

# Some complexes containing carbon chains end-capped with tungsten or ruthenium groups and tricobalt carbonyl clusters

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## Abstract

The Pd(0)/Cu(I)-catalysed reactions between  $\text{Co}_3(\mu_3\text{-CBr})(\text{CO})_9$  and  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$  gives the  $\text{C}_5$  complex  $\{\text{Cp}(\text{OC})_3\text{W}\}-\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\text{CO})_9\}$  (**2**). Similarly,  $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$  and  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$  or  $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$  give  $\{\text{Cp}(\text{OC})_3\text{W}\}-\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$  and  $\{\text{Cp}^*(\text{dppe})\text{Ru}\}-\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$  (**5**). An attempt to prepare a  $\text{C}_3$  analogue from  $\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$  and  $\text{Co}_3(\mu_3\text{-CBr})(\text{CO})_9$  gave instead the acyl derivative  $\{\text{Cp}(\text{Ph}_3\text{P})_2\text{Ru}\}-\text{C}\equiv\text{CC}(\text{O})-\text{C}\{\text{Co}_3(\text{CO})_8(\text{PPh}_3)\}$  (**7**). The X-ray structures of **2**, **5** and **7** are reported: the  $\text{C}_5$  chains in **2** and **5** have an essentially unperturbed  $-\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv$  formulation.

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## 1. Introduction

Current interest in the synthesis and properties of molecules containing carbon chains end-capped by transition metals is driven by their potential as models for molecular-scale wires in which electron/hole transfer between redox-active groups occurs via the chain [1,2]. These materials may then be used as components of a variety of electronic devices [3–6]. Reported examples of complexes of this type are dominated by systems containing even-numbered  $\text{C}_n$  bridges, largely as a result of the synthetic methods employed, which depend upon the use of ethynyl or poly-ynyl synthons [1]. Considering possible valence representations of the  $\text{M}-\text{C}_n-\text{M}$  bridge, three have been described (neglecting radical-based formulations), namely **A**, **B** and **C** in Chart 1. These materials are often obtained when mono- or poly-acetylenic

synthons are used. In the odd-numbered series, two representations **D** and **E** may be drawn, with either one (in **D**) or two (in **E**) metal–carbon multiple bonds. Syntheses of these molecules requires either that modification of an existing  $\text{M}-\text{C}$  single bond occur, or that a precursor containing either  $\text{M}=\text{C}$  double or  $\text{M}\equiv\text{C}$  triple bond be used.

A few examples containing  $\text{C}_3$  and  $\text{C}_5$  systems have been described. These include the dianion  $[\{\text{Tp}^*(\text{OC})_2\text{W}\}-\text{C}=\text{C}=\text{C}=\{\text{M}(\text{CO})_2\text{Tp}^*\}]^{2-}$  [ $\text{M}=\text{Mo}$ ,  $\text{W}$ ;  $\text{Tp}^* = \text{HB}(\text{dmpz})_3$ ], formed by attack of the anionic vinylidene  $[\text{M}(\text{C}=\text{CH}_2)(\text{CO})_2\text{Tp}^*]^-$  on  $\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{Tp}^*$ , followed by deprotonation of the resulting  $\text{Tp}^*(\text{OC})_2\text{M}\equiv\text{CCH}_2\text{C}\equiv\text{Mo}(\text{CO})_2\text{Tp}^*$  [7]; the heterometallic dianion can be oxidised to a mixture of  $\text{Tp}^*(\text{OC})_2\text{M}\equiv\text{CC}\equiv\text{CM}'(\text{O})_2\text{Tp}^*$  ( $\text{M}, \text{M}' = \text{Mo}, \text{W}$  and  $\text{W}, \text{Mo}$ ). The complex  $\{\text{Cp}^*(\text{Ph}_3\text{P})(\text{NO})\text{Re}\}(\text{C}\equiv\text{C})_n\text{C}\equiv\{\text{Mn}(\text{CO})_2\text{Cp}'\}$  ( $\text{Cp}' = \text{Cp}, \eta\text{-C}_5\text{H}_4\text{Cl}, \eta\text{-C}_5\text{Cl}_5; n = 1, 2$ ) is obtained from  $\text{Mn}(\text{CO})_3\text{Cp}'$  and  $\text{Li}(\text{C}\equiv\text{C})_n\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*$ , followed by treatment with  $[\text{OMe}_3]\text{BF}_4$  [8]. Complexes containing metal

