Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 36.[1] Reactions of the Dimetal Compounds $[ReM(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (M = Cr, Mo, or W) with Octacarbonyldicobalt; Crystal Structures of $[Co_2WRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ and $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$*

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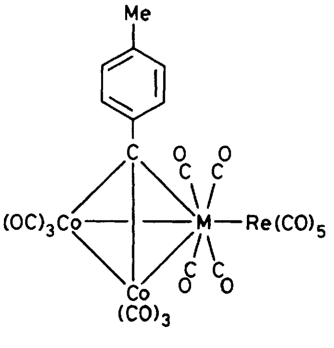
Treatment of the compounds $[ReM(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (M = Cr, Mo, or W) with $[Co_2(CO)_8]$ in light petroleum at room temperature afforded the tetranuclear metal complexes $[Co_2MRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$. The structure of the tungsten-containing species has been established by *X*-ray diffraction. Crystals are monoclinic (space group $P2_1$), with two crystallographically independent molecules in the asymmetric unit. The two cobalt atoms and the tungsten form a triangle [mean Co–W 2.72(1), mean Co–Co 2.482(3) Å], to which the rhenium atom is attached *via* the tungsten [mean Re–W 3.13(2) Å]. The Co_2W triangle is capped by the tolylmethylidyne ligand [mean μ-C–W 2.08(2), mean μ-C–Co 1.94(2) Å]. The carbonyl ligands are all terminally bound; five to the rhenium, four to the tungsten, and three to each cobalt. When toluene solutions of the tetranuclear metal compounds are heated to *ca.* 100 °C, they are converted into a dicobaltrhenium complex $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$, with concomitant formation of the hexacarbonyls $[M(CO)_6]$. An *X*-ray crystallographic study established the structure of the dicobaltrhenium species. Crystals are monoclinic (space group $P2_1/c$). The metal-atom triangle [Co–Co 2.535(1), mean Co–Re 2.70(2) Å] is asymmetrically triply bridged by the tolylmethylidyne group [μ_3-C–Re 2.189(6), mean μ_3-C–Co 1.89(1) Å]. The carbonyl ligands are terminally bound to the metal atoms; four to the rhenium, and three to each cobalt. Spectroscopic data (i.r. and n.m.r.) for the new compounds are reported and discussed.

Several heteronuclear metal complexes have been prepared from reactions between the tolylmethylidynetungsten compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) and organo-dimetal complexes. Examples of cluster species made in this manner include $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ from $[Co_2(CO)_8]$,[2] $[Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$ from $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$,[3] $[MRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (M = Co or Rh) from $[MRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[3,4] and $[Mo_2W(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$ from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[5] Although there are strong indications that the dimetal compounds react *via* a dissociative pathway, these syntheses represent an important and systematic route to complexes containing a CM_2W (M = Co, Rh, Ni, Mo, or W) core structure.[6]

In order to extend the scope of this preparative route to heteronuclear metal clusters, we have studied reactions of the compounds $[ReM(\equiv CR)(CO)_9]$ (M = Cr, Mo, or W) with dimetal carbonyl complexes and herein report results using octacarbonyldicobalt. In the compounds $[ReM(\equiv CR)(CO)_9]$, the carbyne ligand is terminally bound to the sub-Group 6 metal atom and is *trans* to the $Re(CO)_5$ moiety.[7,8] Hence with $[Co_2(CO)_8]$ it was envisaged that clusters would be formed containing a CCo_2M core with an external $Re(CO)_5$ group attached to the Cr, Mo, or W atoms. Such species, if formed, might be precursors to other clusters.



	M
(1a)	Cr
(1b)	Mo
(1c)	W

Results and Discussion

In light petroleum at room temperature, the compounds $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ and $[Co_2(CO)_8]$ afford a green complex (**1a**), characterised by microanalysis and spectroscopic properties (Tables 1 and 2). Similar compounds (**1b**) and (**1c**) were prepared from the dimetal complexes $[ReM(\equiv CR)(CO)_9]$ (M = Mo or W), data for which are also given in the Tables. A characteristic feature of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the three products (**1**) was the absence of a resonance attributable to an alkylidyne group ligating a single metal atom or bridging two metal atoms. Instead, signals were observed [δ 294.2 (**1a**), 272.0 (**1b**), and 260.0 (**1c**)] characteristic for carbon atoms of alkylidyne groups capping a trimetal centre.[9] The $^{13}C\text{-}\{^1H\}$

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* 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-3-(pentacarbonylrhenio)-μ_3-(*p*-tolylmethylidyne)-*triangulo*-dicobalt-tungstenand 1,1,1,2,2,2,3,3,3,3-decacarbonyl-μ_3-(*p*-tolylmethylidyne)-*triangulo*-dicobaltrhenium respectively.

