Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 73.[1] Reactions of $[WCo(\equiv CR)(CO)_8]$ (R = C_6H_4Me-4 or Me) with Alkynes. Crystal Structures of $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$ and $[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)][BF_4]$*

Ian J. Hart, John C. Jeffery, Markus J. Grosse-Ophoff, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

In light petroleum at room temperature the compound $[WCo(\equiv CR)(CO)_8]$ (R = C_6H_4Me-4) reacts with MeC≡CMe or EtC≡CEt to give the complexes $[WCo\{\mu\text{-}C(R)C(R^1)C(R^1)C(O)\}(CO)_7]$ (R^1 = Me or Et), whereas MeC≡CEt affords an inseparable mixture of the species $[WCo\{\mu\text{-}C(R)C(R^1)C(R^2)\text{-}C(O)\}(CO)_7]$ (R^1 = Me, R^2 = Et; R^1 = Et, R^2 = Me). Reactions between $[WCo(\equiv CMe)(CO)_8]$ and MeC≡CMe or MeC≡CPh yield the compounds $[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_7]$ and $[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(O)\}(CO)_7]$, respectively. Treatment of these various products with PPh_3 leads to substitution of a CO ligand on the cobalt atom by the phosphine, and the structure of one of these derivatives $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$ has been established by *X*-ray diffraction. The W–Co bond [2.737(1) Å] is spanned by the $C(C_6H_4Me\text{-}4)\text{-}C(Me)C(Me)C(O)$ fragment, with the terminal carbon atoms of the chain σ bonded to the cobalt, and with the carbon atoms of the $C(C_6H_4Me\text{-}4)C(Me)C(Me)$ moiety η^3 co-ordinated to the tungsten. The latter carries four terminal CO groups, and the cobalt two such ligands and the PPh_3 group [Co–P 2.237(2) Å, P–Co–W 146.4(1)°]. Protonation of the complex $[WCo\{\mu\text{-}C(Me)C(Me)C(Me)\text{-}C(O)\}(CO)_7]$ with $HBF_4\cdot Et_2O$ affords the salt $[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(OH)\}(CO)_7][BF_4]$. Three PPh_3 derivatives of the alkyne-adducts of $[WCo(\equiv CR)(CO)_8]$ (R = C_6H_4Me-4 or Me) have also been protonated, and the structure of the salt $[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)]$ $[BF_4]$ has been established by *X*-ray diffraction. The results confirm that in the latter the phenyl group is attached to the carbon atom at the end of the μ-C_4 chain, and that this carbon atom and that of the C(OH) group are σ bonded to the cobalt. The tungsten atom is ligated by all four carbon atoms of the bridging ligand, by the cobalt atom [W–Co 2.660(1) Å], and by four terminal carbonyl groups. The cobalt atom carries two terminal carbonyl ligands and the PPh_3 group [Co–P 2.261(1) Å] with the latter sited transoid to the W–Co bond [P–Co–W 144.8(1)°]. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed in relation to their structures.

We are currently exploring the chemistry of the compounds $[WM(\equiv CR)(CO)_4L_n]$ [R = C_6H_4Me-4, ML_n = $Co(CO)_4$ (**1a**), $Mo(CO)_3(\eta\text{-}C_5H_5)$ (**1c**), or $Re(CO)_5$ (**1d**); R = Me, ML_n = $Co(CO)_4$ (**1b**)],[2] and in this paper report reactions of (**1a**) and (**1b**) with some alkynes. The new results are related to the recently reported[3] synthesis of the complexes $[MoW\{\mu\text{-}C(R)C(Me)C(Me)\}(CO)_3(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)]$ (**2**) and $[MoW\{\mu\text{-}C(R)C(=CH_2)CH(Me)C(O)\}(CO)_6(\eta\text{-}C_5H_5)]$ (**3**), species obtained by treating (**1c**) with MeC≡CMe. Formation of (**2**) and (**3**) is a consequence of a linking of the terminal W≡CR group in (**1c**) with but-2-yne. Moreover, the bridging C_3 ligand present in (**2**) is also found in the dimetal complexes $[WM\{\mu\text{-}C(R)C(Me)C(Me)\}(CO)_2(L_n)(L')]$ [R = C_6H_4Me-4, ML_n = $Fe(CO)_3$ (**4a**), $Co(\eta\text{-}C_5Me_5)$ (**4b**), $Rh(\eta^5\text{-}C_9H_7)$ (**4c**) (C_9H_7 = indenyl), L′ = $\eta\text{-}C_5H_5$; ML_n = $Fe(CO)_3$, L′ = $\eta\text{-}C_5Me_5$ (**4d**)].[4] The compounds (**4**) are also obtained as a result of coupling of the fragments $C(C_6H_4Me\text{-}4)$ and MeC≡CMe, but the precursors in these syntheses contain *p*-tolylmethylidyne groups which bridge heteronuclear metal–metal bonds, rather than being terminal ligands as in the complexes (**1**). An interesting feature, therefore, of the reaction between (**1c**) and but-2-yne is that the process results in migration of the $C(C_6H_4Me\text{-}4)$ fragment from its terminal position so that it becomes incorporated in the bridging groups found in (**2**) and (**3**). The reactions described herein involving the dimetal compounds (**1a**) and (**1b**) were carried out in order to establish whether alkylidyne–alkyne coupling reactions would occur with these species also, and to find out if in these reactions organic fragments bridging heteronuclear metal–metal bonds are formed.