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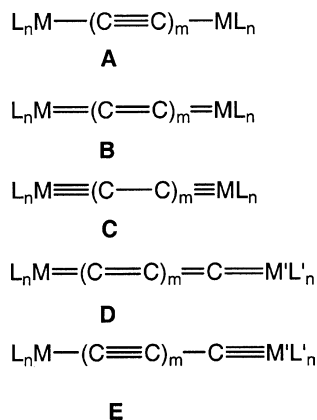


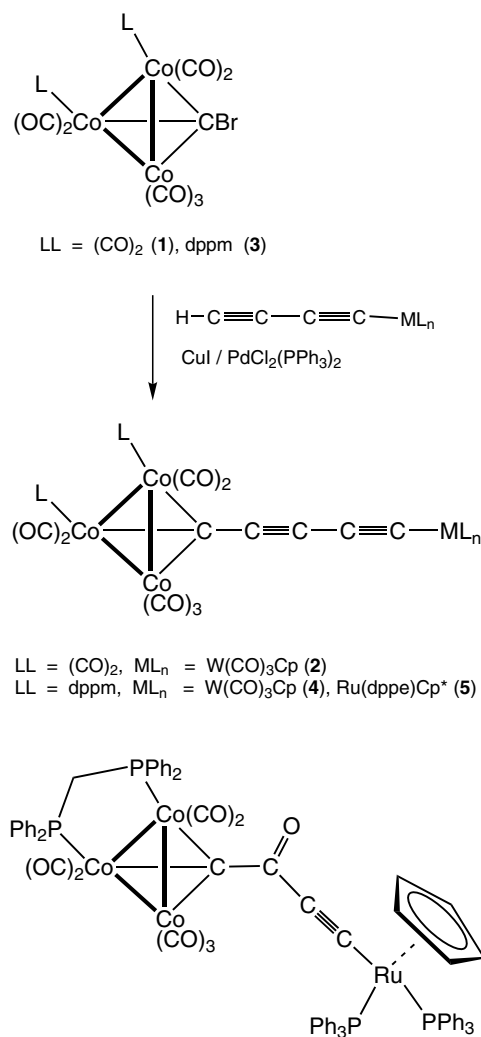
Chart 1.

clusters at one or both ends of a C<sub>3</sub> chain are exemplified by Os<sub>3</sub>{μ<sub>3</sub>-C<sub>2</sub>C[Re(NO)(PPh<sub>3</sub>)Cp\*]}(μ-OMe)(CO)<sub>10</sub> [9].

We have recently described the syntheses of a variety of complexes containing carbon chains of various lengths by elimination of phosphine-gold(I) halides in reactions between halogen-C(sp) or -C(sp<sup>2</sup>) bonds with alkynyl- or poly-ynyl-gold(I) phosphine complexes [10]. Among these were several cobalt cluster derivatives containing C<sub>5</sub> chains, including Co<sub>3</sub>(μ<sub>3</sub>-CC<sub>4</sub>R)(μ-dppm)(CO)<sub>7</sub> [R = Fc, Au(PPh<sub>3</sub>), W(CO)<sub>3</sub>Cp] [11]. In our search for routes to compounds containing odd-numbered carbon chains, we had earlier explored the coupling reaction between Co<sub>3</sub>(μ<sub>3</sub>-CBr)(CO)<sub>9</sub> and diyne-metal complexes carried out under the normal Cadot-Chodzkiwicz conditions [secondary amine, CuI/Pd(0)]. This paper describes three complexes containing C<sub>5</sub> chains end-capped by tungsten or ruthenium groups. However, as described elsewhere [12], the major products were formed by attack of the secondary amine on a cobalt cluster precursor, probably via an intermediate such as [Co<sub>3</sub>(μ<sub>3</sub>-CCO)(CO)<sub>9</sub>]<sup>+</sup>. This intermediate is probably the source of Co<sub>3</sub>{μ<sub>3</sub>-CC(O)C≡C[Ru-(PPh<sub>3</sub>)<sub>2</sub>Cp]}(CO)<sub>8</sub>(PPh<sub>3</sub>) which is also described below.

## 2. Results and discussion

Although the gold-halide elimination reaction has proved to be the methodology of choice for this type of complex, we had also pursued the original reaction as a possible alternative source and were gratified to find that use of a tertiary amine allowed access to the desired products, albeit in low yield. For example, the reaction between W(C≡CC≡CH)(CO)<sub>3</sub>Cp and Co<sub>3</sub>(μ<sub>3</sub>-CBr)(CO)<sub>9</sub> (1) in NEt<sub>3</sub> afforded the bright red complex {Cp(OC)<sub>3</sub>W}C≡CC≡CC{Co<sub>3</sub>(CO)<sub>9</sub>} (2) in 16% yield (Scheme 1). This complex, which is somewhat unstable, especially in solution, has been identified by elemental analysis, and from its IR spectra [five bands between



Scheme 1.