Supplementary data available (No. SUP 56229, 10 pp.): H-atom coordinates, thermal parameters, complete bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical[a] and physical data for the tri- and tetra-nuclear metal compounds

Compound	M.p.[b] (θ_c/°C)	Colour	Yield (%)	ν(CO)[c]/cm^{-1}	Analyses (%)	
					C	H
(**1a**) $[Co_2CrRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$	119	Green	69	2 123w, 2 084s, 2 052vs, 2 039s, 2 028s, 2 024s, 1 997w, 1 983w, 1 926w, br	31.2 (31.4)	0.8 (0.8)
(**1b**) $[Co_2MoRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$	112	Green	64	2 116w, 2 081s, 2 052vs, 2 039s, 2 033s, 2 019s, 2 016s, 1 989m, 1 952w, br	29.9 (30.8)	0.8 (1.0)
(**1c**) $[Co_2WRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$		Green	75	2 118w, 2 083s, 2 053s, 2 040m, 2 032s, 2 021s, 2 016s, 1 990m, 1 945w, br	27.4 (27.3)	0.8 (0.7)
(**2**) $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$	84	Red	90	2 101w, 2 058vs, 2 045s, 2 035s, 2 014m, 2 004m, 1 991w(sh), 1 964w	31.6 (31.5)	1.0 (1.0)
(**3**) $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta^6\text{-}C_6H_5Me)]$		Brown	15	2 105w, 2 066m, 2 049w, 2 022s, 1 996m, 1 977m, 1 932m, br	37.3 (37.9)	2.1 (2.2)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In light petroleum.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the tri- and tetra-nuclear metal compounds

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(**1a**)	2.38 (s, 3 H, Me-4), 7.21 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8]	294.2 (μ_3-C), 236.6 [Cr(CO)], 200.8 [br, Co(CO)], 190.1 [4 CO, Re(CO)], 179.4 [1 CO, Re(CO)], 157.9 [$C^1(C_6H_4)$], 137.8, 128.9, 128.1 (C_6H_4), 21.3 (Me-4)
(**1b**)	2.37 (s, 3 H, Me-4), 7.17 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8]	272.0 (μ_3-C), 222.1 [Mo(CO)], 199.1 [br, Co(CO)], 190.7 [4 CO, Re(CO)], 179.9 [1 CO, Re(CO)], 157.0 [$C^1(C_6H_4)$], 136.7, 127.8, 127.0 (C_6H_4), 20.1 (Me-4)
(**1c**)	2.39 (s, 3 H, Me-4), 7.17 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8][d]	260.0 (μ_3-C), 212.0 [W(CO), *J*(WC) 118], 198.7 [br, Co(CO)], 190.6 [4 CO, Re(CO)], 180.7 [1 CO, Re(CO)], 159.0 [$C^1(C_6H_4)$], 137.6, 128.8, 128.1 (C_6H_4), 21.2 (Me-4)
(**2**)	2.44 (s, 3 H, Me-4), 7.23 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8]	297.9 (μ_3-C), 196.5 (CO), 157.0 [$C^1(C_6H_4)$], 141.1, 131.1, 129.0 (C_6H_4), 21.5 (Me-4)
(**3**)	2.06 (s, 3 H, C_6H_5Me), 2.41 (s, 3 H, Me-4), 5.74 (m, 2 H, C_6H_5), 5.93 (m, 3 H, C_6H_5), 7.28 [$(AB)_2$ system, 4 H, C_6H_4, *J*(AB) 8][d]	287.9 (μ_3-C), 199.6, 196.4, 190.8 (br, CO), 161.7 [$C^1(C_6H_4)$], 138.4, 130.9, 128.7 (C_6H_4), 109.6, 100.0 98.3, 97.7, 97.2, 96.9 (C_6H_5), 21.5 (Me-4), 19.6 (C_6H_5Me)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$; measured in CD_2Cl_2–CH_2Cl_2. [d] Measured in CD_2Cl_2.

n.m.r. spectra of the compounds (**1**) were also informative in the CO region, showing the expected two resonances for a $Re(CO)_5$ group (relative intensity 4:1) (Table 2).

In order to establish firmly the molecular structure of these products, an *X*-ray diffraction study was carried out on (**1c**) for which suitable crystals were available. Selected internuclear distances and angles are summarised in Table 3.

The unit cell contains two crystallographically independent molecules (i) and (ii). Close inspection of the relevant parameters reveals some differences between the two molecules but the principal structural features are identical, and only molecule (ii) is shown in Figure 1 and its data discussed here. As expected a Co_2W triangle of metal atoms is capped by the tolylmethylidyne ligand. The dimensions of the CCo_2W core [μ-C–W 2.07(2), mean μ-C–Co 1.94(2), Co–Co 2.482(3), mean Co–W 2.724(2) Å] are very similar to those previously found in the complex $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ [μ-C–W 2.103(7), μ-C–Co 1.953(6), Co–Co 2.488(1), Co–W 2.672(1) Å].[2] The two cobalt atoms each carry three essentially terminal and orthogonal carbonyl ligands, whilst the tungsten atom has a distorted planar array of four terminal carbonyl groups which are bent towards the attached $Re(CO)_5$ moiety. The four radial CO ligands of the latter are staggered with respect to the four similar groups on the tungsten atom, and the resulting molecule has an approximate plane of mirror symmetry defined by the Re, W, and μ-C atoms, and the midpoint of the Co–Co vector.

