(3)
<i>b</i> (Å)	7.601(1)		18.644(3)	17.288(1)	16.335(2)	19.852(3)
<i>c</i> (Å)	15.550(3)	8.2930(8)	25.152(5)	19.467(2)	17.771(2)	20.674(3)
α (°)					100.130(2)	102.608(3)
β (°)	107.736(3)		120.285(3)	99.253(1)	97.087(2)	107.572(3)
γ (°)					105.095(2)	113.062(3)
<i>V</i> (Å ³)	2176	10509	10604	4913	3267	5815
ρ_c (g cm ⁻³)	1.49 ₇	1.38 ₉	1.51 ₉	1.70 ₁	1.54 ₂	1.39 ₁
<i>Z</i>	4	18	8	4	2	4
2 θ _{max} (°)	53	50	50	50	58	50
μ (Mo K α) (mm ⁻¹)	0.71	0.67	1.32	3.45	1.29	0.58
<i>T</i> _{min/max}	0.75	0.86	0.70	0.77	0.87	0.91
Crystal dimensions (mm ³)	0.32 × 0.11 × 0.09	0.08 × 0.08 × 0.05	0.30 × 0.23 × 0.14	0.23 × 0.21 × 0.19	0.56 × 0.28 × 0.08	0.50 × 0.12 × 0.12
<i>N</i> _{tot}	20104	25070	38640	45371	30189	41379
<i>N</i> (<i>R</i> _{int})	4447 (0.046)	4087 (0.12)	8879 (0.076)	8616	15579 (0.038)	18752 (0.049)
<i>N</i> ₀	3853	2674	5214	6784	10071	13468
<i>R</i>	0.071	0.059	0.071	0.043	0.097	0.083
<i>R</i> _w	0.117	0.073	0.094	0.088	0.16	0.161

(C₆D₆): δ 78.44 (s, 2P, dppe). ¹³C NMR (C₆D₆): δ 10.67 (s, C₅Me₅), 13.30, 15.59, 16.62 (3 × s, pz-C₃Me), 29.78 (m, CH₂CH₂), 56.41 (s, C≡C), 95.07 (s, C₅Me₅), 106.28/106.47, 143.51/143.86, 151.51/151.66 (6 × s, pz-ring C), 123.80–141.57 (m, Ph), 230.95 (s, CO), 254.47 (s, Mo≡C). ES MS (positive ion, MeOH + NaOMe, *m/z*): 1143, [M + Na]⁺; 1121, [M + H]⁺; 667, [Ru(MeOH)(dppe)Cp*]⁺; 635, [Ru(dppe)Cp*]⁺.

4.3.12. {Tp*(OC)₂Mo}≡CC≡CC≡C{Ru(dppe)Cp*} (13)

A mixture of Mo(≡CBr)(CO)₂Tp* (25 mg, 0.046 mmol), Ru{C≡CC≡CAu(PPh₃)}(dppe)Cp* (53 mg, 0.046 mmol), Pd(PPh₃)₄ (10 mg, 0.009 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (10 ml) at r.t. for 1 h. The solvent was then removed and the resulting residue purified by preparative t.l.c. eluting with acetone/hexane (3/7) to obtain {Tp*(OC)₂Mo}≡CC≡CC≡C{Ru(dppe)Cp*} (13) as a red band (*R_f* 0.38) (20 mg, 67%). Anal. Calc. (C₅₈H₆₁BMoN₆O₂P₂Ru·CH₂Cl₂): C, 59.38; H, 5.32; N, 7.04; M (unsolvated), 1144. Found: C, 59.62; H, 5.32; N, 6.90. IR (thf, cm⁻¹): ν (BH) 2484w, ν (CO) 2021s, 1947s, 1881s. ¹H NMR (C₆D₆): δ 1.45 (s, 15H, Cp*), 1.68, 2.32 (2 × m, 2 × 2H, CH₂CH₂), 2.11, 2.43 (2 × s, 2 × 3H, Me), 2.19, 2.75 (2 × s, 2 × 6H, 5Me), 5.30 (CH₂Cl₂), 5.37 (s, 1H, H³), 5.56 (s, 2H, H³), 6.79–7.73 (m, 20H, Ph). ³¹P NMR (C₆D₆): δ 53.66 (CH₂Cl₂), 79.05 (s, 2P, dppe). ¹³C NMR (C₆D₆): δ 10.42 (s, C₅Me₅), 13.03, 15.40, 16.58 (3 × s, 3 × pz-C₃Me), 29.99 (m, CH₂CH₂), 53.66, 92.65 (s, C≡C), 94.87 (s, C₅Me₅), 106.62/106.67, 143.80/144.38, 151.64/152.08 (6 × s, pz-ring C), 128.08–148.65 (m, Ph), 230.29 (s, CO), 260.85 (s, Mo≡C). ES MS (*m/z*): 635, [Ru(dppe)Cp*]⁺; 676, [Ru(MeCN)(dppe)Cp*]⁺; 1167, [M + Na]⁺.