2100 and 1958 cm<sup>-1</sup> which approximates to a superposition of the ν(CC) and ν(CO) spectra of the reaction components], a Cp singlet at δ 5.69 in the <sup>1</sup>H NMR spectrum, and a molecular ion in the ES mass spectrum at *m/z* 820. X-ray quality crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane and the structure of a molecule of 2 is shown in Fig. 1.

The molecule of 2 consists of a W(CO)<sub>3</sub>Cp group linked to a Co<sub>3</sub>(CO)<sub>9</sub> cluster by a five-carbon chain, which is σ-bonded to tungsten and attached by C(5) to the three cobalt atoms. Consequently, it can also be considered to be another example of the well-known CCo<sub>3</sub> clusters now bearing a buta-1,3-diyndiyl-tungsten (C<sub>4</sub>-W) group. Structural parameters are similar to those found in previous examples of these two systems, with the W-C(1) bond [2.131(3) Å] similar to that found in W(C≡CC≡CFc)(CO)<sub>3</sub>Cp [2.12(2) Å] [13], for example, and the Co(2-4)-C(5) separations [1.918–1.926(5) Å] similar to those found in Co<sub>3</sub>{μ<sub>3</sub>-C(C≡C)<sub>2</sub>SiMe<sub>3</sub>}(CO)<sub>9</sub> [1.908–1.914(6) Å] [14]. Of interest are the dimensions of

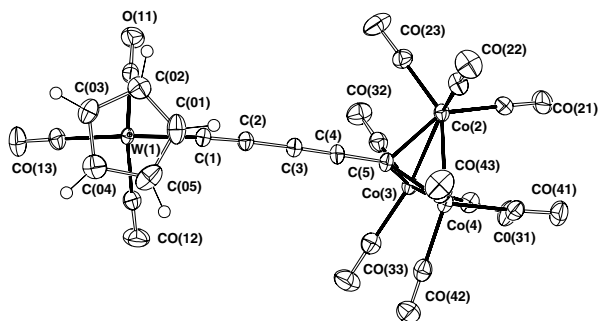


Fig. 1. Plot of a molecule of  $\{\text{Cp}(\text{OC})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\text{CO})_9\}$  (**2**).

the  $\text{C}_5$  chain. The C–C separations have a short–long–short–long pattern [1.211, 1.365, 1.228 and 1.385(5) Å], again similar to those in  $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_2\text{SiMe}_3\}(\text{CO})_9$  [1.212, 1.376, 1.183 and 1.367(8) Å] and consistent with an unperturbed  $\text{-C}\equiv\text{C}\text{-C}\equiv\text{C}\text{-C}\equiv$  formulation. In **2**, bending at individual carbon atoms decreases along the chain from C(1) [176.1(4)°] to C(4) [179.1(4)°].

In an effort to stabilise the cobalt cluster, we have prepared the dppm derivative of the bromo-carbyne precursor,  $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$  (**3**), from the reaction between **1** and dppm in the presence of  $\text{Me}_3\text{NO}$  [12]. Black crystals of **3** were obtained in 61% yield and characterised by elemental analyses, and its IR [ $\nu(\text{CO})$  between 2065 and 1974  $\text{cm}^{-1}$ ],  $^1\text{H}$  NMR [ $\delta$  3.30, 4.49 ( $\text{CH}_2$ ), 7.02–7.51 (Ph)] and  $^{31}\text{P}$  NMR spectra ( $\delta$  32.3). As with **2**, the  $^{13}\text{C}$  NMR resonances for the chain carbons have not yet been observed: that for the  $\text{Co}_3\text{C}$  nucleus is usually broadened as a result of the  $^{59}\text{Co}$  quadrupole, while the instability of **2** in solution has precluded observation of the resonances of the carbon chain. An X-ray structural study of **3** has confirmed the structure with the dppm bridging one of the basal Co–Co vectors [12].

The reaction between **3** and  $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{-Cp}$ , also carried out in  $\text{NEt}_3$ , afforded  $\{\text{Cp}(\text{OC})_3\text{-W}\}\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_9\}$  (**4**), identical in all respects with the product obtained from the reaction between **3** and  $\text{W}\{\text{C}\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)\}_2(\text{CO})_3\text{Cp}$  which has been described earlier [11].