No compounds with rhenium–tungsten bonds which are unsupported by bridging groups appear to have been previously studied by *X*-ray diffraction. The Re–W separation [3.138(1) Å] in (**1c**) is somewhat longer than those reported for the two complexes $[ReW\{\mu\text{-}C(C_6H_4Me\text{-}4)(PMe_3)\}(\mu\text{-}CO)(CO)_7(PMe_3)]$ [2.968(2) Å][8] and $[N(PPh_3)_2][ReW\{\mu\text{-}$

Table 3. Selected internuclear distances (Å) and angles (°) for [$Co_2WRe(\mu_3-CC_6H_4Me-4)(CO)_{15}$] (**1c**)

Molecule (i)		Molecule (ii)		Molecule (i)		Molecule (ii)	
W(1)–Re(1)	3.112(1)	W(2)–Re(2)	3.138(1)	W(1)–Co(11)	2.735(2)	W(2)–Co(21)	2.725(2)
W(1)–Co(12)	2.704(2)	W(2)–Co(22)	2.722(2)	W(1)–C(11)	2.02(2)	W(2)–C(21)	2.01(2)
W(1)–C(12)	2.00(2)	W(2)–C(22)	2.03(1)	W(1)–C(13)	2.02(2)	W(2)–C(23)	2.01(2)
W(1)–C(14)	2.04(2)	W(2)–C(24)	2.05(2)	W(1)–C(120)	2.09(1)	W(2)–C(220)	2.07(2)
Re(1)–C(15)	1.91(2)	Re(2)–C(25)	1.92(2)	Re(1)–C(19)	2.01(2)	Re(2)–C(26)	1.96(2)
Re(1)–C(18)	1.98(2)	Re(2)–C(27)	1.92(2)	Re(1)–C(17)	1.96(2)	Re(2)–C(28)	1.96(2)
Re(1)–C(16)	2.01(2)	Re(2)–C(29)	1.97(2)	Co(11)–Co(12)	2.482(3)	Co(11)–Co(22)	2.482(3)
Co(11)–C(110)	1.81(2)	Co(21)–C(210)	1.76(2)	Co(11)–C(111)	1.81(2)	Co(21)–C(211)	1.80(2)
Co(11)–C(112)	1.78(2)	Co(21)–C(212)	1.181(2)	Co(11)–C(120)	1.93(1)	Co(21)–C(220)	1.94(2)
Co(12)–C(113)	1.85(2)	Co(22)–C(213)	1.82(2)	Co(12)–C(115)	1.76(2)	Co(22)–C(214)	1.79(2)
Co(12)–C(114)	1.76(2)	Co(22)–C(215)	1.79(2)	Co(12)–C(120)	1.93(2)	Co(22)–C(220)	1.94(2)
Mean C–O(W)	1.16(2)	Mean C–O(W)	1.16(2)	Mean C–O(Re)	1.13(3)	Mean C–O(Re)	1.17(2)
Mean C–O(Co)	1.14(3)	Mean C–O(Co)	1.14(2)				
Re(1)–W(1)–Co(11)	149.0(1)	Re(2)–W(2)–Co(21)	148.7(1)	Re(1)–W(1)–Co(12)	150.9(1)	Re(2)–W(2)–Co(22)	54.2(1)
Co(11)–W(1)–Co(12)	54.3(1)	Co(21)–W(2)–Co(22)	54.2(1)	Re(1)–W(1)–C(120)	155.9(4)	Re(2)–W(2)–C(220)	156.5(4)
Co(11)–W(1)–C(120)	44.7(4)	Co(21)–W(2)–C(220)	45.3(4)	Co(12)–W(1)–C(120)	45.3(4)	Co(22)–W(2)–C(220)	45.4(4)
W(1)–Co(11)–Co(12)	62.2(1)	W(2)–Co(21)–Co(22)	62.8(1)	W(1)–Co(11)–C(120)	49.6(4)	W(2)–Co(21)–C(220)	49.2(5)
Co(12)–Co(11)–C(120)	50.0(4)	Co(22)–Co(21)–C(220)	50.3(4)	W(1)–Co(12)–Co(11)	63.5(1)	W(2)–Co(22)–Co(21)	63.0(1)
W(1)–Co(12)–C(120)	50.2(4)	W(2)–Co(22)–C(220)	49.3(5)	Co(11)–Co(12)–C(120)	49.9(4)	Co(21)–Co(22)–C(220)	50.3(5)
W(1)–C(120)–Co(11)	85.7(5)	W(2)–C(220)–Co(21)	85.5(6)	W(1)–C(120)–Co(12)	84.5(5)	W(2)–C(220)–Co(22)	85.3(6)
Co(11)–C(120)–Co(12)	80.0(5)	Co(21)–C(220)–Co(22)	79.4(5)	W(1)–C(120)–C(121)	131.9(9)	W(2)–C(220)–C(221)	137.0(10)
Co(11)–C(120)–C(121)	128.2(8)	Co(21)–C(220)–C(221)	124.5(10)	Co(12)–C(120)–C(121)	128.9(9)	Co(22)–C(220)–C(221)	126.5(10)
Mean W–C–O	175(2)	Mean W–C–O	176(3)	Mean Re–C–O	177(2)	Mean Re–C–O	176(2)
Mean Co–C–O	177(2)	Mean Co–C–O	177(2)				