Results and Discussion

Treatment of (**1a**) with MeC≡CMe in light petroleum at room temperature afforded the orange complex $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_7]$ (**5a**) (Scheme 1), characterised by the data given in Tables 1 and 2. The i.r. spectrum in the CO stretching region shows seven bands, and there is an absorption at 1 649 cm^{-1} attributable to the acyl carbonyl group. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data are in agreement with the formulation of (**5a**). The $^{13}C\text{-}\{^1H\}$ spectrum was measured at −50 °C to reduce ^{59}Co quadrupolar broadening of some signals. The C_6H_4 fragment shows six resonances in the range δ 143.4—129.3 p.p.m., indicating that this group is in a fixed position due to restricted rotation about the C–C_6H_4 bond.[2d] There is a peak for the Me-4 group at δ 21.4 p.p.m., and two other methyl group signals at δ 18.9 and 14.8 p.p.m. The carbonyl region shows four resonances. That at δ 212.3 p.p.m. can be unambiguously

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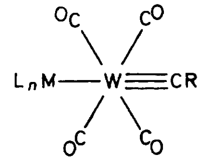
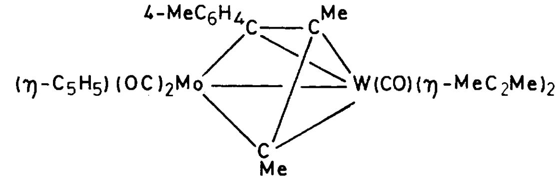
* 1,1,2,2,2,2-Hexacarbonyl-μ-[2,3-dimethyl-1-oxo-4-*p*-tolylbut-3-en-1,2,4-triyl-$C^{1,4}$(Co)C^{2-4}(W)]-1-(triphenylphosphine)cobalt-tungsten-(*Co–W*) and 1,1,2,2,2,2-hexacarbonyl-μ-[1-hydroxy-2,3-dimethyl-4-phenylbuta-1,3-dien-1,4-diyl-$C^{1,4}$(Co)C^{1-4}(W)]-1-(triphenylphosphine)cobalt-tungsten(*Co-W*) tetraphenylborate respectively.

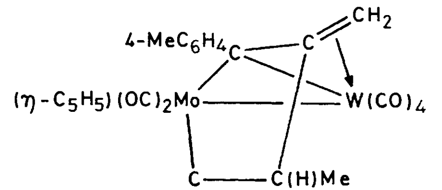
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



	ML_n	R
(**1a**)	$Co(CO)_4$	C_6H_4Me-4
(**1b**)	$Co(CO)_4$	Me
(**1c**)	$Mo(CO)_3(\eta$-$C_5H_5)$	C_6H_4Me-4
(**1d**)	$Re(CO)_5$	C_6H_4Me-4



(**2**)



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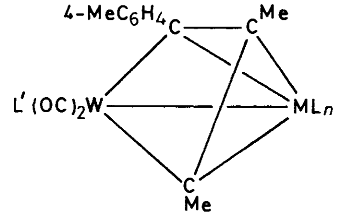


	ML_n	L'		ML_n	L'
(**4a**)	$Fe(CO)_3$	η-C_5H_5	(**4c**)	$Rh(\eta^5$-$C_9H_7)$	η-C_5H_5
(**4b**)	$Co(\eta$-$C_5Me_5)$	η-C_5H_5	(**4d**)	$Fe(CO)_3$	η-C_5Me_5

assigned to the four CO ligands of the W(CO)$_4$ group, in view of the observation of ^{183}W–^{13}C coupling (125 Hz). The appearance of one peak indicates site-exchange of these four CO groups even at −50 °C. The signal at δ 209.7 p.p.m., slightly broadened due to the ^{59}Co quadrupolar effect, is assigned to the cobalt-ligated acyl group, and the broad resonances at 198.7 and 193.8 p.p.m. to the three carbonyl groups co-ordinated to the cobalt.