Extension of the reaction to that between **3** and  $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$  [15] afforded dark red crystalline  $\{\text{Cp}^*(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$  (**5**), obtained in 39% yield, along with  $\text{Co}_3\{\mu_3\text{-CC}(\text{O})\text{-NEt}_2\}(\mu\text{-dppm})(\text{CO})_7$  (**6**) which has been described elsewhere [12]. Complex **5** was characterised from its X-ray structure (Fig. 2) which clearly showed the  $\text{C}_5$  chain linking the two metal–ligand end-caps. The  $\text{C}(n) - \text{C}(n + 1)$  ( $n = 1\text{--}4$ ) separations [1.225, 1.361, 1.224 and 1.392(5) Å] indicate that the alternating  $\text{C}\equiv\text{C}$  and  $\text{C}\text{-C}$  bonds are preserved in the chain, while angles at C(1–4) are 172.3(4)°, 177.8(6)°, 178.5(6)° and 177.2(5)°. The geometries of the end-caps are similar

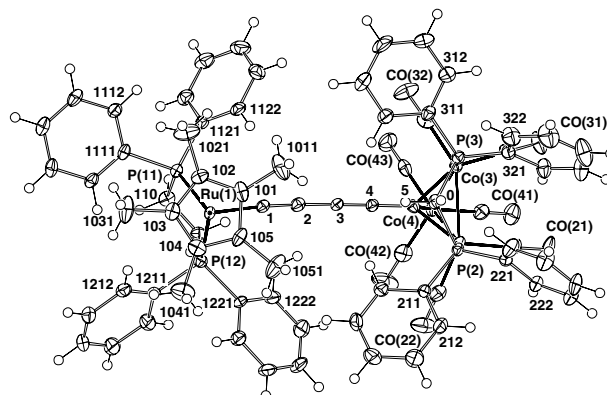


Fig. 2. Plot of a molecule of  $\{\text{Cp}^*(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}$  (**5**).

to those found in many other of their derivatives. Thus, Ru–P, Ru–C( $\text{Cp}^*$ ) and Ru–C(1) distances of 2.278(1), 2.26(2) (av.) and 1.976(4) Å are measured, with corresponding bond angles P(1)–Ru–P(2) and P(1,2)–Ru–C(1) of 83.16(5)°, 91.1° and 80.1(1)°, respectively. Within the  $\text{Co}_3$  cluster, Co–Co distances are between 2.484 and 2.491(1) Å, with Co–P separations of 2.196 and 2.205(1) Å. The three Co–C(5) distances are between 1.898 and 1.952(5) Å, the longest being to Co(4) which is not attached to the dppm ligand.

In an attempt to obtain a similar complex containing a  $\text{C}_3$  bridge, the reaction between  $\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$  [16] and  $\text{Co}_3(\mu_3\text{-CBr})(\text{CO})_9$  was examined under similar conditions. A low yield (17%) of brown  $\text{Co}_3\{\mu_3\text{-CC}(\text{O})\text{C}\equiv\text{C}[\text{Ru}(\text{PPh}_3)_2\text{Cp}]\}(\text{CO})_8(\text{PPh}_3)$  (**7**) was obtained. The spectroscopic properties of **7** were in accord with the solid-state structure determined from a single-crystal X-ray study. Only terminal  $\nu(\text{CO})$  bands were found between 2078 and 1966  $\text{cm}^{-1}$  for the Co–CO groups; no absorption assignable to the ketonic CO group in the chain was found. The  $^1\text{H}$  NMR spectrum contained resonances at C:  $\delta$  4.31 (Cp) and between 7.20 and 7.53 (Ph), while the  $^{31}\text{P}$  NMR spectrum contained two resonances for the  $\text{PPh}_3$  ligands at  $\delta$  37.1 and 50.4 in a 1:2 intensity ratio, assigned to these ligands on Co and Ru, respectively. The ES – MS was obtained from solutions containing NaOMe and showed  $[\text{M} + \text{Na}]^+$  and  $[\text{M} + \text{OMe}]^-$  ions.

The molecular structure (Fig. 3) consists of a  $\text{C}_4\text{O}$  chain linking  $\text{Ru}(\text{PPh}_3)_2\text{Cp}$  and  $\text{Co}_3(\text{CO})_8(\text{PPh}_3)$  end-caps. This novel feature is characterised by Ru–C(1) and Co–C(4) distances of 1.977(3) and 1.886–1.924(3) Å, the longest of the latter involving Co(3). The  $\text{C}(n) - \text{C}(n + 1)$  separations along the non-linear chain are 1.235, 1.412 and 1.476(4) Å, with angles at C(1–3) of 177.8°, 168.7° and 117.9(3)°. The  $\text{sp}^2$  hybridisation of C(3), which is also attached to O(3) [C(3)–O(3), 1.248(4) Å], is also confirmed by the other angles [C(2,4)–C(3)–O(3) 121.4°, 120.7(3)°; sum 360.0°].