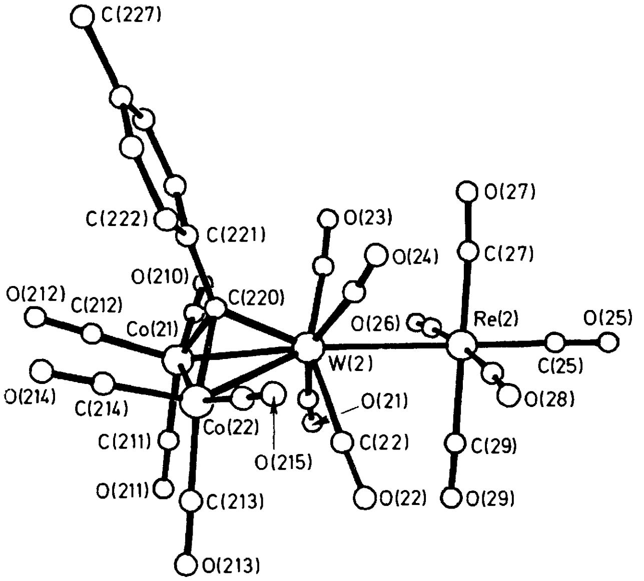


Figure 1. The molecular structure of $[Co_2WRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (**1c**) showing the atom-numbering scheme for molecule (ii) in the asymmetric unit (see text)

$CH(C_6H_4Me\text{-}4)\}(CO)_9]$ [3.033(1) Å],[10] both of which contain bridging ligands. The contraction of metal–metal separations by bridging ligands, other than hydride, is commonly observed.[11]

When the complexes (**1**) are heated in toluene, the colour of the solution changes from green to red. Chromatography of the mixture affords a new air-stable compound (**2**). This transformation proceeds in a matter of minutes for (**1a**) and (**1b**), but for (**1c**) refluxing in toluene for several hours is required for the conversion to be complete. Moreover, in the thermolysis of (**1c**) small quantities of a further product (**3**) can be isolated. Monitoring of the reaction involving (**1c**) by i.r. revealed that the conversion into (**2**) is accompanied by the formation of hexacarbonyltungsten.

Data for (**2**) and (**3**) are given in Tables 1 and 2. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra for both species showed the characteristic resonance for a μ_3-C nucleus: δ 297.9 p.p.m. for (**2**) and 287.9 p.p.m. for (**3**). However, the spectroscopic data alone were insufficient to characterise structurally the compounds and an *X*-ray diffraction study was carried out on (**2**). Selected distances and angles are summarised in Table 4, and the structure is shown in Figure 2.

The molecule possesses a trimetallatetrahedrane CCo_2Re core. Since the groups $Co(CO)_3$, $Re(CO)_4$, and CR are isolobal,[12] the structure is closely related to that of the long known compounds $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = H, alkyl, or aryl).[13,14] It is interesting to compare the Co–Co [2.535(1) Å] and μ-C–Co [mean 1.89(1) Å] separations in (**2**) with the corresponding distances in $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ [mean Co–Co 2.468(7), mean μ_3-C–Co 1.90(2) Å].[15] The somewhat longer Co–Co bond in (**2**) may be attributed to replacement of a $Co(CO)_3$ group in the homonuclear tricobalt compound by the larger $Re(CO)_4$ fragment. Compound (**2**) appears to be the first example of a species with a Co–Re bond studied by *X*-ray crystallography, and hence comparison of this metal–metal bond distance [mean 2.70(2) Å] with others involving these elements is not possible. The μ-C–Re distance [2.189(6) Å] is somewhat shorter than that recently found [2.248(12) Å] for the triply-bridging tolylmethylidyne ligand in the complex $[ReW_2(\mu\text{-}Br)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$.[16]

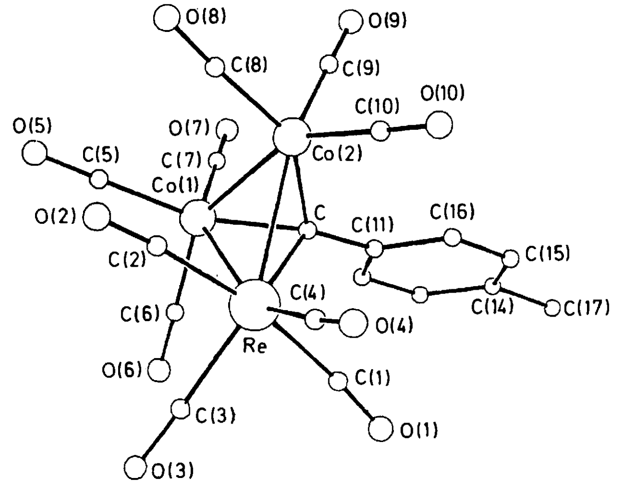
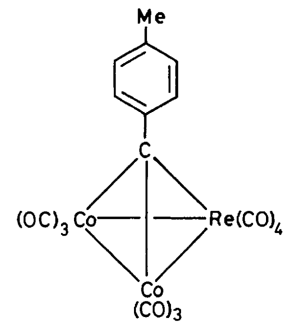
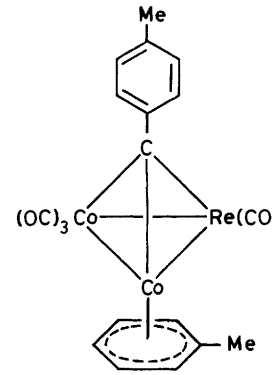