4.3.13. {Tp*(CO)₂Mo}≡C(C≡C)₃{Ru(dppe)Cp*} (14)

A mixture of Mo(≡CBr)(CO)₂Tp* (23 mg, 0.04 mmol), Ru{(C≡C)₃Au(PPh₃)}(dppe)Cp* (50 mg, 0.04 mmol), Pd(PPh₃)₄ (10 mg, 0.009 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (10 ml) at r.t. for 1 h. The solvent was then removed and the resulting residue purified by preparative t.l.c. eluting with acetone/hexane (3/7) to obtain {Tp*(OC)₂Mo}≡C(C≡C)₃{Ru(dppe)Cp*} (14) as a mauve band (*R_f* 0.33) (23 mg, 49%). Anal. Calc. (C₆₀H₆₁BMoN₆O₂P₂Ru·CH₂Cl₂): C, 58.48; H, 5.07; N, 6.71; M (unsolvated), 1112. Found: C, 59.06; H, 5.01; N, 6.38. IR (thf, cm⁻¹): ν (C≡C) 2116w, 2069w, 2010w, ν (CO) 1990m, 1916m, 1868s. ¹H NMR (C₆D₆): δ 1.43 (s, 15H, Cp*), 1.72, 2.34 (2m, 2 × 2H, CH₂CH₂), 2.01, 2.23 (2 × s, 2 × 3H, Me), 2.10, 2.53 (2 × s, 2 × 6H, Me), 5.29 (s, 1H, H³), 5.51 (s, 2H, H³), 6.98–7.62 (m, 20H, Ph). ³¹P NMR (C₆D₆): δ 78.88 (s, 2P, dppe). ¹³C NMR (C₆D₆): δ 10.55 (s, C₅Me₅), 13.06, 14.72, 16.44 (3 × s, 3 × pz-C₃Me), 28.54 (m, CH₂CH₂), 72.60, 78.20, 87.43 (s, C≡C), 95.30 (s, C₅Me₅), 107.17, 144.00/145.65, 151.77/152.03 (5 × s, pz-ring C), 127.95–170.80 (m, Ph), 227.55 (s, CO). ES MS (positive ion, MeOH + NaOMe, *m/z*): 1191, [M + Na]⁺.

4.4. Structure determinations

Full spheres of diffraction data were measured using a Bruker AXS CCD area-detector instrument. *N*_{tot} reflections were merged to *N* unique (*R*_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), *N*₀ with *F* > 4σ(*F*) being used in the full matrix least squares refinements. All data were measured using monochromatic Mo Kα radiation, λ = 0.71073 Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being constrained at estimated values. Conventional residuals *R*, *R*_w are quoted at convergence Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [27]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% (low temperature determinations) or 20% probability amplitude displacement ellipsoids (r.t. determinations) and hydrogen atoms with arbitrary radii of 0.1 Å) and Tables 1 and 3.

4.5. Variata

Complex 1. Rotational disorder is evident for the CF₃ and SiMe₃ groups, each over two sets of sites, the latter also entailing displacement of the C₃ string; site occupancies of each component were set at 0.5 after trial refinement. The disordered CF₃ groups lie about the *bc* face of the cell, the SiMe₃ groups about *x* = 0.5. Refinement was on |*F*|, reflection weights being [σ²(*F*) + 0.004*F*²]⁻¹.

Complex 2. Difference map residues were modelled in terms of disordered CH₂Cl₂ of solvation. The crystal packing is of interest, the quasi-3 axis of the molecule being aligned parallel to crystallographic *c*. Refinement was on |*F*|, reflection weights being [σ²(*F*) + 0.002*F*²]⁻¹.

Complex 7. Difference map residues were modelled in terms of CH₂Cl₂ of solvation, disordered about an inversion centre; the CO groups around Co(3) are also disordered (site occupancies 0.5).

Complex 8. Refinement was on *F*², reflection weights being [σ²(*F*² + 60*F*²)]⁻¹.

Complex 9. Displacement amplitudes of the CHCl₃ were very high but disorder was not resolvable. Refinement was on *F*², reflection weights being [σ²(*F*²) + 2*F*²]⁻¹.

Complex 12. Weak and limited data would support meaningful anisotropic displacement parameter refinement for Ru, Mo, P only. Refinement was on *F*², reflection weights being [σ²(*F*²) + 10.2*F*²]⁻¹.

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Appendix A. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 293398–293402 (**1**, **2**, **7**, **9**, **12**) and 612585 (**8**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.043.

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