The resonance at δ 175.6 p.p.m. can be assigned to the μ-*C*(C$_6$H$_4$Me-4) nucleus, with the signal slightly broadened due to the proximity of the cobalt nucleus. The resonances due to the two ligated *C*(Me) groups occur at δ 123.0 and 97.1 p.p.m. A specific assignment is made possible by reference to the ^{13}C-{^1H} n.m.r. data for the two cyclopentadienone complexes [Fe(CO)$_3${η^4-C(H)C(H)C(H)C(H)C(O)}][5] and [Co{η^4-C(H)C(Ph)C(H)C(Ph)C(O)}(η-C_5H_5)].[6] Because of the isolobal relationship existing between the fragments Co(CO)$_3$ and CH or CPh,[7] these iron and cobalt cyclopentadienone complexes are structurally related to compound (**5a**), *i.e.* the latter may be viewed as a cobaltacyclopentadienone–tungsten tetracarbonyl complex (Scheme 2). In the ^{13}C-{^1H} n.m.r. spectra of the cyclopentadienone–iron and –cobalt complexes the resonance for the C(O)*C*(R) nucleus is less deshielded than that for the C(O)C(R)*C*(R) (R = H or Ph) nucleus. Hence the peaks in the spectrum of (**5a**) at 97.1 and 123.0 p.p.m. may be assigned to the C(O)*C*(Me) and C(O)C(Me)*C*(Me) nuclei, respectively.

As mentioned above, the W(CO)$_4$ group gives rise to only one ^{13}C resonance. If (**5a**) is viewed as a metallacyclopentadienone complex of the W(CO)$_4$ fragment, the observation of one signal is readily understandable in terms of rotation of this group about an axis through the tungsten and the mid-point of the Co(CO)$_3$C(O)C(Me)C(Me)C(C$_6$H$_4$Me-4) five-membered ring system.

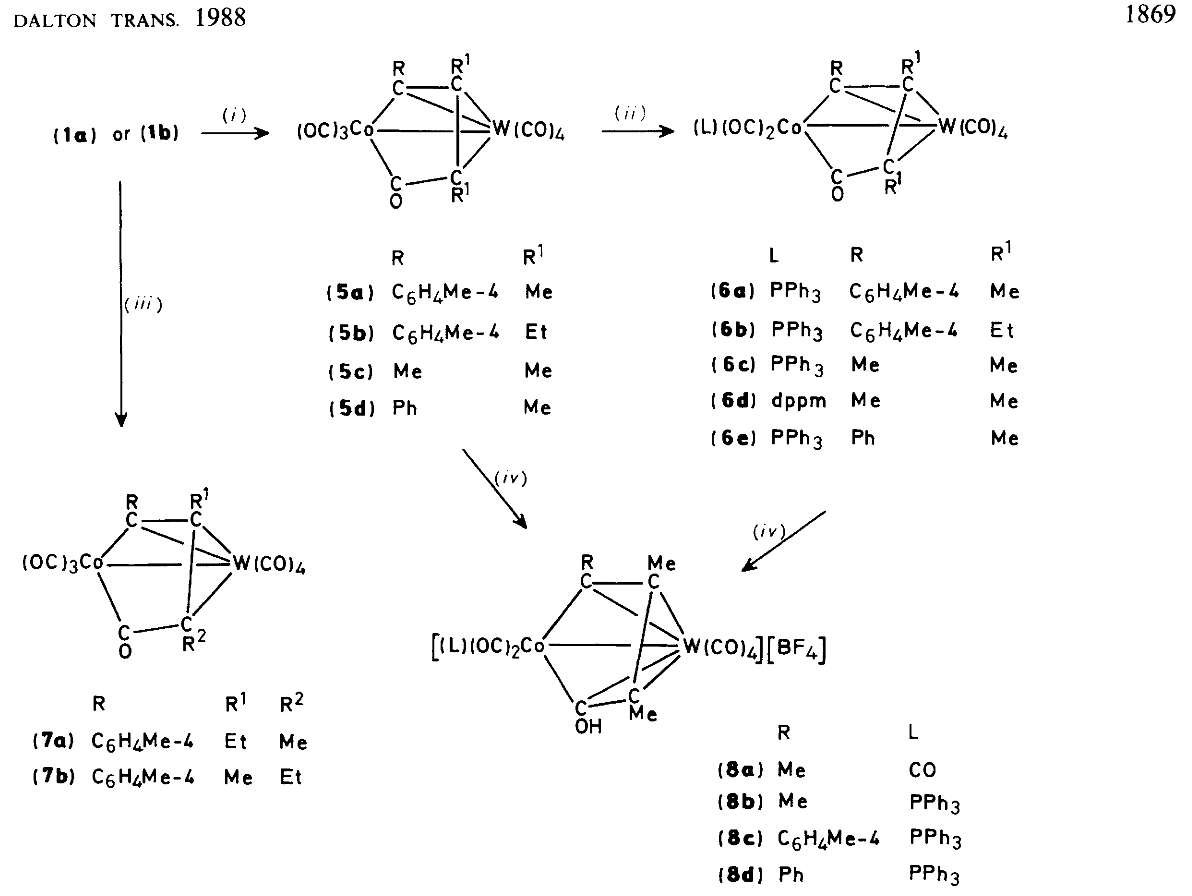
In the ^1H n.m.r. spectrum of (**5a**) (Table 2) there are two Me group signals at δ 1.97 and 2.38 of relative intensity 1:2. The peak at δ 1.97, being the most shielded, is assigned to the C(O)C(Me) group, while that at δ 2.38, corresponding to six protons, is assigned to a coincidence of the resonances for the C(O)C(Me)C(*Me*) and Me-4 groups.