Figure 2. The molecular structure of $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (**2**) showing the atom-numbering scheme



(2)



(3)

The carbonyl groups in (**2**) are all terminally bound to the metal atoms, three to each cobalt and four to the rhenium. While the molecule is not subject to any crystallographically imposed symmetry, it does have virtual C_s symmetry with an approximate mirror plane passing through the atoms Re and C and the midpoint of the Co(1)–Co(2) vector.

Having established the molecular structure of (**2**), it is possible to identify the side product (**3**) of the thermolysis of (**1c**) as the η^6-toluene complex shown. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra support the structure proposed. Both spectra show resonances due to the presence of a C_6H_5Me ligand (Table 2). Evidently under the relatively vigorous conditions required to convert (**1c**) to (**2**) in refluxing toluene, three CO ligands on one of the cobalt atoms are replaced by a toluene molecule.

Table 4. Selected internuclear distances (Å) and angles (°) for $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (**2**)

Re–Co(1)	2.686(1)	Re–C(2)	1.999(7)	Co(1)–C	1.896(6)	Co(1)–C(7)	1.794(7)
Re–Co(2)	2.720(1)	Re–C(3)	1.951(7)	Co(2)–C	1.880(6)	Co(2)–C(8)	1.821(7)
Re–C	2.189(6)	Re–C(4)	1.933(6)	Co(1)–C(5)	1.828(7)	Co(2)–C(9)	1.800(8)
Re–C(1)	1.993(8)	Co(1)–Co(2)	2.535(1)	Co(1)–C(6)	1.756(8)	Co(2)–C(10)	1.795(7)
Mean C–O(Re)	1.133(9)			Mean C–O(Co)	1.14(2)		

Co(1)–Re–Co(2)	55.9(1)	Re–Co(1)–Co(2)	62.7(1)	Re–Co(2)–Co(1)	61.3(1)	Co(1)–C–Co(2)	84.4(3)
Co(1)–Re–C	44.3(2)	Re–Co(1)–C	53.8(2)	Re–Co(2)–C	53.1(2)	Co(1)–C–Re	81.9(2)
Co(2)–Re–C	43.4(2)	Co(2)–Co(1)–C	47.6(2)	Co(1)–Co(2)–C	48.1(2)	Co(2)–C–Re	83.5(2)
Co(1)–Re–C(1)	107.3(2)	Re–Co(1)–C(5)	105.8(2)	Re–Co(2)–C(8)	108.6(2)	Co(1)–C–C(11)	131.4(4)
Co(1)–Re–C(2)	81.5(2)	Re–Co(1)–C(6)	82.7(2)	Re–Co(2)–C(9)	148.3(2)	Co(2)–C–C(11)	130.2(4)
Co(1)–Re–C(3)	106.8(2)	Re–Co(1)–C(7)	150.5(2)	Re–Co(2)–C(10)	92.2(2)	Re–C–C(11)	127.9(4)
Co(1)–Re–C(4)	153.3(2)	Co(2)–Co(1)–C(5)	100.7(2)	Co(1)–Co(2)–C(8)	99.8(2)		
Co(2)–Re–C(1)	113.8(2)	Co(2)–Co(1)–C(6)	142.6(3)	Co(1)–Co(2)–C(9)	98.1(2)		
Co(2)–Re–C(2)	77.4(2)	Co(2)–Co(1)–C(7)	99.5(2)	Co(1)–Co(2)–C(10)	151.2(2)		
Co(2)–Re–C(3)	156.5(2)	Mean Re–C–O	176(2)				
Co(2)–Re–C(4)	97.9(2)	Mean Co–C–O	177(2)				