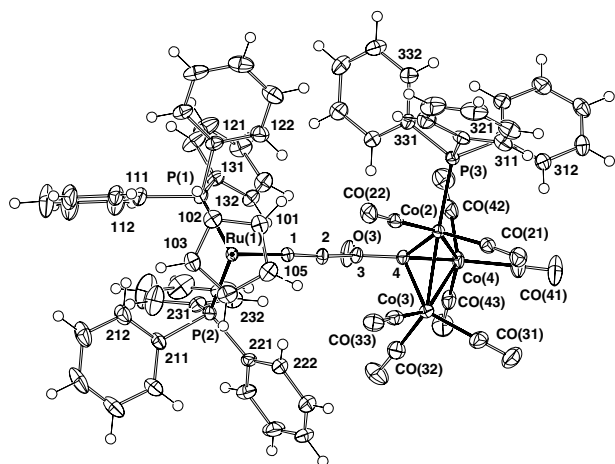


Fig. 3. Plot of a molecule of  $\{Cp(Ph_3P)_2Ru\}C\equiv CC(O)C\{Co_3(\mu-dppm)(CO)_7\}$  (**7**).

Formation of the ketonic bridge is probably related to reactions which have afforded amido complexes in reactions of  $Co_3C$  clusters carried out in the presence of amines or other bases [17]. Partial deprotonation of the ruthenium reagent to form the alkynyl anion is followed by attack on  $[Co_3(CCO)(CO)_9]^+$  present in the reaction mixture. The species CCCC $O$  has been obtained in gas-phase ion–molecule studies [18], but this is the first example of a metal complex stabilising this entity. The nearest congener is the CCCC $O$  ligand present in  $Cr(CCCC(O)CO)_5$  [19].

In conclusion, we have demonstrated that it is possible to obtain novel carbon chain complexes by the conventional coupling of alkynes with tricobalt–halocarbyne cluster complexes, although the yields are low and other products form in competitive reactions involving the amine solvents.

### 3. Experimental

#### 3.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

#### 3.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in  $CH_2Cl_2$  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 Bruker AM300WB or ACP300 ( $^1H$  at 300.13 MHz,  $^{13}C$  at 75.47 MHz,  $^{31}P$  at 121.503 MHz)

instruments. Samples were dissolved in  $CDCl_3$ , unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for  $^1H$  and  $^{13}C$  NMR spectra and external  $H_3PO_4$  for  $^{31}P$  NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [20]. Elemental analyses were performed at CMAS, Belmont, Australia.

#### 3.3. Reagents

The compounds  $W(C\equiv CC\equiv CH)(CO)_3Cp$  [21],  $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$  [15],  $Ru(C\equiv CH)(PPh_3)_2Cp$  [16],  $Co_3(\mu_3-CBr)(CO)_9$  [22] and  $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$  [12] were made by the cited methods.

#### 3.4. $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(CO)_9\}$ (**2**)

$W(C\equiv CC\equiv CH)(CO)_3Cp$  (49 mg, 0.13 mmol), **1** (100 mg, 0.19 mmol),  $PdCl_2(PPh_3)_2$  (18 mg, 0.26 mol) and  $CuI$  (5 mg) were added sequentially to a Schlenk tube containing degassed  $NEt_3$  (20 ml). After 2 h at r.t., removal of solvent and preparative TLC of the residue (silica gel, acetone/hexane: 1/4) afforded  $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(CO)_9\}$  (**2**) (17 mg, 16%) from the major band of several which developed. Anal. Calc. ( $C_{22}H_5Co_3O_{12}W$ ): C, 32.15; H, 0.61;  $M$ , 820. Found: C, 32.64; H, 0.52%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2100m, 2077m, 2055vs, 2039vs, 1958s (br)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.69 (s, 5H, Cp). ES – MS (negative ion, NaOMe added,  $m/z$ ): 851,  $[M + OMe]^-$ ; 820,  $M^-$ .

