Cluster Chemistry. Part 92.[1] Directed Syntheses and Crystal Structures of $[\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2\}\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]\cdot CH_2Cl_2$, $[\{Os_3(CO)_{11}\}(\mu\text{-}PPh_2C_2C_2)\{Co_2Os_3(\mu\text{-}PPh_2)(CO)_{13}\}]$ and $[Co_2Os_3Re\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]\cdot CH_2Cl_2$ *

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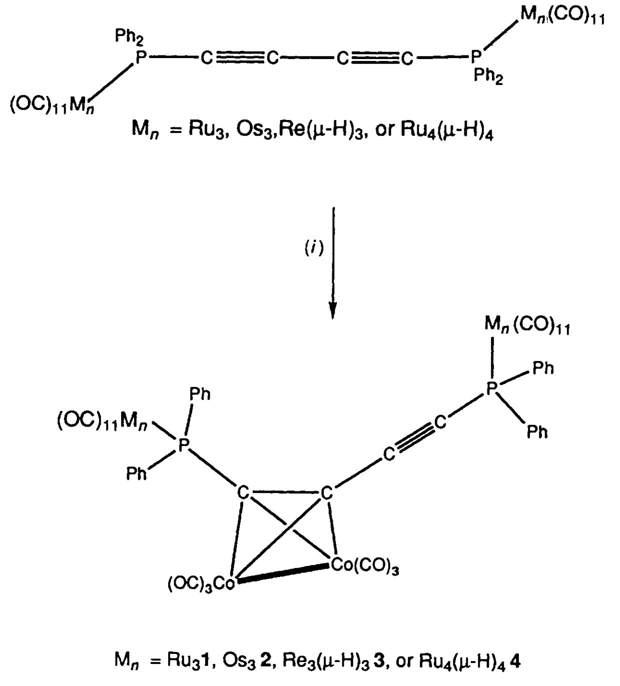
Reactions of $[Co_2(CO)_8]$ with $[\{M_n(CO)_{11}\}_2(\mu\text{-bdpp})]$ [$M_n = Ru_3$, Os_3, $Re_3(\mu\text{-}H)_3$, or $Ru_4(\mu\text{-}H)_4$; bdpp = $PPh_2C_2C_2PPh_2$] afforded $[\{M_n(CO)_{11}\}_2\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}]$ [$M_n = Ru_3$ **1**, Os_3 **2**, $Re_3(\mu\text{-}H)_3$ **3** or $Ru_4(\mu\text{-}H)_4$ **4**] in which the $Co_2(CO)_6$ moiety bonds to one of the C≡C triple bonds of the bridging bdpp ligand. Pyrolysis of **1** yielded $[\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2\}\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **5**, which is formed by concomitant addition of a P–C(sp) bond to one Ru_3 cluster and elimination of a $Ru(CO)_4$ fragment. In $[\{Os_3(CO)_{11}\}(\mu\text{-}PPh_2C_2C_2)\{Co_2Os_3(\mu\text{-}PPh_2)(CO)_{13}\}]$ **8**, obtained by heating **2**, the Co_2Os_3 cluster consists of three edge-sharing triangles; the C_2 fragment interacts with all five metal atoms. Reaction of the mixed-metal complex $[\{Os_3(CO)_{11}\}(\mu\text{-bdpp})\{Re_3(\mu\text{-}H)_3(CO)_{11}\}]$ **10** with $[Co_2(CO)_8]$ yielded a 1:1 isomeric mixture of $[\{Os_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}\{Re_3(\mu\text{-}H)_3(CO)_{11}\}]$ **11a** and $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}\{Os_3(CO)_{11}\}]$ **11b**. Pyrolysis of **11a** afforded $[Co_2Os_3Re\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]$ **12** in which all three transition metals form a cluster about the C_4P fragment of the original bdpp ligand, which has also added one H atom to the carbon adjacent to the PPh_2 group. The second PPh_2 group bridges an Os–Os bond. Molecular structures of **5**, **8** and **12** were determined by X-ray crystallography.

Previous papers have described the synthesis of transition-metal complexes containing the linear bidentate bis(tertiary phosphine) 1,4-bis(diphenylphosphino)buta-1,3-diyne, $PPh_2C_2C_2PPh_2$ (bdpp).[1,2] These complexes have been shown to be sources of the C_4 ligand[2,3] and because of the longer carbon chain can interact with $[Co_2(CO)_6]$ and other transition-metal alkynophiles *via* the acetylenic C≡C bond, a feature not available to derivatives of the analogous monoacetylenic ligand dppa $C_2(PPh_2)_2$.[4] Two objectives of this work have been (*a*) the synthesis of complexes containing the C_4 ligand, produced by cleavage of the P–C(sp) bonds, and (*b*) incorporation of both P- and C≡C-bonded ML_n fragments into polynuclear aggregates held together by the four-carbon unit. The preceding paper[1] has described some successes in the first part of the work: this paper reports the synthesis and characterisation of some cluster complexes containing the bdpp–$Co_2(CO)_6$ ligand and the thermal transformation of some of these to more highly condensed clusters.

Results and Discussion

We have found that cluster complexes of the type $[\{M_n(CO)_{11}\}_2(\mu\text{-bdpp})]$ [$M_n = Ru_3, Os_3, Re_3(\mu\text{-}H)_3$ or $Ru_4(\mu\text{-}H)_4$] react readily with $[Co_2(CO)_8]$ under mild conditions (ether solvents, room temperature, overnight) to give 85–95% yields of the corresponding derivatives containing a $Co_2(CO)_6$ moiety attached to one of the C≡C triple bonds, namely the complexes $[\{M_n(CO)_{11}\}_2\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}]$ [$M_n = Ru_3$ **1**, Os_3 **2**, $Re_3(\mu\text{-}H)_3$ **3** or $Ru_4(\mu\text{-}H)_4$ **4**] (Scheme 1). As expected, all these novel compounds were obtained as black microcrystalline powders and were characterised by a combination of elemental analysis and spectroscopic methods, the most useful (but not



Scheme 1 (*i*) $[Co_2(CO)_8]$

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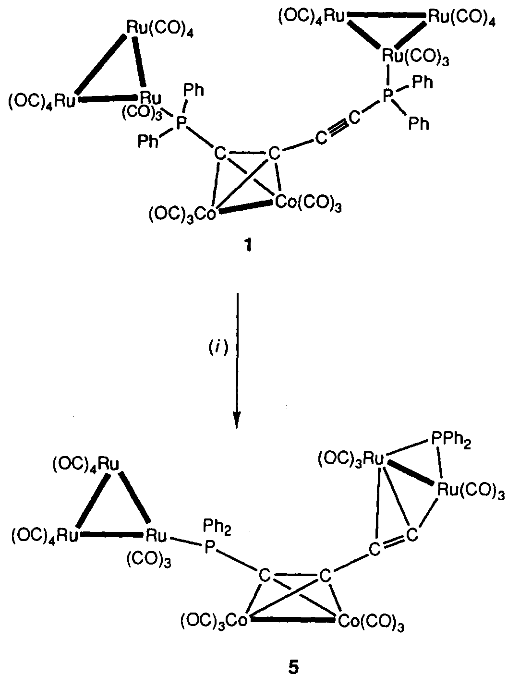
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

solely definitive) being FAB mass spectrometry. Molecular ions were found for all except **3**, which had $[M - 3CO]^+$ as highest mass ion at *m*/*z* 2360. The IR ν(CO) spectra contained a multitude of bands in the terminal CO region which were not particularly diagnostic for structural determinations, but which nevertheless approximated to a superposition of the bands of the precursor complexes and those associated with the $Co_2(CO)_6$ fragment.

A minor product isolated in 5% yield from the reaction between the Ru_3 precursor and $[Co_2(CO)_8]$ was prepared in larger amount by heating a solution of **1** in cyclohexane (80 °C, 1 h) (Scheme 2). Preparative TLC separated the reaction product into bands containing $[Ru_3(CO)_{12}]$ (37%) and a brown pentanuclear complex subsequently identified by an X-ray diffraction study as $[\{Ru_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2\}\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **5**, isolated in 56% yield.



Scheme 2 (*i*) Heat

Molecular Structure of Complex **5**.—The molecular structure of complex **5**, characterised as a dichloromethane solvate, is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. There is evidence of disorder, in particular associated with the Ru_3 triangle and hence with the CO positions. Nevertheless the stoichiometry of the complex has been determined unambiguously. The molecule consists of an $Ru_3(CO)_{11}(PPh_2R)$ unit, where R is a C_4 moiety attached to $Co_2(CO)_6$ and $Ru_2(\mu\text{-}PPh_2)(CO)_6$ fragments. All of these structural components have extensive precedents and the bond parameters in the present example show no significant differences for those found previously. Thus, the Ru_3 triangle has Ru–Ru separations of 2.842(6), 2.876(5) and 2.927(4) Å, the longest being adjacent to the tertiary phosphine ligand. In a comprehensive survey of similar complexes, a range of 2.846(1)–2.953(1) Å was found.[5] The P(1)–Ru(1) distance is 2.347(6) Å, again not significantly different from values found in related complexes.