Treatment of (**5a**) with PPh$_3$ in light petroleum affords the complex [WCo{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)C(O)}(CO)$_6$(PPh$_3$)] (**6a**), data for which are given in Tables 1—3. The structure of (**6a**) was established by an *X*-ray diffraction study, the results of which are summarised in Table 4, and the structure is shown in Figure 1. This study was of considerable assistance in interpreting the n.m.r. data for (**6a**) and those of other new compounds reported herein.

The W–Co bond [2.737(1) Å] is comparable in length with those found in the compounds [WCo$_2${μ$_3$-C(C$_6$H$_4$Me-4)}(CO)$_8$(η-C_5H_5)] [2.672(1) Å],[8] [WCo{μ-C(C$_6$H$_4$Me-4)}(CO)$_3$(η-C_5H_5)(η-C_5Me_5)] [2.758(1) Å],[9] and [WCo{μ-C$_4$(CF$_3$)$_4$}(CO)$_4$(η-C_5H_5)] [2.664(1) Å],[10] but is appreciably longer than that in [WCo{μ-σ:η^3-C(C$_6$H$_4$Me-4)C(Me)C(Me)H}(μ-CO)(CO)(η-C_5H_5)(η-C_5Me_5)][BF$_4$] [2.552(1) Å].[11] However, the latter is an electronically unsaturated dimetal species (32 valence electrons), whereas (**6a**) has an 18-electron configuration at each metal centre and is thus a 34 valence electron dimetal complex.

The disposition of the bridging ligand is such that the tungsten atom is ligated by C(8), C(9), and C(10) [W–C(8) 2.381(7), W–C(9) 2.291(6), and W–C(10) 2.219(6) Å], but is not bonded to the acyl group. The cobalt atom is linked to the bridging ligand *via* the acyl group [Co–C(1) 1.967(6) Å] and *via* the carbon atom carrying the C$_6$H$_4$Me-4 fragment [Co–C(10) 1.996(6) Å]. It is interesting to compare the bonding of the bridging ligand in (**6a**) with the bonding of the μ-C$_3$ fragments in the compounds [W$_2${μ-C(H)C(H)C(SiMe$_3$)}(μ-CSiMe$_3$)(OPr^i)$_4$] and [W$_2${μ-C(Ph)C(Ph)C(SiMe$_3$)}(μ-CSiMe$_3$)(CH$_2$SiMe$_3$)$_4$].[12] In both ditungsten compounds the μ-C$_3$ ligand is η^3-co-ordinated to one metal centre and σ bonded to the other *via* the two terminal carbon atoms. The μ-C–W separations to the η^3-bonded tungsten atom in these complexes are 2.33(1), 2.23(1), and 2.14(1) Å for [W$_2${μ-C(H)C(H)C(SiMe$_3$)}(μ-CSiMe$_3$)(OPr^i)$_4$], and 2.24(1), 2.45(1), and 2.29(1) Å for [W$_2${μ-C(Ph)C(Ph)C(SiMe$_3$)}(μ-CSiMe$_3$)(CH$_2$SiMe$_3$)$_4$]. These distances are similar to the W–C distances to the η^3-ligated tungsten atom in (**6a**) [W–C(8) 2.381(7), W–C(9) 2.291(6), and W–C(10) 2.219(6) Å].