Table 5. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for (**1c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	2 333(1)	5 000	4 582(1)	C(23)	3 429(12)	8 846(13)	8 757(11)
Re(1)	3 382(1)	3 353(1)	3 396(1)	O(23)	4 061(10)	8 703(11)	8 176(9)
W(2)	2 333(1)	9 136(1)	9 719(1)	C(24)	3 351(11)	9 925(13)	10 307(10)
Re(2)	3 512(1)	7 392(1)	10 446(1)	O(24)	3 925(11)	10 371(12)	10 590(9)
Co(11)	1 981(2)	5 880(2)	6 198(1)	C(25)	4 310(14)	6 412(15)	10 918(12)
Co(12)	1 831(2)	6 917(2)	4 883(1)	O(25)	4 715(9)	5 757(11)	11 207(9)
Co(21)	1 145(2)	9 787(2)	8 538(1)	C(26)	3 493(14)	6 683(15)	9 333(12)
Co(22)	1 003(2)	10 634(2)	9 986(1)	O(26)	3 443(12)	6 228(13)	8 712(11)
C(11)	3 547(10)	4 890(12)	5 197(9)	C(27)	4 713(13)	8 039(15)	9 980(13)
O(11)	4 287(11)	4 790(12)	5 462(10)	O(27)	5 418(11)	8 467(14)	9 645(10)
C(12)	3 212(12)	5 814(14)	3 725(11)	C(28)	3 409(12)	8 164(13)	11 534(11)
O(12)	3 682(11)	6 264(12)	3 149(10)	O(28)	3 283(11)	8 618(13)	12 208(10)
C(13)	1 710(11)	3 757(12)	5 133(10)	C(29)	2 254(12)	6 754(14)	10 871(11)
O(13)	1 318(11)	3 078(11)	5 481(10)	O(29)	1 531(10)	6 350(11)	11 131(9)
C(14)	1 386(10)	4 821(11)	3 663(9)	C(210)	1 755(14)	9 151(16)	7 632(12)
O(14)	874(9)	4 776(10)	3 136(8)	O(210)	2 167(12)	8 769(13)	7 017(11)
C(15)	4 050(12)	2 344(15)	2 679(11)	C(211)	−5(14)	9 135(16)	8 703(12)
O(15)	4 408(11)	1 713(13)	2 222(10)	O(211)	−697(12)	8 671(13)	8 786(11)
C(16)	4 616(12)	4 138(15)	3 460(11)	C(212)	836(13)	10 843(15)	7 904(12)
O(16)	5 312(10)	4 529(11)	3 527(9)	O(212)	652(12)	11 472(13)	7 459(11)
C(17)	3 089(12)	4 089(15)	2 353(11)	C(213)	−172(14)	10 127(16)	10 462(12)
O(17)	2 885(11)	4 505(13)	1 734(10)	O(213)	−909(11)	9 848(13)	10 795(10)
C(18)	2 106(11)	2 678(12)	3 380(10)	C(214)	611(12)	11 800(14)	9 589(11)
O(18)	1 370(9)	2 318(10)	3 377(8)	O(214)	378(10)	12 536(12)	9 347(9)
C(19)	3 621(13)	2 694(14)	4 526(12)	C(215)	1 490(14)	11 130(15)	10 927(13)
O(19)	3 737(12)	2 309(13)	5 138(11)	O(215)	1 795(12)	11 487(15)	11 525(11)
C(110)	1 957(13)	4 741(14)	6 817(11)	C(120)	1 141(9)	5 724(11)	5 285(9)
O(110)	1 917(11)	4 070(13)	7 235(10)	C(121)	39(4)	5 512(8)	5 387(6)
C(111)	3 108(15)	6 414(17)	6 489(14)	C(122)	−393(4)	4 994(8)	6 123(6)
O(111)	3 829(12)	6 753(14)	6 694(11)	C(123)	−1 405(4)	4 838(8)	6 242(6)
C(112)	1 075(11)	6 513(13)	6 923(11)	C(124)	−1 985(4)	5 200(8)	5 626(6)
O(112)	483(11)	6 887(11)	7 430(9)	C(125)	−1 533(4)	5 718(8)	4 891(6)
C(113)	3 045(12)	7 511(15)	4 853(11)	C(126)	−541(4)	5 875(8)	4 772(6)
O(113)	3 792(12)	7 829(13)	4 860(11)	C(127)	−3 123(15)	5 057(18)	5 801(14)
C(114)	1 553(13)	7 168(14)	3 814(12)	C(220)	2 139(10)	10 477(11)	9 106(9)
O(114)	1 317(11)	7 317(13)	3 118(10)	C(221)	2 793(8)	11 307(7)	8 679(7)
C(115)	1 002(14)	7 784(15)	5 416(12)	C(222)	2 868(8)	12 201(7)	9 122(7)
O(115)	483(10)	8 350(13)	5 770(10)	C(223)	3 415(8)	12 979(7)	8 711(7)
C(21)	1 593(12)	7 978(13)	9 303(11)	C(224)	3 887(8)	12 861(7)	7 857(7)
O(21)	1 257(10)	7 234(11)	9 076(9)	C(225)	3 812(8)	11 967(7)	7 415(7)
C(22)	1 525(11)	8 947(11)	10 912(10)	C(226)	3 266(8)	11 189(7)	7 826(7)
O(22)	1 108(9)	8 831(10)	11 610(8)	C(227)	4 434(23)	13 737(26)	7 363(21)

Substitution reactions of this kind have been previously observed[17] with the tricobalt compounds $[Co_3(\mu_3\text{-}CR)(CO)_9]$, and an *X*-ray crystallographic study has confirmed that the arene ligand is bonded to one of the cobalt atoms of the Co_3 triangle.[18]

Formation of (**2**), *via* reaction of the complexes $[ReM(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ with $[Co_2(CO)_8]$, and the intermediacy of the compounds (**1**), is of considerable interest. The overall process involves transfer of an alkylidyne group, terminally bound to Cr, Mo, or W, to a Co_2Re cluster. The formation of (**2**) and $[M(CO)_6]$ (M = Cr, Mo, or W) from (**1a**)—(**1c**) is not stoicheiometric and must involve either scavenging of CO molecules or formation of other sub-Group 6 metal by-products.