The $(\mu\text{-}C_2)Co_2(CO)_6$ fragment has a Co–Co distance of 2.460(5) Å, essentially identical to separations of 2.453, 2.458(4) Å found in $[\{W(CO)_5\}_2\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}]$ **6** studied earlier.[2] The Co–C(alkyne) distances of 1.95–1.98(2) are also similar to the ones found in that complex. In the $(\mu\text{-}C_2)Ru_2(\mu\text{-}PPh_2)(CO)_6$ fragment the Ru–Ru separation [2.750(3) Å] is similar to that found in $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}(\mu\text{-}PPh_2C_2)\{Ru_2(\mu\text{-}PPh_2)(CO)_6\}]$ **7** [2.770(2) Å],[6] although the Ru–P(2) distances of 2.321, 2.324(7) Å are somewhat shorter than those found in complex **7** [2.339, 2.364(4) Å]; the

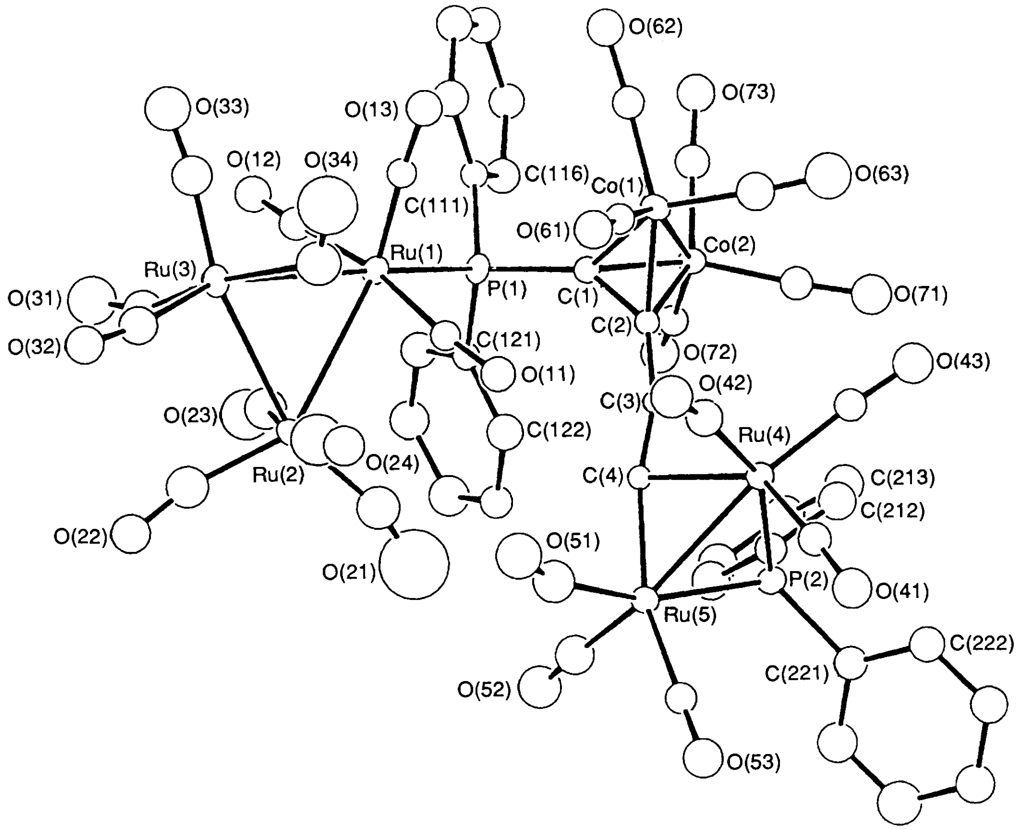


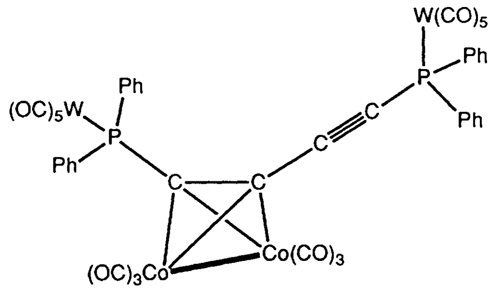
Fig. 1 Plot of a molecule of complex **5**, showing the atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids

Table 1 Selected bond lengths (Å) and angles (°) for [{$Ru_3(CO)_{11}$}{μ-$PPh_2[C_2Co_2(CO)_6]C_2$}{Ru_2(μ-PPh_2)$(CO)_6$}]·CH_2Cl_2 **5**

Co(1)–Co(2)	2.460(5)	Co(1)–C(1)	1.97(2)
Ru(1)–Ru(2)	2.927(4)	Co(1)–C(2)	1.95(2)
Ru(1)–Ru(2′)	2.781(7)	Co(2)–C(1)	1.95(2)
Ru(1)–Ru(3)	2.876(5)	Co(2)–C(2)	1.98(2)
Ru(2)–Ru(3)	2.842(6)	Ru(4)–C(3)	2.49(2)
Ru(2′)–Ru(3)	2.441(9)	Ru(4)–C(4)	2.03(2)
Ru(2)–Ru(2′)	1.220(9)	Ru(5)–C(4)	2.25(2)
Ru(4)–Ru(5)	2.750(3)	C(1)–P(1)	1.80(2)
Ru(1)–P(1)	2.347(6)	C(1)–C(2)	1.42(3)
Ru(4)–P(2)	2.321(7)	C(2)–C(3)	1.39(3)
Ru(5)–P(2)	2.324(7)	C(3)–C(4)	1.26(3)
Co–CO	range 1.70–1.76(3), average 1.73		
Ru–CO	range 1.72(4)–2.48(5), average 1.94		
C–O	range 1.06(5)–1.25(4), average 1.16		
P–C(Ph)	range 1.83–1.85(2), average 1.83		
Ru(1)–P(1)–C(1)	119.3(8)	C(3)–C(4)–Ru(5)	165(2)
P(1)–C(1)–C(2)	141(2)	C(3)–Ru(4)–C(4)	30.3(7)
C(1)–C(2)–C(3)	140(2)	C(4)–C(3)–Ru(4)	64(1)
C(2)–C(3)–C(4)	160(2)	C(4)–Ru(4)–Ru(5)	46.6(6)
C(2)–C(3)–Ru(4)	136(2)	C(4)–Ru(5)–Ru(4)	53.6(6)
C(3)–C(4)–Ru(4)	85(1)		

Table 2 Selected bond lengths (Å) and angles (°) for [{$Os_3(CO)_{11}$}(μ-$PPh_2C_2C_2$){Co_2Os_3(μ-PPh_2)$(CO)_{13}$}] **8**

Co(1)–Co(2)	2.532(6)	Os(6)–P(2)	2.34(1)
Co(1)–Os(1)	2.693(5)	Co(1)–C(71)	1.87(3)
Co(2)–Os(1)	2.655(5)	Co(2)–C(71)	2.00(3)
Co(2)–Os(2)	2.643(5)	Os(1)–C(71)	2.10(3)
Os(1)–Os(2)	2.881(2)	Os(2)–C(71)	2.31(3)
Os(1)–Os(3)	2.936(2)	Os(2)–C(72)	2.16(3)
Os(2)–Os(3)	2.756(2)	Os(3)–C(72)	2.06(3)
Os(4)–Os(5)	2.872(2)	C(71)–C(72)	1.40(5)
Os(4)–Os(6)	2.858(2)	C(72)–C(73)	1.40(5)
Os(5)–Os(6)	2.874(2)	C(73)–C(74)	1.27(5)
Co(2)–P(1)	2.20(1)	C(74)–P(2)	1.76(4)
Os(2)–P(1)	2.29(1)		
Co–CO	range 1.66(4)–1.78(5), average 1.72		
Os–CO	range 1.76(4)–1.95(5), average 1.86		
C–O	range 1.13(4)–1.25(5), average 1.17		
P – C(Ph)	range 1.79–1.81(2), average 1.80		
C(71)–C(72)–C(73)	124(3)	C(73)–C(74)–P(2)	179(3)
C(72)–C(73)–C(74)	177(4)	C(74)–P(2)–Os(6)	113(1)
Dihedral angles			
Os(1)–Co(1)–Co(2)/Os(1)–Os(2)–Co(2)	122.1		
Os(1)–Os(2)–Co(2)/Os(1)–Os(2)–Os(3)	140.1		



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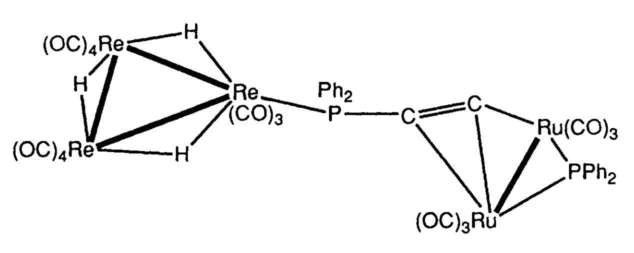

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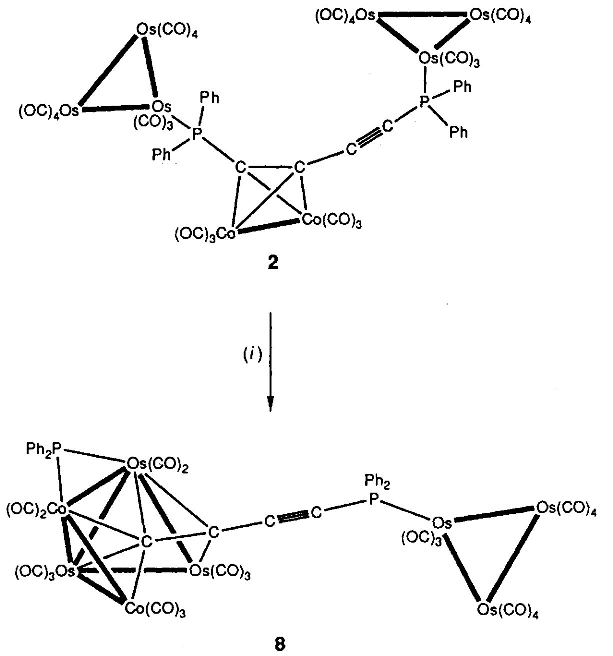


Scheme 3 (*i*) Heat

μ-PPh_2 group bridges the Ru–Ru bond more symmetrically in **5**.