The C(1)–C(8) [1.467(9)], C(8)–C(9) [1.413(9)], and



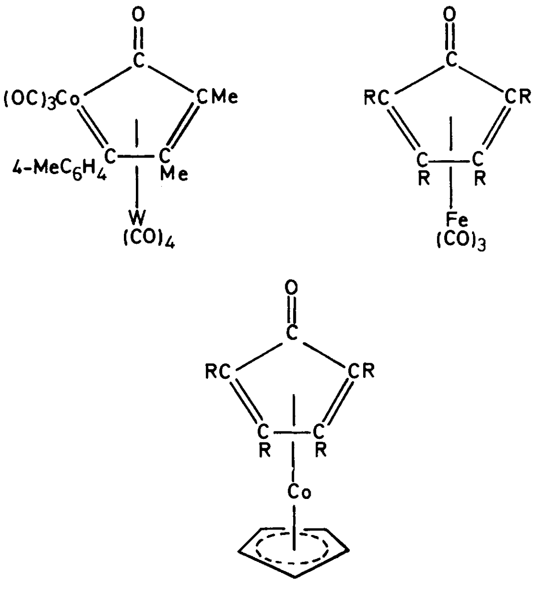
	R	R1
(5a)	C6H4Me-4	Me
(5b)	C6H4Me-4	Et
(5c)	Me	Me
(5d)	Ph	Me

	L	R	R1
(6a)	PPh3	C6H4Me-4	Me
(6b)	PPh3	C6H4Me-4	Et
(6c)	PPh3	Me	Me
(6d)	dppm	Me	Me
(6e)	PPh3	Ph	Me

	R	R1	R2
(7a)	C6H4Me-4	Et	Me
(7b)	C6H4Me-4	Me	Et

	R	L
(8a)	Me	CO
(8b)	Me	PPh3
(8c)	C6H4Me-4	PPh3
(8d)	Ph	PPh3

Scheme 1. (*i*) MeC≡CMe, EtC≡CEt, or MeC≡CPh; (*ii*) PPh_3 or dppm; (*iii*) MeC≡CEt; (*iv*) $HBF_4\cdot Et_2O$



Scheme 2. The structural relationship between compounds of type (**5**) and cyclopentadienone complexes of the fragments $Fe(CO)_3$ and $Co(\eta\text{-}C_5H_5)$, based on the isolobal mapping $Co(CO)_3 \overset{o}{\longleftrightarrow}$ CR (R = H, alkyl, or aryl). The groups $W(CO)_4$, $Fe(CO)_3$, and $Co(\eta\text{-}C_5H_5)$ are isolobal with CH^+

C(9)–C(10) [1.427(8) Å] distances in (**6a**) are all very similar, being intermediate between those expected for a single and a double bond. Moreover, these internuclear separations are close to those found for the two C–C distances [1.437(8) and 1.441(8) Å] in the μ_3-C ligand of compound (**4c**).[4b]

As expected, the tungsten atom in (**6a**) carries four terminal CO groups, and the cobalt atom has two such ligands. The PPh_3 ligand is bonded to the cobalt atom [Co–P 2.237(2) Å], being transoid to the metal–metal bond [P–Co–W 146.4(1)°].

Having established the molecular structure of (**6a**), the n.m.r. data (Tables 2 and 3) are readily interpretable. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a single resonance at δ 37.4 p.p.m. The absence of ^{183}W–^{31}P coupling is as expected, since the signal is due to a $CoPPh_3$ rather than a $WPPh_3$ group. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, resonances at δ 219.2 and 213.1 p.p.m. may be assigned to the *C*(O)C(Me) and $W(CO)_4$ groups, respectively, with the very broad signal at 190—200 p.p.m. being due to the $Co(CO)_2$ moiety. All the other peaks in the spectra are as expected on the basis of the structure established by *X*-ray diffraction.

The reaction between (**1a**) and hex-3-yne was next investigated. The product was the orange crystalline complex $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(Et)C(O)\}(CO)_7]$ (**5b**), data for which are listed in Tables 1 and 2. The spectroscopic properties of (**5b**) establish that it is structurally similar to (**5a**). Treatment of (**5b**) with PPh_3 in light petroleum affords the red-orange complex $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(Et)C(O)\}(CO)_6(PPh_3)]$ (**6b**), characterised by the data given in Tables 1—3. Structurally (**6b**) is similar to (**6a**).