Initially we had considered the possibility that on heating in a suitable solvent the complexes (**1**) might undergo a cluster expansion reaction affording stable 60-electron tetranuclear metal compounds of composition $[Co_2MRe(\mu_3\text{-}CR)(CO)_{13}]$. However, no evidence for these species was obtained, nor for 62-electron clusters with a 'butterfly' metal-atom core. Nevertheless, this does not preclude their possible intermediacy prior to ejection of an $M(CO)_n$ fragment. Comparison between the formation of (**2**) and earlier work is merited. Vahrenkamp and co-workers[19] have prepared several heteronuclear cluster compounds *via* cluster expansion reactions followed by subsequent loss of mononuclear metal fragments. Thus treatment of the tricobalt compounds $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = H, alkyl, aryl, or halide) with the organometal arsenide complexes $[M(AsMe_2)(CO)_3(\eta\text{-}C_5H_5)]$ (M = Cr, Mo, or W) affords in the first step substitution products in which a CO ligand on the alkylidyne(nonacarbonyl)tricobalt cluster is displaced by the $AsMe_2$ moiety of the reactant. The resulting CCo_3 clusters contain pendant $As(Me_2)M(CO)_3(\eta\text{-}C_5H_5)$ groups, and on heating metal exchange occurs to give the clusters $[Co_2M(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ and a $Co(AsMe_2)(CO)_3$ species is eliminated. Application of this type of reaction to the compound $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ clearly identified a step-wise process with the intermediacy of a tetranuclear metal cluster having a SCo_2FeM core structure, which subsequently ejected $[Co(AsMe_2)(CO)_3]_x$.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. The instrumentation used to obtain spectroscopic information has been listed previously.[4] The compounds $[ReM(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (M = Cr, Mo, or W) were prepared by the method described earlier.[7,8] Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Compounds $[Co_2MRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (M = Cr, Mo, *or* W).—The three complexes were prepared in a similar manner, the following synthesis of compound (**1a**) illustrating the method employed.

A mixture of $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (0.30 g, 0.50 mmol) and $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol) in light petroleum (15 cm^3) was stirred at room temperature for 1 h. The supernatant liquid was removed and the dark green residue extracted with light petroleum (4 × 10 cm^3). The mother-liquor and the extracts were combined and chromatographed on a Florisil column (*ca.* 20 × 2 cm). Elution with light petroleum afforded, after removal of solvent *in vacuo*, dark green *microcrystals* of $[Co_2CrRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (**1a**) (0.30 g).

Formation of the Complex $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$.—A solution of (**1a**) (0.44 g, 0.50 mmol) in toluene (20 cm^3) was warmed to *ca.* 100 °C for 10 min, a colour change from green to red being observed. Solvent was removed *in vacuo* and the residue extracted with light petroleum (5 × 10 cm^3), the extracts being combined and chromatographed on a Florisil column. Elution with the same solvent gave a single red eluate, which after removal of volatile material *in vacuo* afforded red *microcrystals* of $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (**2**) (0.42 g).

Thermolysis of (**1b**) under similar conditions gave (**2**) in somewhat lower (70%) yield. Conversion of (**1c**) into (**2**) required more vigorous conditions, *ca.* 5 h in refluxing toluene (yields 50—60%). Compound (**3**) was also formed (< 15%) in this reaction and separated by column chromatography.

Table 6. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for (**2**)

Atom	x	y	z
Re	2 070(1)	1 567(1)	2 468(1)
Co(1)	1 705(1)	813(1)	993(1)
Co(2)	4 287(1)	1 106(1)	1 548(1)
C	2 743(6)	2 004(5)	1 298(3)
C(1)	1 480(9)	3 018(6)	2 414(4)
C(2)	2 445(7)	109(5)	2 724(4)
C(3)	253(8)	1 349(5)	2 970(4)
C(4)	3 222(7)	1 906(5)	3 427(4)
C(5)	1 559(7)	−559(5)	1 111(4)
C(6)	−92(8)	1 210(6)	1 081(4)
C(7)	1 975(7)	892(5)	−46(4)
C(8)	4 841(7)	−197(5)	1 747(4)
C(9)	5 118(7)	1 267(5)	622(4)
C(10)	5 585(7)	1 750(5)	2 205(4)
C(11)	2 747(6)	3 020(4)	945(3)
C(12)	1 667(7)	3 341(5)	382(4)
C(13)	1 653(7)	4 318(5)	78(4)
C(14)	2 716(8)	5 008(5)	311(4)
C(15)	3 778(8)	4 701(5)	857(4)
C(16)	3 812(7)	3 718(5)	1 156(4)
C(17)	2 670(9)	6 081(6)	6(5)
O(1)	1 064(7)	3 821(4)	2 422(4)
O(2)	2 595(6)	−702(4)	2 926(3)
O(3)	−824(6)	1 190(5)	3 244(4)
O(4)	3 955(6)	2 069(4)	3 974(3)
O(5)	1 445(7)	−1 413(4)	1 136(4)
O(6)	−1 302(6)	1 467(5)	1 079(4)
O(7)	2 111(7)	951(5)	−705(3)
O(8)	5 229(7)	−1 001(4)	1 845(3)
O(9)	5 643(6)	1 371(4)	45(3)
O(10)	6 425(6)	2 139(4)	2 615(3)