The interaction of the C_4 chain with the various groups attached to it is of interest. The P(1)–C(1) bond length of 1.80(2) Å is identical with that found in complex **6**. Along the C_4 chain, the C–C separations are 1.42(3), 1.39(3) and 1.26(3) Å, values expected for a C≡C triple bond bridging the two Co atoms [*cf.* 1.36, 1.32(4) Å in **6**], a C(sp)–C(sp) single bond and a C_2 unit bridging the Ru_2 system [*cf.* 1.218(4) Å in **7**], respectively. The Ru(4)–C(4) separation is 2.03(2) Å, which is identical with the value found in **7**. The interactions with the various metal atoms destroy the linearity of the C_4 chain, as shown by the angles at C(1), C(2) and C(3) of 141(2), 140(2) and 160(2)°, respectively.

A similar reaction of complex **2** in toluene (100–105 °C, 8 h, with nitrogen purge) gave (Scheme 3) black crystals of the octanuclear complex [{$Os_3(CO)_{11}$}(μ-$PPh_2C_2C_2$){Co_2Os_3(μ-PPh_2)$(CO)_{13}$}] **8** which, however, was isolated in only 21% yield; 16% of precursor **2** was recovered. The molecular structure of **8** was determined by a single-crystal X-ray study.

Molecular Structure of Complex **8**.—A molecule of complex **8** is depicted in Fig. 2 and selected bond lengths and angles are given in Table 2; although the X-ray analysis is less than optimum the molecular geometry has been determined unambiguously. The molecule is an $Os_3(CO)_{11}(PPh_2R)$ complex, where the R group is an extensively modified C_4 fragment attached to a Co_2Os_3 cluster. Within the Os_3 triangle, the pattern of Os–Os separations [2.872(2), 2.858(2) and 2.874(2) Å] resembles that found in the similar ruthenium system in **5**, as expected from previous studies. The Os(6)–P(2) distance [2.34(1) Å] is also unexceptional.

The Co_2Os_3 cluster formed by incorporation of the (μ-C_2)$Co_2(CO)_6$ fragment into the second Os_3 cluster consists of three edge-fused triangles [Co_2Os, $CoOs_2$, Os_3] sharing Co–Os

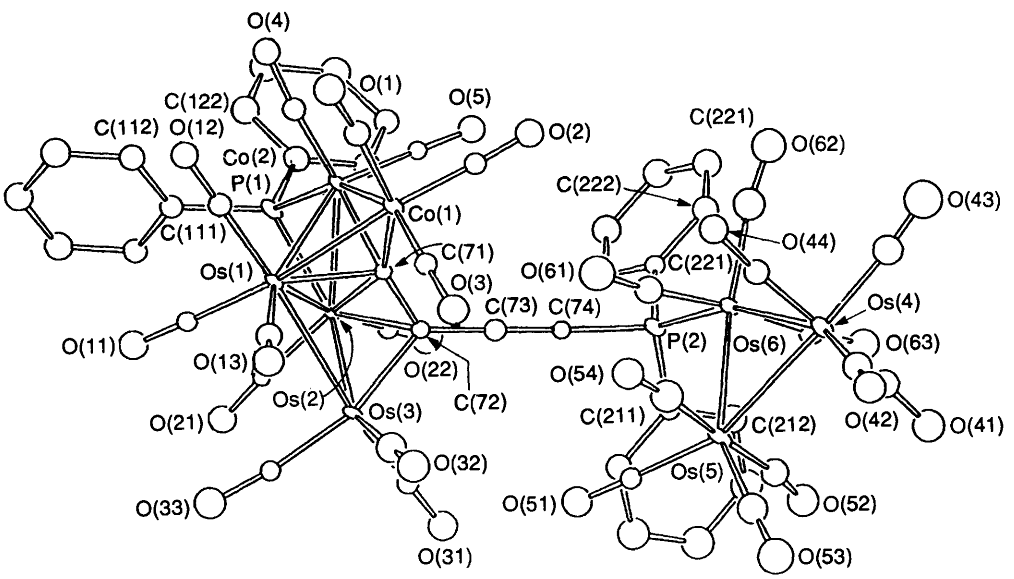
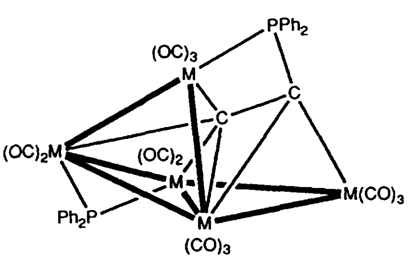
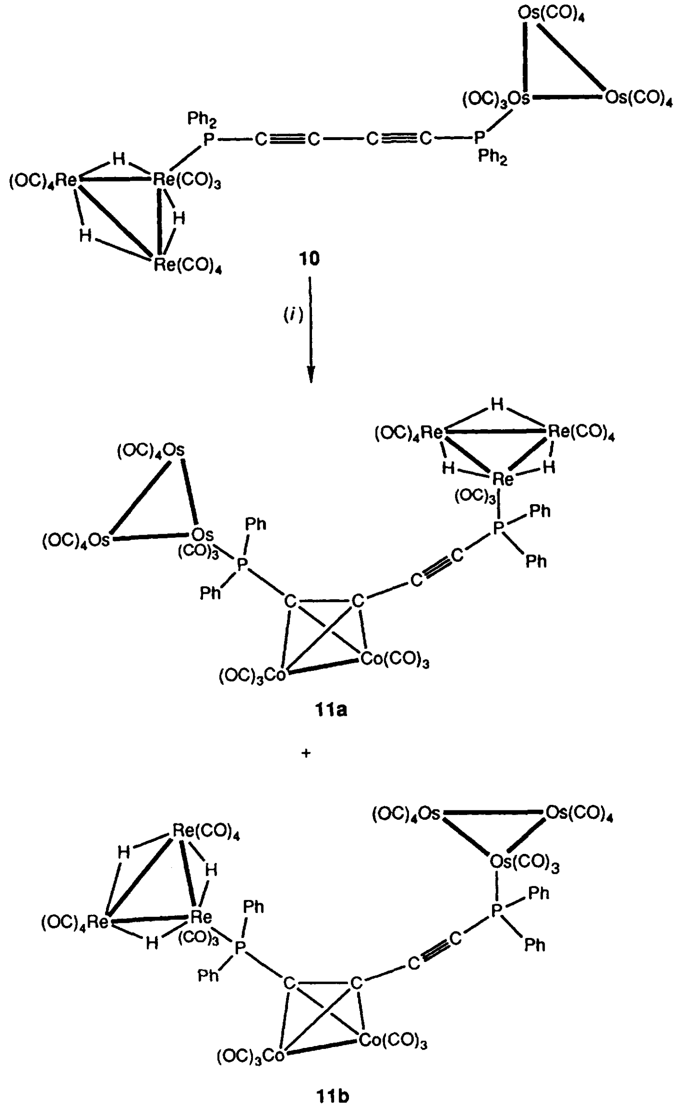


Fig. 2 Plot of a molecule of complex **8**, showing the atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids



9 M = Ru or Os



Scheme 4 (*i*) $[Co_2(CO)_8]$

and Os–Os edges. The conformation is the same as that found in the open M_5 clusters **9** which are formed by heating $[\{M_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (M = Ru or Os), which we have previously termed swallow clusters. The single Co–Co distance is 2.532(6) Å, Co–Os distances range between 2.643 and 2.693(5) Å, and the three Os–Os distances are 2.756(2), 2.881(2) and 2.936(2) Å. The Co(2)–Os(2) vector is bridged by P(1) of the μ-PPh_2 group [Co(2)–P(1) 2.20(1), Os(2)–P(1) 2.29(1) Å].

The C(71)–C(72) fragment of the C_4 chain is attached to all five metal atoms, C(71) spanning the Co(1)Co(2)Os(1)Os(2) butterfly, interacting strongly with Co(1) [1.87(3) Å] and Os(1) [2.10(3) Å], but less so with Co(2) [2.00(3) Å] and Os(2) [2.31(3)]; C(72) somewhat asymmetrically bridges the Os(2)–Os(3) vector [2.16, 2.06(3) Å, respectively]. Overall, the bonding of C(71) to the cluster closely resembles that found for the corresponding carbons in complexes **9**. Along the C_4 chain, C–C distances are 1.40, 1.40 and 1.27(5) Å for the three atoms C(71), C(72) and C(73), consistent with an uncomplexed C≡C triple bond between C(73) and C(74); however, we note the high errors associated with these parameters which limit the usefulness of these assignments. The P(2)–C(74) distance is 1.76(4) Å [*cf.* 1.72, 1.77(3) Å for the C(sp)–P separation in **6**].

Co-ordination of the metal atoms in the Co_2Os_3 cluster is completed by 13 CO groups; all ligands supply 26 (13CO) + 3 (PPh_2) + 5 (C_2R) = 34 electrons, which with 42 electrons from the metal atoms give a total electron count of 76 as anticipated for a swallow geometry with seven M–M bonds.