The dimetal methylidyne complex (**1b**) is thermally less stable than (**1a**). Nevertheless, (**1b**) reacts with but-2-yne at *ca.* 0 °C to afford the compound $[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_7]$ (**5c**). Moreover, the yield of (**5c**) is significantly higher than that of its analogue (**5a**), a feature which may be rationalised in terms of the probable mechanism of these reactions, discussed later. The properties of (**5c**) (Tables 1 and 2)

Table 1. Analytical[a] and physical data for the tungsten–cobalt complexes

	Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$			Analysis (%) C	Analysis (%) H
(5a)	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_7]$	Orange	41	2 096s, 2 034s, 1 943s,	2 052vs, 2 002s, 1 649br,m	2 047vs, 1 966s,	37.9 (38.5)	2.3 (2.1)
(5b)	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(Et)C(O)\}(CO)_7]$	Orange	40	2 094s, 2 033s, 1 942s,	2 051vs, 2 001s, 1 658br,m	2 046vs, 1 966s, 1 645br,m	39.7 (40.5)	2.9 (2.6)
(5c)	$[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_7]$	Orange	62	2 095s, 2 031s, 1 942s,	2 052vs, 2 004s, 1 643br,m	2 043vs, 1 962s,	30.6 (30.7)	1.8 (1.6)
(5d)	$[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(O)\}(CO)_7]$	Orange	40	2 095s, 2 035m, 1 944s,	2 053vs, 2 002m, 1 652br,m	2 048s, 1 967s,	37.5 (37.4)	1.9 (1.8)
(6a)	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_6\text{-}(PPh_3)]$	Red	96	[c] 2 063vs, 1 952s,	2 021s, 1 924s,	2 003s (sh), 1 585br,m	51.7 (51.8)	3.3 (3.3)
(6b)	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(Et)C(O)\}(CO)_6\text{-}(PPh_3)]$	Red-orange	94	[c] 2 062vs, 1 950s,	2 020s, 1 921s,	2 002s (sh), 1 591br,m	52.8 (52.7)	3.6 (3.7)
(6c)	$[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$	Red	96	[c] 2 062vs, 1 947s,	2 018s, 1 921s,	2 000s (sh), 1 590br,m	48.0 (47.6)	3.4 (3.1)
(6d)	$[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_6(dppm)]$	Orange	96	[c] 2 062vs, 1 946s,	2 018s, 1 922s,	2 000s, 1 566br,m	50.6 (50.4)	3.5 (3.4)
(6e)	$[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$	Red-orange	98	[c] 2 064vs, 1 953m,	2 022s, 1 925s,	2 004s (sh), 1 603m,	51.1 (51.2)	3.2 (3.1)
(7a)[d] **(7b)**[d]	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Et)C(Me)C(O)\}(CO)_7]$ $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Et)C(O)\}(CO)_7]$	Orange	39	2 095s, 2 034s, 1 944s,	2 052vs, 2 001s, 1 650br,m	2 046vs, 1 967s,	39.7 (39.5)	2.8 (2.4)
(8a)	$[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(OH)\}(CO)_7][BF_4]$	Yellow	93	[c] 2 127m, 2 030 (sh),	2 090vs, 2 004br,s	2 060m,	27.0 (26.4)	1.8 (1.6)
(8b)	$[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)]\text{-}[BF_4]$	Yellow	96	[c] 2 092vs, 1 990br,s	2 060s,	2 036s (sh),	42.1 (42.8)	2.9 (2.9)
(8c)	$[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(OH)\}(CO)_6\text{-}(PPh_3)][BF_4]$	Yellow	95	2 093vs, 2 021s,	2 061s, 1 997s,	2 039s, 1 979s	47.4 (47.0)	3.4 (3.1)
(8d)	$[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)]\text{-}[BF_4]$	Yellow	100	[c] 2 093vs, 2 022s,	2 063s, 2 002s,	2 039s, 1 980s	45.5 (46.4)	2.9 (2.9)

[a] Calculated values are given in parentheses. [b] In light petroleum unless otherwise stated. [c] In CH_2Cl_2. [d] Isomeric mixture, see text.

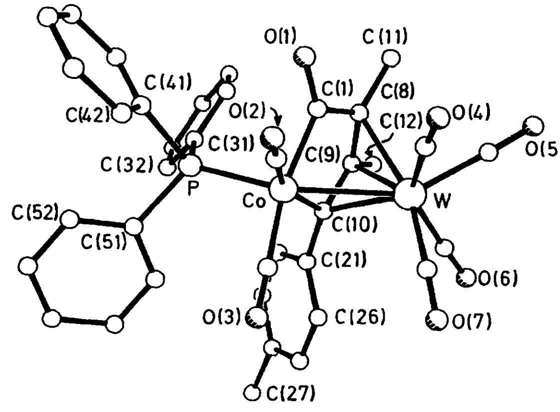


Figure 1. The molecular structure of $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$ (**6a**) showing the crystallographic atom labelling scheme