#### 3.5. $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(\mu-dppm)(CO)_7\}$ (**4**)

$NEt_3$  (20 ml) was added to a mixture of  $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$  (100 mg, 0.12 mmol),  $W(C\equiv CC\equiv CH)(CO)_3Cp$  (46 mg, 0.12 mmol),  $Pd(PPh_3)_4$  (14 mg, 0.012 mmol) and  $CuI$  (3 mg, 0.015 mmol) and the suspension was stirred overnight at r.t. The brown precipitate which formed was filtered off, washed with hexane and crystallised ( $CH_2Cl_2$ /hexane) to give small red crystals of  $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(\mu-dppm)(CO)_7\}$  (**4**) (94 mg, 69%). X-ray quality crystals were obtained from chloroform. Anal. Found: C, 45.30; H, 1.97. Calc. ( $C_{45}H_{27}Co_3O_{10}P_2W \cdot 0.5CH_2Cl_2$ ): C, 45.12; H, 2.27;  $M$ , 1150. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2058s, 2037m, 2008vs, 1955m (br)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  3.36, 4.43 ( $2 \times m$ ,  $2 \times 1H$ ,  $CH_2$ ), 5.71 (s, 5H, Cp), 7.09–7.47 (m, 20H, Ph).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  39.13 [s (br),  $CH_2$ ], 53.48, 96.01, 114.03 ( $3 \times s$ , C5 chain), 91.91 (s, Cp), 128.01–132.11 (m, Ph), 210.19 (s, CO).  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  33.57 (s, 2P, dppm), 49.42 (s, 2P,  $PPh_3$ ). ES – MS (positive ion, MeOH + NaOMe,  $m/z$ ): 1173,  $[M + Na]^+$ ; 1145,  $[+Na - CO]^+$ ; 1117,

$[M + Na - 2CO]^+$ ; (negative ion, MeOH): 1150,  $M^-$ . Concentration of the mother liquor and separation by preparative TLC (silica gel, hexane/acetone: 7/3) afforded a brown band ( $R_f$  0.42) containing **4** (1.7 mg, total yield 70.5%), together with minor fractions appearing a several multi-coloured bands ( $R_f$  0.52, 0.48, 0.29) which were not further investigated.

### 3.6. Reaction between $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ and $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$

A mixture of  $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$  (42.5 mg, 0.05 mmol),  $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$  (34.1 mg, 0.05 mmol),  $Pd(PPh_3)_4$  (6 mg, 0.005 mmol) and  $CuI$  (2 mg, 0.01 mmol) in  $NEt_3$  (15 ml) was stirred at r.t. overnight to give a brown solution containing a dark coloured precipitate. Removal of solvent and separation of a dichloromethane extract by preparative TLC (silica gel, hexane/acetone: 4/1) gave several bands. Of these, a

red-brown fraction ( $R_f$  0.33) contained  $\{Cp^*(dppe)-Ru\}C\equiv CC\equiv CC\{Co_3(\mu-dppm)(CO)_7\}$  (**5**) (28 mg, 39%; very dark red crystals from toluene/MeOH). Anal. Found: C, 60.25; H, 4.17. Calc. ( $C_{73}H_{61}Co_3O_7P_4Ru$ ): C, 60.38; H, 4.23;  $M$ , 1452. IR (cyclohexane):  $\nu(CO)$  2062w, 2044m, 2009s, 2003vs, 1989 (sh), 1976w, 1968vw, 1952vw  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.59 (s, 15H,  $C_5Me_5$ ), 2.03, 2.69 (2  $\times$  m, 4H,  $CH_2$ -dppe), 3.21, 4.52 (2  $\times$  m, 2H,  $CH_2$ -dppm), 7.03–7.70 (m, 40H, Ph).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  10.13 (s,  $C_5Me_5$ ), 29.69 [s (br),  $CH_2$ -dppe], 38.38 [s (br),  $CH_2$ -dppm], 86.08, 96.09, 109.60, 137.61 ( $C_5$  chain), 93.64 (s,  $C_5Me_5$ ), 127.42–133.38 (m, 40H, Ph), 202.83, 203.35, 210.32 [s (br), CO].  $^{31}P$  NMR ( $CDCl_3$ ):  $\delta$  33.5 (s, 2P, dppm), 79.45 (s, 2P, dppe). ES – MS (positive ion, MeOH,  $m/z$ ): 1452,  $M^+$ ; 1424,  $[M - CO]^+$ ; 1396,  $[M - 2CO]^+$ ; (positive ion, MeOH + NaOMe): 1475,  $[M + Na]^+$ ; (negative ion, MeOH): 1452,  $M^-$ . A dark green band ( $R_f$  0.35) contained  $Co_3\{\mu_3-CC(O)NEt_2\}(\mu-dppm)(CO)_7$  (**6**) [12], while two