Earlier we also reported the synthesis of complexes containing different cluster moieties attached to each end of a bdpp ligand.[1] One of these, the mixed $Re_3(\mu\text{-}H)_3/Os_3$ species **10**, was treated with $[Co_2(CO)_8]$ to give a mixture of two isomeric products which were separable by TLC (Scheme 4). These were probably the two expected complexes formed by addition of the $Co_2(CO)_6$ group to the C≡C bond nearer to the rhenium (**11a**) or to the osmium clusters (**11b**), and were isolated in 42 and 38%

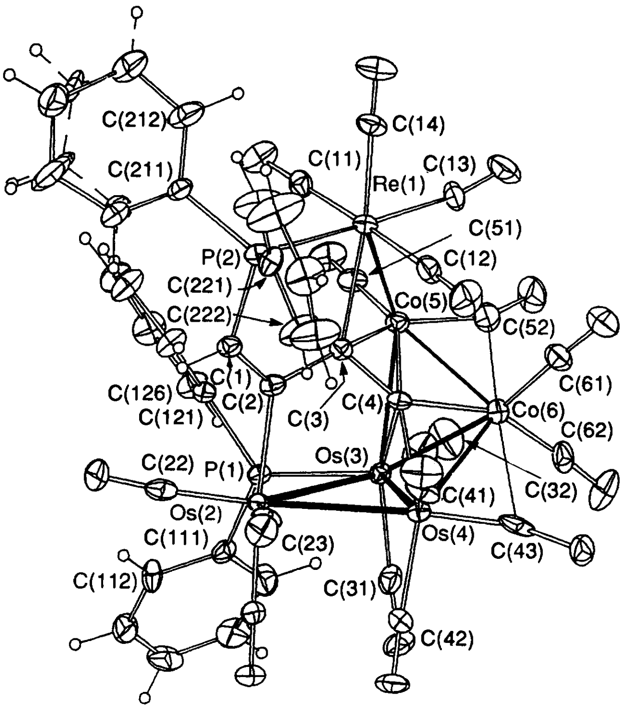


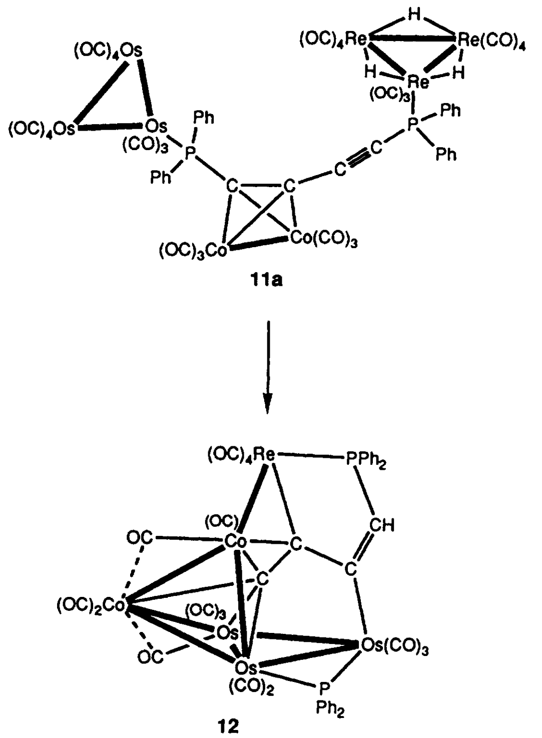
Fig. 3 Plot of a molecule of complex **12**, showing the atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å

yields, respectively. The spectroscopic properties were similar, with ν(CO) bands coinciding within ± 1 cm^{-1} except for the two lowest-energy weak absorptions. The FAB mass spectra were also similar, with identical highest-mass ions and fragmentation by loss of up to 28 CO groups. However, for **11b**, the ions $[M - n\mathrm{CO}]^+$ (n = 1, 2 or 4) were not observed.

Pyrolysis of complex **11a** afforded at least three products, but only one (Scheme 5), obtained as black crystals in 19% yield, has been characterised by a single-crystal X-ray analysis; it was found to have the composition $[Co_2Os_3Re\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]$ **12** and contains an unusual Co_2Os_3Re cluster.

Molecular Structure of Complex **12**.—A molecule of complex **12** is depicted in Fig. 3 and selected bond lengths and angles are given in Table 3. The molecule contains an extended heterometallic core, partly assembled around the PC_4 moiety of a bdpp ligand which has added one P–C bond across as Os–Os vector. A pentanuclear Co_2Os_3 core, which resembles that found in **8**, is metallated by a single Re atom at the Co wing-tip. Within the Os_3 triangle, Os–Os distances of between 2.717 and 3.044(3) Å are found; the other M–M bonds are from Os(3) and Os(4) to Co(6) [Co(6)–Os(3,4) 2.659, 2.689(3) Å] and between Os(3) and Co(5) [2.680(3) Å] and Co(6) [2.511(4) Å]. The single Re atom is bonded to Co(5) [2.819(2) Å].

One carbon of the C_4 chain interacts with the atoms of the edge-fused $Co_2Os/CoOs_2$ triangles [C(4)–Co(5,6) 1.96, 1.93(2); C(4)–Os(3,4) 2.22, 2.11(2) Å], but not with the third Os atom. Atom C(2) is attached to Os(2) [C(2)–Os(2) 2.14(1) Å] and is doubly bonded to C(1) [1.31(2) Å]; this latter carbon is attached to P(2) [1.79(2) Å] which in turn is co-ordinated to Re(1) [Re(1)–P(2) 2.443(5) Å]. Atom C(3) bridges the Co(5)–Re(1) vector [Co(5)–C(3) 2.01(1), Re(1)–C(3) 2.28(1) Å] and is singly bonded to C(2) [1.48(2) Å]. Atom C(4) spans the Co(5)-Co(6)Os(3)Os(4) butterfly and with C(3) forms an η^2-attachment to Co(5) [C(3,4)–Co(5) 2.01(1), 1.96(1) Å]. The geometry about C(1) [C(2)–C(1)–P(2) 120(1)°] and the observation of a resonance at δ 6.52 in the ^1H NMR spectrum both suggest that this carbon also carries a hydrogen atom, but it was not located definitively by the X-ray work.



Scheme 5 (*i*) Heat

Table 3 Selected bond lengths (Å) and angles (°) for $[Co_2Os_3Re\{\mu_6\text{-}C_2C{=}CH(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{14}]\cdot CH_2Cl_2$ **12**

Co(5)–Co(6)	2.511(4)	Os(2)–C(2)	2.14(1)
Co(5)–Os(3)	2.680(3)	Os(3)–C(3)	3.06(2)
Co(5)–Re(1)	2.819(2)	Os(3)–C(4)	2.22(1)
Co(6)–Os(3)	2.659(3)	Os(4)–C(4)	2.11(2)
Co(6)–Os(4)	2.689(3)	Re(1)–C(3)	2.28(1)
Os(2)–Os(3)	2.999(2)	Os(4)–C(43)	1.81(2)
Os(2)–Os(4)	3.044(3)	Co(6)–C(43)	2.50(2)
Os(3)–Os(4)	2.717(3)	Co(6)–C(52)	2.24(2)
Os(2)–P(1)	2.416(5)	Co(5)–C(52)	1.82(2)
Os(3)–P(1)	2.297(5)	P(2)–C(1)	1.79(2)
Re(1)–P(2)	2.443(5)	C(1)–C(2)	1.31(2)
Co(5)–C(3)	2.01(1)	C(2)–C(3)	1.48(2)
Co(5)–C(4)	1.96(1)	C(3)–C(4)	1.42(2)
Co(6)–C(4)	1.93(2)		
Co–CO	range 1.74–1.78(2), average 1.75		
Os–CO	range 1.79–1.97(2), average 1.89		
Re–CO	range 1.95–1.98(2), average 1.97		
C–O	range 1.10–1.25(2), average 1.16		
P–C(Ph)	range 1.80–1.86(2), average 1.84		
Os(3)–Co(5)–Re(1)	132.82(9)	C(2)–C(3)–C(4)	116(1)
P(2)–C(1)–C(2)	120(1)	C(3)–C(4)–Co(6)	146(1)
C(1)–C(2)–C(3)	118(1)	C(4)–C(3)–Re(1)	119(1)
Dihedral angle			
Os(2)–Os(3)–Os(4)/Os(3)–Os(4)–Co(6)	35.41(7)		

Co-ordination of the various metal atoms is completed by sixteen CO groups, two of which semi-bridge the Co(5)–Co(6) and Os(4)–Co(6) vectors [Co(5)–C(52) 1.82(2), Co(6)–C(52) 2.24(2) Å, Co(5)–C(52)–Co(6) 75.7(6)°; Os(4)–C(43) 1.81(2), Co(6)–C(43) 2.50(2) Å, Os(4)–C(43)–Co(6) 75.4(7)°]. The ligands supply a total of 32 (16CO) + 3 (PPh_2) + 8 (C_4HPPh_2) = 43 electrons to the cluster, which with 49 electrons from the metal core is thus a 92e system, as expected for a six-atom cluster with eight M–M bonds.