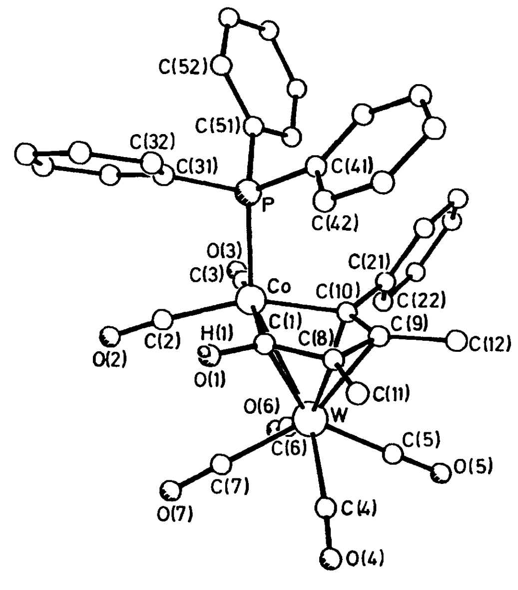


Figure 2. The structure of the cation of the salt $[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)][BF_4]$ (**8d**) showing the crystallographic atom labelling scheme

established that it is structurally similar to (**5a**). The i.r. spectrum of (**5c**) shows the characteristic band for the acyl carbonyl group at 1 643 cm^{-1}. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table 2, the resonances for the ligating carbon nuclei of the bridge system [*C*(O)C(Me), *C*(Me)Co, C(O)C(Me)*C*(Me), and C(O)*C*(Me)] have very similar shifts to those observed for the corresponding signals in the spectrum of (**5a**).

Like (**5a**), compound (**5c**) reacts readily with PPh_3. The product, $[WCo\{\mu\text{-}C(Me)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$ (**6c**), data for which are given in Tables 1—3, is clearly very similar to (**6a**). The only feature of interest arises in the ^1H n.m.r.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the tungsten–cobalt complexes