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

Compound	<b>2</b>	<b>5</b>	<b>7<sup>a</sup></b>
<i>Bond distances (Å)</i>			
M–C(1)	2.131(3) [W]	1.976(4) [Ru]	1.977(3) [Ru]
C(1)–C(2)	1.211(5)	1.225(5)	1.235(4)
C(2)–C(3)	1.365(5)	1.361(5)	1.412(4)
C(3)–C(4)	1.228(4)	1.224(5)	1.476(4)
C(4)–C(5)	1.385(4)	1.392(5)	
C(5)–Co(2,3,4)	1.926, 1.918, 1.918(3)	1.917, 1.898, 1.952(5)	1.889, 1.924, 1.886(3) [C(4)]
W–CO(13)	2.004(5)		
W–CO(11,12)	2.013, 1.987(5)		
Ru–P(11)		2.278(1)	2.3182(9) [P(1)]
Ru–P(12)		2.279(1)	2.2967(8) [P(2)]
M–C(Cp)	2.313–2.376(5) [W]	2.240–2.279(5) [Ru]	2.236–2.272(3) [Ru]
(av.)	2.34(3)	2.26(2)	2.252(14)
M–C(0) <sub>Cp</sub>	2.003	1.897	1.895
Co(2)–Co(3)	2.4654(9)	2.491(1)	2.4814(6)
Co(2)–Co(4)	2.4668(9)	2.484(1)	2.5014(6)
Co(3)–Co(4)	2.4796(8)	2.488(1)	2.4711(6)
Co(2)–P(2)		2.205(1)	
Co(3)–P(3)		2.196(1)	2.2382(9) [Co(2)]
Co( <i>n</i> )–CO( <i>n</i> 1) (ax) <sup>b</sup>	1.833, 1.828, 1.827(4)	1.791, 1.804, 1.815(4)	1.808, 1.824, 1.823(4)
Co( <i>n</i> )–CO( <i>n</i> 2) (eq) <sup>b</sup>	1.798, 1.807, 1.811(4)	1.772, 1.788, 1.785(6)	1.798, 1.812, 1.801(4)
Co( <i>n</i> )–CO( <i>n</i> 3) (eq) <sup>b</sup>	1.803, 1.806, 1.810(4)	–, –, 1.794(6) [ <i>n</i> = 4]	–, 1.797, 1.800(4)
<i>Bond angles (°)</i>			
X(11)–M–X(12)	108.8(2) [C,W]	83.16(5) [P, Ru]	98.57 [P, Ru]
C(11)–W–C(13)	78.3(2)		
C(12)–W–C(13)	76.8(2)		
X(11)–M–C(1)	74.2(1) [C,W]	91.1(1) [P, Ru]	92.78(9) [P, Ru]
X(12)–M–C(1)	72.5(2) [C,W]	80.1(1) [P, Ru]	85.76(8) [P, Ru]
C(0)–M–P(1,2)	–	130.6, 136.1	121.9, 125.2
M–C(1)–C(2)	176.1(4) [W]	172.3(4) [Ru]	177.8(3) [Ru]
C(1)–C(2)–C(3)	177.1(5)	177.8(6)	168.7(3)
C(2)–C(3)–C(4)	178.3(5)	178.5(6)	117.9(3)
C(3)–C(4)–C(5)	179.1(4)	177.2(5)	
C(4)–C(5)–Co(2,3,4)	129.6, 133.8, 132.6(3)	135.2, 131.4, 128.1(4)	137.9, 120.7, 132.4(2) <sup>a</sup>

Other data: For **2**: C(0)–W–C(11,12,13) 125.6, 125.1, 118.0; C(1)–W–C(13) 128.8(2)°.

For **5**: P(2,3)–C(0) 1.841, 1.832(5) Å; P(2)–C(0)–P(3) 107.8(2)°; For **7**: C(3)–O(3) 1.248(4) Å; C(2)–C(3)–O(3) 121.4(3), C(4)–C(3)–O(3) 120.7(3)°.

<sup>a</sup> For C(4), C(5), read C(3), C(4).

<sup>b</sup> CO(ax) and CO(eq) are, respectively, approximately perpendicular to and coplanar with, the  $Co_3$  plane.