In summary, therefore, three of the four carbon atoms of the original bdpp ligand are involved in bonding to all five metal atoms, the fourth having acquired a hydrogen atom, presumably from the original $Re_3(\mu\text{-}H)_3$ cluster. One of the PPh_2 groups bridges an Os–Os vector, while the other, still attached to the C_4 chain, bonds to Re(1): atoms P(2)–C(1)–C(2)–C(3) chelate this metal atom to form an ReC_3P metallacycle.

Discussion

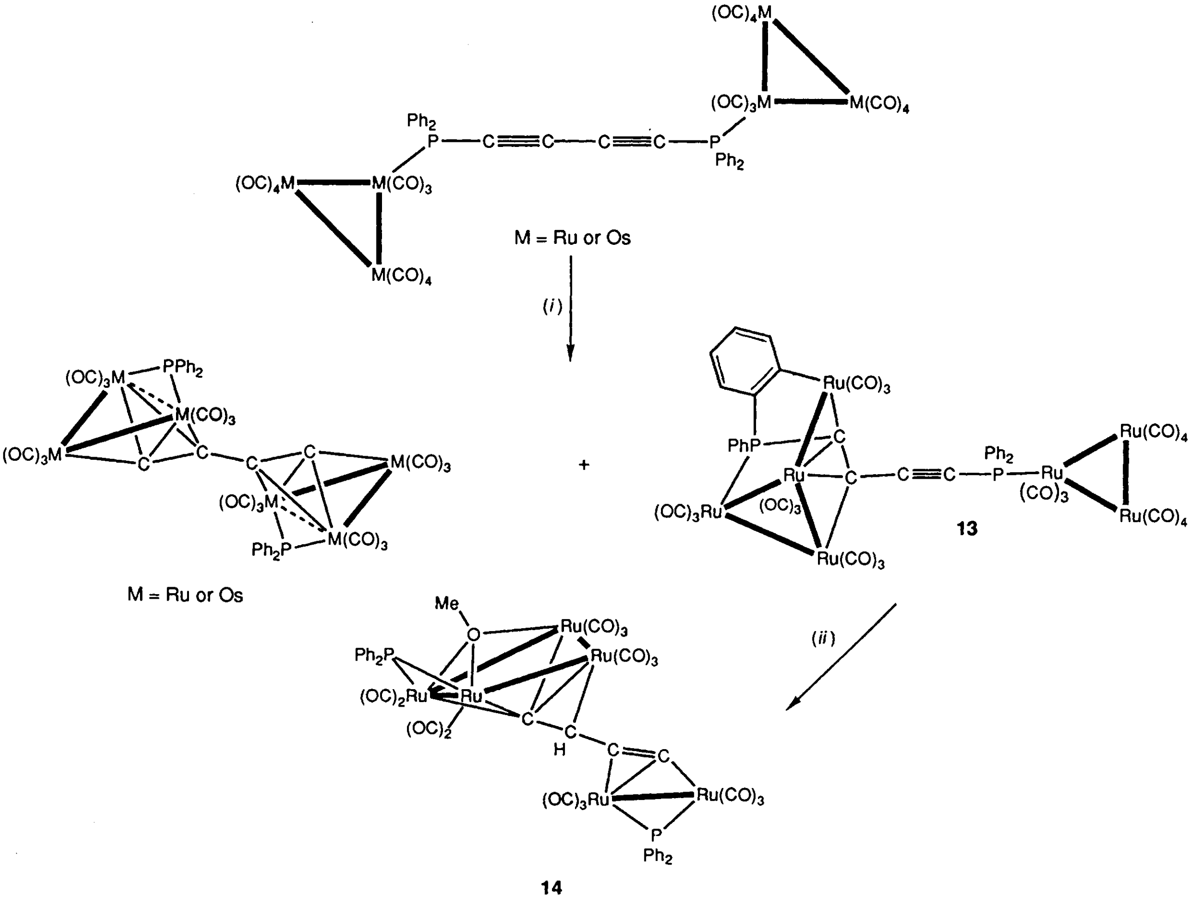
This work has again demonstrated that the *P*-bonded cluster complexes of bdpp are sufficiently open to allow co-ordination of one $Co_2(CO)_6$ group to a C≡C triple bond of the ligand, as found previously with bdpp-bridged mononuclear complexes.[2] In the case of the mixed-metal system, the two isomeric complexes can be separated by TLC. The subsequent behaviour of three of these complexes on heating is of interest.

The formation of **5** by heating **1** further illustrates the previously described behaviour of complexes containing the $C{\equiv}CPPh_2\{Ru_3(CO)_{11}\}$ fragment. Thus, on heating $[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ complex **13** was isolated, but was converted into **14** in MeOH solution (Scheme 6). While pyrolysis of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ gives the open Ru_5 cluster $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$, similar treatment of the mixed $\{Ru_3\}/\{Re_3(\mu\text{-}H)_3\}$ derivative gave **7**, in which one $Ru(CO)_4$ group has been eliminated concomitantly with addition of the P–C bond across the remaining Ru–Ru bond. Such reactions have many precedents in the chemistry of acetylenic phosphines, $PPh_2(C{\equiv}CR)$, established by Carty and his group.[7] In the present case, co-ordination of the $Co_2(CO)_6$ group to one of the C≡C bonds of the bdpp ligand protects it from further involvement, allowing the transformation of the $C{\equiv}CPPh_2\{Ru_3(CO)_{11}\}$ fragment to the familiar $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2R)(CO)_6$ derivative.

A different version of this reaction occurs with complex **2**. In the product **8** the $C{\equiv}CPPh_2\{Os_3(CO)_{11}\}$ fragment (R_{Os}) survives the reaction conditions, while the $Co_2(CO)_6$ unit combines with the second Os_3 cluster to give the Co_2Os_3 which resembles that present in the Ru_5 cluster mentioned above. The C_2 unit interacts with all five metal atoms after cleavage of the P–C(sp) bond while retaining the R_{Os} substituent unchanged.

Involvement of both C_2 units of the bdpp ligand is found in one of the products obtained by heating complex **11a**. As described in detail above, the metal cluster in **12** contains an Os_3 triangle bonded to the Co_2 unit, to which a single rhenium atom is attached. The bdpp ligand has formally added to one Os–Os edge, the original carbon interacting with the Co_2Os_2 system. The second half of the bdpp ligand retains the C–P bond, the phosphine being bonded to a rhenium atom and the C_2 unit interacting with the third Os atom. One hydrogen, probably from the Re_3 cluster, has migrated to the carbon not bonded to a metal atom to generate a $=CHPR_2$ system.

In complexes **8** and **12** quite complicated rearrangements of the metal cores have occurred. These are facilitated by having the C_4P backbone which may act as a template to guide the formation of the final product. Possibly **12** is formed *via* an intermediate with a structure akin to that of **8**. Whilst it might appear that addition of the first P–C(sp) bond to a cluster deactivates the second towards such reactions, this must only be the result of the additional complexation of the $Co_2(CO)_6$ fragment to one of the C≡C triple bonds, as we have shown before that some cobalt-free complexes can be transformed on heating, with cleavage of both P–C(sp) bonds, to novel complexes containing the C_4 ligand.



Scheme 6 (*i*) Heat; (*ii*) MeOH

Conclusion

This paper describes some studies of the synthesis and transformations of cluster complexes containing the bdpp ligand bridging two cluster nuclei together with a $Co_2(CO)_6$ group attached to one of the C≡C triple bonds. As expected,[8] facile incorporation of the cobalt atoms into cluster frameworks is observed. A feature of these reactions is the ease of rearrangement of the metal core about the organic ligand; this, together with facile elimination of small metal carbonyl fragments, does not yet allow prediction of the final geometry of these clusters. Similar adaptability of the Ru_5 cluster to the organic ligand has been observed throughout our studies of the chemistry of the related complex $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$.[9] Further examination of the scope of these reactions, taking advantage of the variety of metal–ligand combinations from across the Periodic Table which are now known to enter into η^2 bonding with C≡C triple bonds, which can be used to build up unusual mixed-metal clusters in a partially empirical way, is in progress.

Experimental

General Conditions.—All reactions were carried out under dry, high-purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. Thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Reagents.—The complexes $[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$, $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$, $[\{Os_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ and $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ were prepared as described earlier;[1] $[Co_2(CO)_8]$ (Strem) was used as received.

Instrumentation.—Infrared: Perkin Elmer 1700X FT-IR or 683 double beam, NaCl optics. NMR: Bruker CXP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz). FAB mass spectrometry: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Reactions with $[Co_2(CO)_8]$.—$[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$. A solution of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ (151 mg, 0.092 mmol) and $[Co_2(CO)_8]$ (500 mg, 1.46 mmol) in tetrahydrofuran (40 cm^3) was stirred for 24 h. The solvent was removed and the residue purified by preparative TLC [light petroleum (b.p. 60–80 °C)–acetone, 3:1] to yield two products. The major black band (R_f 0.5) was complex **1** (123 mg, 85%). IR: ν(CO) (cyclohexane) 2104m, 2095m, 2074m, 2068m, 2062 (sh), 2046s, 2028m, 2025m, 2015vs, 1999 (sh), 1990m, 1981 (sh), 1962s and 1946vw cm^{-1}. FAB mass spectrum: *m/z* 1928, M^+. A second minor brown band (R_f 0.55) was recrystallised from CH_2Cl_2–MeOH to yield black crystals of **5** (5 mg, 3%), m.p. > 300 °C (decomp.) [Found: C, 35.65; H, 1.35%; *M* 1687 (mass spectrometry). $C_{51}H_{20}Co_2O_{23}P_2Ru_5$ requires C, 34.90; H, 1.05%; *M* 1687]. IR: ν(CO) (cyclohexane) 2102m, 2093s, 2086s, 2083 (sh), 2078 (sh), 2068s, 2060m, 2053m, 2045 (sh), 2042s, 2029s, 2021 (sh), 2014vs, 2003 (sh), 1990m, 1979w, 1961w and 1945vw cm^{-1}. FAB mass spectrum: *m/z* 1687, M^+; 1603, 1547–1041, $[M - n\text{CO}]^+$ (n = 3, 5–23); 964, $[M - 23\text{CO} - \text{Ph}]^+$.