Crystal Structure Determinations.—(*a*) $[Co_2WRe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (**1c**). Crystals of compound (**1c**) grow as deep green prisms. Diffracted intensities were recorded at 298 K from a crystal of dimensions *ca.* 0.40 × 0.45 × 0.20 mm. Of the 5 180 independent reflections ($2\theta \leqslant 50°$), measured on a Nicolet *P*3*m* four-circle diffractometer (ω scans), 4 730 had $I \geqslant 3\sigma(I)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by a semi-empirical method based upon azimuthal scan data.[20]

Crystal data for (**1c**). $C_{23}H_7Co_2O_{15}ReW$, M = 1 011.2, monoclinic, a = 13.726(5), b = 13.504(4), c = 15.316(3) Å, β = 82.96(2)°, U = 2 817(2) Å^3, Z = 4, D_c = 2.38 g cm^{-3}, $F(000)$ = 1 872, space group $P2_1$ (no. 4), $\mu(Mo\text{-}K_\alpha)$ = 97.3 cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å.

The solution and refinement of the structure was similar to that described for compound (**2**) below, except in the following respects: only the metal atoms were refined with anisotropic thermal parameters, and hydrogen atoms were not included in the refinement. The aryl ring system was refined as a rigid group (C–C = 1.395 Å) with the constituent atoms being given individual, refined, isotropic thermal parameters. Refinement with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ converged at R = 0.038 (R' = 0.039). Refinement of the alternative enantiomeric configuration was marginally worse (R = 0.042). The final electron-density difference synthesis showed no peaks $\geqslant$ 1 e Å^{-3}.

(*b*) $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (**2**). Crystals of (**2**) grow as well formed red rectangular prisms. That chosen for data collection was of dimensions *ca.* 0.3 × 0.2 × 0.1 mm. Data were collected as for (**1c**). Of the 2 673 independent reflections (θ–2θ scans, $2\theta \leqslant 45°$), 2 192 with $I \geqslant 3\sigma(I)$ were used for the structure solution and refinement.

Crystal data for (**2**). $C_{18}H_7Co_2O_{10}Re$, $M = 687.4$, monoclinic $a = 9.238(4)$, $b = 13.204(9)$, $c = 16.905(7)$ Å, $\beta = 93.73(4)°$, $U = 2\,058(2)$ Å^3, $Z = 4$, $D_c = 2.22$ g cm^{-3}, $F(000) = 1\,296$, space group $P2_1/c$ (no. 14), $\mu(\text{Mo-}K_\alpha) = 75.9$ cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included in calculated positions and given fixed isotropic thermal parameters 1.2 times $U_{\text{equiv.}}$ of their parent carbon atoms. All remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,3|F|^2]$, converged at $R = 0.025$ ($R' = 0.025$). The final electron-density difference synthesis showed no peaks $\geqslant 0.8$ e Å^{-3}. Scattering factors with corrections for the effects of anomalous dispersion were from ref. 21. All calculations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[20] Atomic co-ordinates for (**1c**) and (**2**) are listed in Tables 5 and 6, respectively.

Acknowledgements

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References

1 Part 35, D. Hodgson, J. A. K. Howard, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1985, 1331.
2 M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitrprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699.
3 M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 2475.
4 C. Marsden, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 1315.
5 M. Green, S. J. Porter, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 513.
6 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, p. 383.
7 E. O. Fischer, T. L. Lindner, F. R. Kreissl, and P. Braunstein, *Chem. Ber.*, 1977, **110**, 3139.
8 W. Uedelhoven, D. Neugebauer, and F. R. Kreissl, *J. Organomet. Chem.*, 1981, **217**, 183.
9 E. Delgado, A. T. Emo, J. C. Jeffery, N. D. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 1323 and refs. therein.
10 J. C. Jeffery, A. G. Orpen, W. T. Robinson, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1984, 396.
11 M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.
12 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.
13 D. Seyferth, *Adv. Organomet. Chem.*, 1976, **14**, 97.
14 B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, 1973, **6**, 73.
15 P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, 1967, **89**, 261.
16 G. A. Carriedo, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597.
17 B. H. Robinson and J. L. Spencer, *J. Chem. Soc. A*, 1971, 2045.
18 R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, 1972, **11**, 1855.
19 H. Vahrenkamp, *Adv. Organomet. Chem.*, 1983, **22**, 169; H. Beurich and H. Vahrenkamp, *Chem. Ber.*, 1982, **115**, 2385; F. Richter and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 531.
20 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P3m X*-ray system, University of Cambridge, 1976; updated Göttingen, 1981.
21 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

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