Table 2  
Crystal data and refinement details

Compound	2	5	7
Formula	C <sub>22</sub> H <sub>5</sub> Co <sub>3</sub> O <sub>12</sub> W	C <sub>73</sub> H <sub>61</sub> Co <sub>3</sub> O <sub>7</sub> P <sub>4</sub> Ru · C <sub>7</sub> H <sub>8</sub>	C <sub>71</sub> H <sub>50</sub> Co <sub>3</sub> O <sub>9</sub> P <sub>3</sub> Ru · 1.5CH <sub>2</sub> Cl <sub>2</sub> · MeOH
MW	821.9	1544.2	1577.4
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.965(1)	12.041(3)	12.106(1)
<i>b</i> (Å)	11.777(1)	12.092(3)	15.550(1)
<i>c</i> (Å)	12.056(1)	26.612(6)	19.211(2)
$\alpha$ (°)	113.241(2)	88.545(7)	86.520(2)
$\beta$ (°)	90.312(2)	78.629(7)	80.947(3)
$\gamma$ (°)	116.147(2)	71.108(6)	74.273(2)
<i>V</i> (Å <sup>3</sup> )	1253	3591	3437
<i>Z</i>	2	2	2
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	2.177	1.428	1.524
$\mu$ (cm <sup>-1</sup> )	66	1.03 mm	1.17 mm
Crystal size (mm)	0.18 × 0.15 × 0.13	0.18 × 0.11 × 0.10	0.34 × 0.16 × 0.08
<i>T</i> <sub>min/max</sub>	0.84	0.86	0.88
2 $\theta$ <sub>max</sub> (°)	68.7	58	75
<i>N</i> <sub>tot</sub>	18,987	38,416	39,060
<i>N</i> ( <i>R</i> <sub>int</sub> )	9621 (0.028)	18569 (0.062)	32416 (0.037)
<i>N</i> <sub>o</sub>	8857	11,248	21,469
<i>R</i>	0.030	0.050	0.060
<i>R</i> <sub>w</sub> ( <i>n</i> <sub>w</sub> )	0.041 (4)	0.051 (4)	0.077 (20)

other green bands with *R*<sub>f</sub> 0.28 and 0.15 were not investigated further. Chromatography was accompanied by significant decomposition.

### 3.7. Reaction between Co<sub>3</sub>(μ<sub>3</sub>-CBr)(CO)<sub>9</sub> and Ru(C≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp

A mixture of Co<sub>3</sub>(μ<sub>3</sub>-CBr)(CO)<sub>9</sub> (21 mg, 0.02 mmol), Ru(C≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp (111 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (21 mg, 0.02 mmol) and CuI (3 mg, 0.015 mmol) in thf/NEt<sub>3</sub> (20/5 ml) was stirred at r.t. for 3 h. Removal of solvent and separation of a dichloromethane extract of the residue by preparative TLC (silica gel, hexane/acetone: 4/1) afforded three bands: orange-brown [*R*<sub>f</sub> 0.82; ν(CO) 2083w, 2034vs, 2020s, 2000w, 1990 (sh), 1942m (br) cm<sup>-1</sup>], purple [*R*<sub>f</sub> 0.76; ν(CO) 2056vs, 2037s, 2021w (br), 1987vw cm<sup>-1</sup>] (both unidentified) and brown (*R*<sub>f</sub> 0.63). The latter afforded brown crystals (from CH<sub>2</sub>Cl<sub>2</sub>/MeOH) of {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C≡CC(O)C-{Co<sub>3</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)} (7) (51.7 mg, 17%). Anal. Found: C, 59.71; H, 3.56. Calc. (C<sub>71</sub>H<sub>50</sub>Co<sub>3</sub>O<sub>9</sub>P<sub>3</sub>Ru): C, 60.14; H, 3.55; *M*, 1418. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2078m, 2038s, 2017vs, 1966w (br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.31 (s, 5H, Cp), 7.20–7.53 (m, 45H, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 37.1 (s, 1P, Co-PPh<sub>3</sub>), 50.4 (s, 2P, Ru-PPh<sub>3</sub>). ES – MS (positive ion, MeOH + NaOMe, *m/z*): 1441, [M + Na]<sup>+</sup>; (negative ion, MeOH + NaOMe): 1445, [M + OMe]<sup>-</sup>.

### 3.8. Crystallography

Full spheres of diffraction data were measured at ca 153 K using a Bruker AXS CCD area-detector instru-

ment with monochromatic Mo Kα radiation, λ = 0.71073 Å. *N*<sub>tot</sub> reflections were merged to *N* unique (*R*<sub>int</sub> cited) after “empirical”/multiscan absorption correction (proprietary software), *N*<sub>o</sub> with *F* > 4σ(*F*) being used in the full matrix least squares refinements. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> being constrained at estimated values. Conventional residuals *R*, *R*<sub>w</sub> on |*F*| are given [weights: (σ<sup>2</sup>(*F*) + 0.000*n*<sub>w</sub>*F*<sup>2</sup>)<sup>-1</sup>]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [23]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and Tables 1 and 2.

For 7, difference map residues were modelled in terms of CH<sub>3</sub>OH (H not located), seemingly hydrogen-bonded to O(3) [O(3)···O(40) 2.747(5) Å] and CH<sub>2</sub>Cl<sub>2</sub>, the latter disordered and with site occupancies set at 0.5 after trial refinement.

## 4. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 227368 (2), 250749 (5) and 250750 (7). 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>).

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