$[\{Os_3(CO)_{11}\}_2(\mu\text{-bdpp})]$. The complexes $[\{Os_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ (20 mg, 0.0092 mmol) and $[Co_2(CO)_8]$ (50 mg, 0.15 mmol) were stirred in diethyl ether (20 cm^3) for 3 d. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 10:3). The major band was recrystallised from CH_2Cl_2–MeOH to yield **2** (22 mg, 96%) as a black powder, m.p. 146–149 °C (decomp.) [Found: C, 27.65; H, 1.00%; *M* 2462 (mass spectrometry). $C_{56}H_{20}Co_2O_{28}Os_6P_2$ requires C, 27.30; H, 0.80%; *M* 2462]. IR: ν(CO) (cyclohexane) 2107m, 2100m, 2074m, 2057s, 2051 (sh), 2034m, 2020vs, 2003m, 1991m, 1981m, 1972 (sh) and 1955vw cm^{-1}. FAB mass spectrum: *m/z* 2462, M^+; 2434–1678, $[M - n\text{CO}]^+$ (n = 1, 3–28).

$[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-bdpp})]$. The complexes $[\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ (69 mg, 0.032 mmol) and $[Co_2(CO)_8]$ (150 mg, 0.44 mmol) were stirred in diethyl ether (50 cm^3) for 3 d. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 5:2). The major band was recrystallised from CH_2Cl_2–MeOH to yield **3** (67 mg, 86%) as a black powder [Found: C, 27.30; H, 1.15%; $[M - 3\text{CO}]^+$ 2360 (mass spectrometry). $C_{56}H_{26}Co_2O_{28}P_2Re_6$ requires C, 27.50; H, 1.05%; *M* − 3CO 2360]. IR: ν(CO) (cyclohexane) 2113m, 2102m, 2089m, 2074m, 2050m, 2034m, 2018vs, 2010 (sh), 2000s, 1952s, 1949m and 1937m cm^{-1}. FAB mass spectrum: *m/z* 2360–1660, $[M - n\text{CO}]^+$ (n = 3–28).

$[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$. The complexes $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-bdpp})]$ (100 mg, 0.054 mmol) and $[Co_2(CO)_8]$ (150 mg, 0.044 mmol) were stirred in diethyl ether (50 cm^3) for 3 d. The solvent was removed and the residue purified by preparative TLC to yield **4** (98 mg, 85%) as a black powder, m.p. 100–105 °C (decomp.) [Found: C, 31.55; H, 1.35%; *M* 2139 (mass spectrometry). $C_{56}H_{28}Co_2O_{28}P_2Ru_8$ requires C, 31.50; H, 1.30%; *M* 2139]. IR: ν(CO) (cyclohexane) 2102m, 2094m, 2073vs, 2069 (sh), 2058vs, 2049m, 2026vs, 2010s, 1998 (sh), 1992 (sh), 1969w and 1960w cm^{-1}. FAB mass spectrum: *m/z* 2139, M^+; 2055, 1915–1355, $[M - n\text{CO}]^+$ (n = 3, 8–28).

$[\{Os_3(CO)_{11}\}(\mu\text{-bdpp})\{Re_3(\mu\text{-}H)_3(CO)_{11}\}]$ **10**. A mixture of complex **10** (82 mg, 0.038 mmol) and $[Co_2(CO)_8]$ (250 mg, 0.73 mmol) was stirred in tetrahydrofuran (30 cm^3) for 24 h. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 20:3) to yield two isomers of $[\{Os_3(CO)_{11}\}\{\mu\text{-}PPh_2[C_2Co_2(CO)_6]C_2PPh_2\}\{Re_3(\mu\text{-}H)_3(CO)_{11}\}]$ **11**. The top band was recrystallised from CH_2Cl_2–MeOH to yield **11a** (39 mg, 42%) as a black powder [Found: *M* 2454 (mass spectrometry). $C_{56}H_{23}Co_2O_{28}Os_3P_2Re_3$ requires *M* 2454]. IR: ν(CO) (hexane) 2109w, 2101w, 2090w, 2075m, 2056m, 2050m, 2035m, 2020vs, 2002m, 1993w, 1974s, 1951w and 1937w cm^{-1}. FAB mass spectrum: *m/z* 2454, M^+; 2426–1670, $[M - n\text{CO}]^+$ (n = 1–28). The bottom band was recrystallised from CH_2Cl_2–MeOH to yield **11b** (35 mg, 38%) as a black powder [Found: *M*, 2454 (mass spectrometry)]. IR: ν(CO) (hexane) 2110w, 2101w, 2091w, 2075m, 2057m, 2050m, 2036m, 2021vs, 2002m, 1994w, 1974s, 1954w and 1945w cm^{-1}. FAB mass spectrum: *m/z* 2454, M^+; 2370, 2314–1670, $[M - n\text{CO}]^+$ (n = 3, 5–28).

Pyrolysis of complex **1**. A solution of complex **1** (123 mg, 0.064 mmol) in cyclohexane (30 cm^3) was heated (oil-bath, 80 °C) for 1 h. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 4:1) to yield two major bands. A yellow band (R_f 0.55) was recrystallised from CH_2Cl_2–MeOH to yield $[Ru_3(CO)_{12}]$ (15 mg, 37%). The major brown band was recrystallised from CH_2Cl_2–isopentane to yield **5** (60 mg, 56%).

Pyrolysis of complex **2**. Nitrogen was bubbled through a solution of complex **2** (70 mg, 0.028 mmol) in toluene (30 cm^3) and heated at 100–105 °C for 8 h. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 5:2). The major band (R_f 0.5) was recrystallised from CH_2Cl_2–MeOH to yield black crystals of **8** (14 mg, 21%), m.p. 213–217 °C (decomp.) [Found: C, 26.55; H, 0.90%; *M* 2350 (mass spectrometry). $C_{52}H_{20}Co_2O_{24}Os_6P_2$ requires C, 26.60; H, 0.85%; *M* 2350]. NMR ($CDCl_3$): ^1H, δ 7.25–7.70 (m, Ph); ^{13}C, δ 83.74 (d, J_{CP} 102.5, P*C*C), 119.64 (d, J_{CP} 15.8, PC*C*), 119.74–132.23 (m, Ph), 135.14 (d, J_{CP} 54.3), 135.98 (d, J_{CP} 55.6), 142.14 (d, J_{CP} 40.4), 142.70 (d, J_{CP} 25.7) (all *ipso*-C of PPh), 170.84 (d, J_{CP} 6)*, 171.72 (s, OsCO), 172.12 (d, J_{CP} 6.7, OsCO), 173.20 (br s)*, 179.05 (s, OsCO), 179.40 (t, J_{CP} 3.3)*, 181.80 (s, OsCO), 183.20 (s, OsCO) and 197.73 (br s, CoCO). Two of the three asterisked low-intensity resonances probably belong to the C atoms co-ordinated to the Co_2Os_3 cluster, while the third is likely to be from an OsCO group. IR: ν(CO) (cyclohexane)

Table 4 Crystal data and refinement details for complexes **5**, **8** and **12**

	5	**8**	**12**
Formula	$C_{51}H_{20}Co_2O_{23}P_2Ru_5\cdot CH_2Cl_2$	$C_{52}H_{20}Co_2O_{24}Os_6P_2$	$C_{44}H_{21}Co_2O_{16}Os_3P_2Re\cdot CH_2Cl_2$
M	1770.8	2349.7	1827.2
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a/Å	11.012(3)	14.887(4)	15.263(4)
b/Å	21.23(1)	15.318(4)	14.862(3)
c/Å	26.16(1)	13.867(4)	11.339(6)
α/°	—	92.66(2)	103.60(3)
β/°	—	96.77(2)	91.23(3)
γ/°	—	77.92(2)	90.22(2)
U/Å^3	6115.8	3070	2499
Z	4	2	2
D_c/g cm^{-3}	1.923	2.542	2.43
F(000)	3400	2128	1684
Crystal size/mm	0.50 × 0.08 × 0.06	0.27 × 0.37 × 0.45	0.20 × 0.12 × 0.18 (fragment)
Transmission (minimum, maximum)	0.191, 0.762	0.091, 0.012	0.32, 0.41
μ/cm^{-1}	18.85	130.05	104.6
No. unique data, *N*	5438	5738	8555
No. data used, N_o	4008	3456	6321
R	0.074	0.068	0.052
R'	—	0.069	0.056

Table 5 Non-hydrogen atomic coordinates (× 10^4) for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3684(2)	2021(1)	3678(1)	O(51)	7628(29)	879(13)	2487(11)
Ru(2)	4879(4)	819(2)	3892(2)	C(52)	5209(34)	−167(17)	1847(13)
Ru(3)	4929(5)	1803(2)	4628(2)	O(52)	4616(24)	−595(13)	1959(9)
Ru(2')	4049(8)	893(3)	4195(3)	C(53)	7217(27)	100(13)	1237(10)
Ru(3')	4430(7)	6944(4)	590(3)	O(53)	8035(23)	−165(11)	1032(9)
Ru(4)	5856(2)	1725(1)	1147(1)	C(61)	4889(27)	3179(13)	2425(10)
Ru(5)	5989(2)	549(1)	1583(1)	O(61)	5848(22)	3204(10)	2606(8)
Co(1)	3428(3)	3093(2)	2162(1)	C(62)	2645(29)	3685(14)	2491(11)
Co(2)	1785(3)	2482(2)	1762(1)	O(62)	2202(21)	4121(10)	2751(8)
P(1)	2232(6)	2011(3)	3021(2)	C(63)	3794(34)	3511(15)	1629(13)
P(2)	4975(7)	810(3)	833(3)	O(63)	3850(28)	3807(13)	1241(11)
C(1)	2628(23)	2320(11)	2404(9)	C(71)	1971(27)	2587(13)	1121(11)
C(2)	3412(22)	2201(10)	1986(8)	O(71)	2081(22)	2694(11)	669(9)
C(3)	4284(20)	1770(10)	1830(7)	C(72)	854(26)	1826(12)	1709(9)
C(4)	4874(21)	1262(10)	1799(8)	O(72)	160(22)	1427(10)	1689(8)
C(11)	5006(25)	1919(12)	3216(9)	C(73)	754(30)	3056(14)	1903(11)
O(11)	5697(19)	1871(9)	2868(7)	O(73)	−17(22)	3448(10)	1980(8)
C(12)	2377(29)	1972(14)	4157(11)	C(111)	855(14)	2478(9)	3158(7)
O(12)	1545(20)	1953(9)	4419(7)	C(112)	983(14)	3021(9)	3454(7)
C(13)	3868(25)	2851(11)	3729(9)	C(113)	−7(14)	3420(9)	3527(7)
O(13)	4040(20)	3422(9)	3737(7)	C(114)	−1125(14)	3278(9)	3305(7)
C(21)	4973(41)	460(19)	3262(15)	C(115)	−1253(14)	2735(9)	3009(7)
O(21)	4870(52)	97(25)	2942(19)	C(116)	−263(14)	2335(9)	2935(7)
C(22)	5250(38)	240(18)	4402(14)	C(121)	1670(15)	1227(9)	2889(7)
O(22)	5712(22)	−155(10)	4654(8)	C(122)	2326(15)	856(9)	2456(7)
C(23)	3138(43)	640(19)	4004(15)	C(123)	1951(15)	241(9)	2442(7)
O(23)	2157(33)	381(15)	4053(12)	C(124)	919(15)	−2(9)	2680(7)
C(24)	6583(53)	1126(24)	3822(21)	C(125)	262(15)	370(9)	3022(7)
O(24)	7442(25)	1285(12)	3700(10)	C(126)	637(15)	984(9)	3127(7)
C(31)	3633(37)	1197(16)	4921(14)	C(211)	3302(20)	750(8)	815(7)
O(31)	2995(31)	1045(14)	5199(12)	C(212)	2669(20)	1154(8)	490(7)
C(32)	6282(35)	1534(15)	5048(13)	C(213)	1421(20)	1079(8)	421(7)
O(32)	6939(22)	1385(10)	5348(9)	C(214)	807(20)	598(8)	677(7)
C(33)	4382(35)	2451(18)	4945(13)	C(215)	1440(20)	193(8)	1002(7)
O(33)	3969(27)	2832(12)	5195(9)	C(216)	2688(20)	269(8)	1071(7)
C(34)	6445(44)	2434(21)	4149(15)	C(221)	5383(21)	437(7)	230(8)
O(34)	6624(43)	2929(20)	4227(15)	C(222)	5828(21)	832(7)	−153(8)
C(41)	7258(29)	1618(14)	776(11)	C(223)	6218(21)	577(7)	−617(8)
O(41)	8136(23)	1492(10)	505(9)	C(224)	6163(21)	−72(7)	−697(8)
C(42)	6820(33)	2209(15)	1630(13)	C(225)	5718(21)	−466(7)	−314(8)
O(42)	7559(25)	2423(12)	1900(9)	C(226)	5328(21)	−212(7)	150(8)
C(43)	5241(28)	2366(14)	729(10)	C(100)	8214(40)	3921(23)	892(17)
O(43)	4878(23)	2760(11)	434(9)	Cl(1)	8675(12)	3128(6)	749(4)
C(51)	7059(38)	664(19)	2206(15)	Cl(2)	6874(16)	3905(8)	1203(10)

The Ru(2) and Ru(3) atoms have site occupancy 0.60; see Experimental section.

Table 6 Non-hydrogen atomic coordinates for (× 10^4) complex **8**

Atom	*x*	*y*	*z*
Os(1)	7 452(1)	7 198(1)	2 737(1)
Os(2)	8 521(1)	5 927(1)	1 501(1)
Os(3)	6 629(1)	6 104(1)	1 228(1)
Os(4)	5 857(1)	1 351(1)	4 451(1)
Os(5)	5 369(1)	2 328(1)	2 682(1)
Os(6)	7 261(1)	1 898(1)	3 529(1)
Co(1)	7 637(3)	6 041(3)	4 186(3)
Co(2)	9 045(3)	6 141(3)	3 370(3)
P(1)	9 776(7)	6 470(7)	2 194(7)
P(2)	8 075(7)	2 315(7)	2 344(7)
O(1)	7 797(22)	7 192(22)	5 938(26)
O(2)	8 492(20)	4 393(20)	5 126(22)
O(3)	5 740(22)	5 768(22)	3 958(24)
O(4)	9 810(18)	7 177(19)	4 887(21)
O(5)	10 101(19)	4 363(19)	3 829(20)
O(11)	7 573(21)	8 497(20)	1 167(23)
O(12)	7 994(19)	8 508(19)	4 305(21)
O(13)	5 406(24)	7 824(23)	2 874(26)
O(21)	8 196(20)	6 880(20)	−396(23)
O(22)	9 437(20)	4 306(20)	523(22)
O(31)	6 420(21)	4 696(22)	−325(24)
O(32)	4 757(24)	6 037(22)	1 897(25)
O(33)	5 856(22)	7 724(22)	−55(25)
O(41)	5 744(22)	−228(23)	3 085(26)
O(42)	3 926(24)	1 419(22)	5 014(25)
O(43)	7 031(30)	176(29)	6 037(34)
O(44)	6 072(20)	2 950(20)	5 771(22)
O(51)	5 411(21)	3 691(21)	1 193(23)
O(52)	5 988(23)	795(23)	1 330(26)
O(53)	3 432(30)	2 030(28)	2 243(31)
O(54)	4 734(23)	3 927(24)	4 033(26)
O(61)	6 742(26)	3 807(28)	4 188(30)
O(62)	8 729(26)	1 433(25)	5 290(29)
O(63)	7 714(22)	−33(23)	2 841(24)
C(1)	7 745(30)	6 687(30)	5 281(34)
C(2)	8 120(26)	5 065(27)	4 755(28)
C(3)	6 526(25)	5 941(24)	4 106(27)
C(4)	9 460(27)	6 770(27)	4 245(31)
C(5)	9 701(23)	5 058(24)	3 618(25)
C(11)	7 515(25)	8 008(25)	1 766(27)
C(12)	7 755(26)	8 002(27)	3 706(30)
C(13)	6 153(31)	7 592(29)	2 743(31)
C(21)	8 295(22)	6 554(22)	348(25)
C(22)	9 074(24)	4 957(25)	907(26)
C(31)	6 481(24)	5 242(25)	258(28)
C(32)	5 477(32)	6 031(31)	1 607(34)
C(33)	6 174(24)	7 012(25)	387(26)
C(41)	5 822(34)	405(35)	3 659(39)
C(42)	4 657(33)	1 313(31)	4 765(34)
C(43)	6 610(35)	564(35)	5 389(40)
C(44)	5 960(27)	2 327(28)	5 201(31)
C(51)	5 391(25)	3 172(25)	1 738(28)
C(52)	5 753(31)	1 336(33)	1 894(36)
C(53)	4 139(37)	2 182(34)	2 467(39)
C(54)	4 963(35)	3 293(37)	3 559(40)
C(61)	6 908(30)	3 076(31)	3 892(33)
C(62)	8 180(34)	1 711(34)	4 662(39)
C(63)	7 482(28)	735(29)	3 084(31)
C(71)	7 838(22)	5 807(22)	2 886(24)
C(72)	7 592(22)	5 249(22)	2 116(24)
C(73)	7 766(26)	4 319(26)	2 159(29)
C(74)	7 890(23)	3 480(24)	2 223(26)
C(111)	9 844(18)	7 600(14)	1 942(18)
C(112)	9 875(18)	8 244(14)	2 684(18)
C(113)	10 025(18)	9 083(14)	2 481(18)
C(114)	10 144(18)	9 277(14)	1 537(18)
C(115)	10 113(18)	8 633(14)	796(18)
C(116)	9 963(18)	7 794(14)	998(18)
C(121)	10 960(14)	5 866(17)	2 210(22)
C(122)	11 676(14)	6 331(17)	2 393(22)
C(123)	12 593(14)	5 867(17)	2 484(22)
C(124)	12 794(14)	4 938(17)	2 393(22)
C(125)	12 078(14)	4 472(17)	2 211(22)
C(126)	11 161(14)	4 937(17)	2 120(22)
C(211)	7 836(18)	1 919(18)	1 122(16)
C(212)	8 106(18)	1 010(18)	905(16)
C(213)	7 872(18)	678(18)	−24(16)
C(214)	7 369(18)	1 255(18)	−736(16)
C(215)	7 098(18)	2 164(18)	−519(16)
C(216)	7 332(18)	2 496(18)	410(16)
C(221)	9 318(12)	2 017(17)	2 488(19)
C(222)	9 793(12)	1 446(17)	3 219(19)
C(223)	10 753(12)	1 182(17)	3 281(19)
C(224)	11 238(12)	1 489(17)	2 611(19)
C(225)	10 764(12)	2 060(17)	1 880(19)
C(226)	9 804(12)	2 324(17)	1 818(19)

2107w, 2093w, 2071s, 2054m, 2045s, 2030m, 2020s, 2012 (sh), 2002m, 1991m, 1980m and 1958w cm^{-1}. FAB mass spectrum: *m*/*z* 2350, M^+; 2322–1677, $[M - n\text{CO}]^+$ (*n* = 1–24). Some starting material was also recovered (R_f 0.55, 11 mg, 16%).

Pyrolysis of complex **11a**. A solution of complex **11a** (top gand; 36 mg, 0.015 mmol) in toluene (15 cm^3) was refluxed for 90 min with a nitrogen purge. The solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 10:3) to yield three bands. A black band (R_f 0.4) was recrystallised from CH_2Cl_2–MeOH to yield **12** (5 mg, 19%), m.p. 275–280 °C (decomp.) [Found: C, 29.75; H, 1.30%; *M* 1744 (mass spectrometry). $C_{44}H_{21}Co_2O_{16}Os_3P_2Re$ requires C, 30.35; H, 1.20%; *M* 1744]. IR: ν(CO) (cyclohexane) 2093w, 2074m, 2051s, 2024vs, 2010s, 1995w, 1986m, 1970m, 1954vw and 1944vw cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.30 (2 H, s, CH_2Cl_2), 6.52 (1 H, d, J_{HP} 17.4 Hz, CHP) and 6.91–7.77 (20 H, m, Ph). FAB mass spectrum: *m*/*z* 1744, M^+; 1716–1296, $[M - n\text{CO}]^+$ (*n* = 1–16).

Crystallography.—Unique data sets were measured at *ca*. 295 K within the limit $2\theta_{max} = 50°$ (40° for complex **8**) using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); *N* independent reflections were obtained, N_o with $I > 3\sigma(I)$ [$2.5\sigma(I)$ for **5** and **8**] being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. For **12**, anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Structure solution and refinement for **5** and **8** were achieved employing the SHELX 76 [10] program with unit weights for **5** and $w = [\sigma^2(F) + 0.009F^2]^{-1}$ for **8**. For **12**, conventional residuals *R*, *R*′ on |*F*| are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used; computation used the XTAL 2.6 program system [11] implemented by S. R. Hall, employing neutral atom complex scattering factors. Crystal data are given in Table 4, final atomic coordinates in Tables 5–7.

Abnormal features/variations in procedure. For complex **5** only the Ru, Co and P atoms were refined anisotropically. Atoms Ru(2) and Ru(3) were found to be disordered over two positions, which were refined such that the site occupancies were 60% for the unprimed atoms. The absolute configuration was determined on the basis of differences in Friedel pairs included in the data set.

For complex **8** a limited data set was obtained as a result of the poor quality of the crystal, hence only Os, Co and P atoms were refined anisotropically.

For complex **12** consideration of difference-map residues and their refinement behaviour led to their modelling in terms of a pair of half-weighted dichloromethane species disposed around a common site. Thermal motion was very high thereon and also on certain phenyl rings: for ring 21, C(214)–C(216)

Table 7 Non-hydrogen positional parameters for complex **12**

Atom	*x*	*y*	*z*
Re(1)	0.080 12(4)	0.822 66(4)	0.911 42(6)
Os(2)	0.338 42(4)	0.626 10(4)	0.679 60(6)
Os(3)	0.402 24(4)	0.749 86(4)	0.914 46(6)
Os(4)	0.322 11(5)	0.589 99(4)	0.931 65(6)
Co(5)	0.259 5(1)	0.854 0(1)	0.972 1(2)
Co(6)	0.303 5(2)	0.747 0(2)	1.104 0(2)
C(11)	0.106(1)	0.923(1)	0.834(1)
O(11)	0.115 2(8)	0.982 6(9)	0.784(1)
C(12)	0.056(1)	0.717(1)	0.985(2)
O(12)	0.046(1)	0.655(1)	1.027(1)
C(13)	0.103(1)	0.900(1)	1.077(2)
O(13)	0.103(1)	0.948(1)	1.172(1)
C(14)	−0.045(1)	0.857(1)	0.932(2)
O(14)	−0.113 8(9)	0.879(1)	0.947(1)
C(21)	0.450(1)	0.560(1)	0.652(1)
O(21)	0.512 8(8)	0.519 7(9)	0.635(1)
C(22)	0.326(1)	0.636(1)	0.526(2)
O(22)	0.311 9(9)	0.646(1)	0.421(1)
C(23)	0.267(1)	0.516(1)	0.662(2)
O(23)	0.223 9(9)	0.447 3(8)	0.634(1)
C(31)	0.504(1)	0.678(1)	0.910(2)
O(31)	0.567 3(8)	0.637(1)	0.911(1)
C(32)	0.462(1)	0.853(2)	1.008(2)
O(32)	0.497(1)	0.919(1)	1.067(1)
C(41)	0.222(1)	0.514(1)	0.916(2)
O(41)	0.156 8(9)	0.474(1)	0.904(2)
C(42)	0.400(1)	0.487(1)	0.872(2)
O(42)	0.445 4(9)	0.427 2(9)	0.842(1)
C(43)	0.332(1)	0.579(1)	1.087(2)
O(43)	0.348(1)	0.552 9(8)	1.181(1)
C(51)	0.286(1)	0.958(1)	0.929(2)
O(51)	0.306 5(9)	1.023 2(8)	0.905(1)
C(52)	0.292(1)	0.901(1)	1.130(2)
O(52)	0.305(1)	0.956 1(9)	1.218(1)
C(61)	0.218(1)	0.747(1)	1.200(2)
O(61)	0.163(1)	0.747(1)	1.270(1)
C(62)	0.389(1)	0.764(1)	1.212(2)
O(62)	0.449(1)	0.773(1)	1.278(1)
P(1)	0.420 7(3)	0.769 7(3)	0.721 6(4)
C(111)	0.532(1)	0.761(1)	0.662(1)
C(112)	0.541(1)	0.729(1)	0.536(1)
C(113)	0.624(1)	0.731(2)	0.492(2)
C(114)	0.695(1)	0.758(1)	0.566(2)
C(115)	0.685(1)	0.791(2)	0.684(2)
C(116)	0.604(1)	0.792(1)	0.736(2)
C(121)	0.378(1)	0.867(1)	0.662(1)
C(122)	0.299(1)	0.865(1)	0.608(2)
C(123)	0.273(1)	0.937(2)	0.555(2)
C(124)	0.327(1)	1.012(1)	0.558(2)
C(125)	0.408(1)	1.014(1)	0.614(2)
C(126)	0.433(1)	0.943(1)	0.665(2)
P(2)	0.043 3(3)	0.729 3(3)	0.708 6(4)
C(211)	−0.005(1)	0.789(1)	0.602(2)
C(212)	−0.062(1)	0.857(1)	0.633(2)
C(213)	−0.098(1)	0.903(1)	0.552(2)
C(214a)^a	−0.086(3)	0.857(4)	0.414(5)
C(215a)^a	−0.060(4)	0.755(4)	0.380(5)
C(216a)^a	−0.010(4)	0.738(4)	0.479(4)
C(214b)^a	−0.067(3)	0.902(3)	0.459(3)
C(215b)^a	0.002(3)	0.843(4)	0.423(4)
C(216b)^a	0.033(3)	0.799(3)	0.503(4)
C(221)	−0.032(1)	0.630(1)	0.703(2)
C(222)	0.002(1)	0.549(1)	0.726(2)
C(223)	−0.053(2)	0.478(1)	0.732(3)
C(224)	−0.137(2)	0.485(2)	0.718(2)
C(225)	−0.171(2)	0.559(2)	0.691(3)
C(226)	−0.118(1)	0.634(1)	0.685(3)
C(1)	0.146(1)	0.684(1)	0.651(1)
C(2)	0.216(1)	0.694(1)	0.723(1)
C(3)	0.206(1)	0.746(1)	0.850(1)
C(4)	0.261 8(9)	0.719(1)	0.937(1)
Cl(11)^a	0.146(2)	1.255(4)	0.860(4)
Cl(12)^a	0.322(2)	1.245(6)	0.818(5)
C(10)^{a,b}	0.244(2)	1.230(5)	0.910(4)
Cl(21)^a	0.224(3)	1.301(3)	1.024(2)
Cl(22)^a	0.235(3)	1.249(3)	0.777(2)
C(20)^{a,b}	0.284(2)	1.249(3)	0.909(2)

^{a} Site occupancy factor = 0.5. ^{b} Refined with isotropic thermal parameters.

were separable into disordered components which were independently refined, with populations ultimately set at 0.5. Thermal parameters for the dichloromethane C atoms were refined using the isotropic form. Assignment of the Re *vs./cf.* Os atoms was largely influenced by the associated chemistry, as was the hydrogen component of the carbon string.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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