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(5a)	1.97 [s, 3 H, C(O)C(Me)], 2.38 [s, 6 H, C(*Me*)C(C_6H_4-*Me*-4)], 7.21 (s, 4 H, C_6H_4)	[d] 212.3 [W(CO), *J*(WC) 125], 209.7 [*C*(O)C(Me)], 198.7, 193.8 [br, Co(CO)], 175.6 [*C*(C_6H_4Me-4)], 143.4 [C^1(C_6H_4)], 138.0, 132.0, 129.8, 129.5, 129.3 (C_6H_4), 123.0 [*C*(Me)C(C_6H_4Me-4)], 97.1 [C(O)*C*(Me)], 21.4 (Me-4), 18.9 [C(*Me*)C(C_6H_4Me-4)], 14.8 [C(O)C(*Me*)]
(5b)	1.23 [t, 3 H, CH_2*Me*, *J*(HH) 7], 1.26 [t, 3 H, CH_2*Me*, *J*(HH) 7], 2.18 [m, 2 H, C(O)C(C*H*$_2$Me)], 2.34 [m, 2 H, C(C*H*$_2$Me)C(C_6H_4Me-4)], 2.38 (s, 3 H, Me-4), 7.22 (s, 4 H, C_6H_4)	[d] 212.0 [W(CO), *J*(WC) 128], 210.2 [*C*(O)C(Et)], 202.2, 194.5 [br, Co(CO)], 179.6 [*C*(C_6H_4Me-4)], 143.5 [C^1(C_6H_4)], 137.8, 131.8, 129.6, 129.3, 129.1 (C_6H_4), 126.4 [*C*(Et)C(C_6H_4Me-4)], 103.2 [C(O)*C*(Et)], 26.8 [C(*C*H$_2$Me)C(C_6H_4Me-4)], 22.9 [C(O)C(*C*H$_2$Me)], 21.2 (Me-4), 16.6, 15.5 (CH_2*Me*)
(5c)	1.96 [s, 3 H, C(O)C(Me)], 2.43 [s, 3 H, C(O)C(Me)C(*Me*)], 3.15 [s, 3 H, C(Me)Co]	[d] 211.8 [W(CO), *J*(WC) 128], 210.4 [*C*(O)C(Me)], 200.5, 193.8 [Co(CO)], 173.9 [br, *C*(Me)Co], 123.6 [C(O)C(Me)*C*(Me)], 98.4 [C(O)*C*(Me)], 31.1 [C(*Me*)Co], 16.0 [C(O)C(Me)C(*Me*)], 15.1 [C(O)C(*Me*)]
(5d)	1.98 [s, 3 H, C(O)C(Me)], 2.38 [s, 3 H, C(*Me*)C(Ph)], 7.28—7.60 (m, 5 H, Ph)	[e,f] 211.6 [W(CO), *J*(WC) 125], 210.4 [*C*(O)C(Me)], 199.0, 194.5, 192.3 [br, Co(CO)], 175.0 [br, *C*(Ph)], 145.5 [C^1(Ph)] 131.5, 129.2, 129.0, 128.4, 127.5 (Ph), 122.5 [*C*(Me)C(Ph)], 96.3 [C(O)*C*(Me)], 18.8 [C(*Me*)C(Ph)], 14.6 [C(O)C(*Me*)]
(6a)	1.93 [s, 3 H, C(O)C(Me)], 2.09, 2.39 [s × 2, 6 H, C(*Me*)C(C_6H_4*Me*-4)], 6.76—7.47 (m, 19 H, C_6H_4, Ph)	[e] 219.2 [br, *C*(O)C(Me)], 213.1 [W(CO), *J*(WC) 125], 200—190 [vbr, Co(CO)], 176.4 [*C*(C_6H_4Me-4)], 145.3 [C^1(C_6H_4)], 136.2—127.5 (C_6H_4, Ph), 119.6 [*C*(Me)C(C_6H_4Me-4)], 98.2 [C(O)*C*(Me)], 21.0 (Me-4), 18.2 [C(*Me*)C(C_6H_4Me-4)], 14.7 [C(O)C(*Me*)]
(6b)	0.81 [t, 3 H, CH_2*Me*, *J*(HH) 7], 1.30 [t, 3 H, CH_2*Me*, *J*(HH) 7], 2.04 [m, 2 H, C(O)C(C*H*$_2$Me)], 2.38 (s, 3 H, Me-4), 2.40 [m, 2 H, C(C*H*$_2$Me)C(C_6H_4Me-4)], 6.95—7.26 (m, 19 H, C_6H_4, Ph)	[g] 221.0 [*C*(O)C(Me)], 213.6 [W(CO), *J*(WC) 124], 204.0, 200.0 [br, Co(CO)], 180.8 [br, *C*(C_6H_4Me-4)], 146.2 [C^1(C_6H_4)], 137.0—127.8 (C_6H_4, Ph), 123.7 [*C*(Et)C(C_6H_4Me-4)], 108.6 [C(O)*C*(Et)], 27.3 [C(*C*H$_2$Me)C(C_6H_4Me-4)], 23.2 [C(O)C(*C*H$_2$Me)], 21.2 (Me-4), 16.5, 16.0 (CH_2*Me*)
(6c)	1.58 [s, 3 H, C(O)C(Me)], 2.10 [d, 3 H, C(O)C(Me)C(*Me*), *J*(PH) 1], 2.85 [d, 3 H, C(Me)Co, *J*(PH) 3], 7.35—7.70 (m, 15 H, Ph)	[e] 219.0 [br, *C*(O)C(Me)], 212.9 [W(CO), *J*(WC) 127], 203.0 [vbr, Co(CO)], 172.9 [*C*(Me)Co], 133.7—128.0 (Ph), 121.7 [C(O)C(Me)*C*(Me)], 98.8 [C(O)*C*(Me)], 31.0 [C(*Me*)Co], 15.3 [C(O)C(Me)C(*Me*)], 14.2 [C(O)C(*Me*)]
(6d)	[d,e] 1.54, 1.59 [s × 2, 6 H, C(O)C(Me)C(Me)], 2.80 [s, 3 H, C(Me)Co], 3.10—3.38 (m, 2 H, PCH_2P), 7.10—7.70 (m, 20 H, Ph)	[d] 221.2 [d, *C*(O)C(Me), *J*(PC) 52], 214.1 [W(CO), *J*(WC) 128], 206—203 [vbr, Co(CO)], 171.8 [br, *C*(Me)Co], 139.7—128.3 (Ph), 124.2 [C(O)C(Me)*C*(Me)], 96.9 [C(O)*C*(Me)], 30.8 [C(*Me*)Co], 29.0 (m, PCH_2P), 14.9, 14.1 [C(O)C(*Me*)C(*Me*)]
(6e)	1.94 [s, 3 H, C(O)C(Me)], 2.11 [s, 3 H, C(*Me*)C(Ph)], 6.84—6.93 (m, 5 H, Ph), 7.24—7.46 (m, 15 H, Ph)	[e,f] 219.7 [*C*(O)C(Me)], 213.2 [W(CO), *J*(WC) 125], 203.8, 199.2 [br, Co(CO)], 175.7 [br, *C*(Ph)], 147.5 [C^1(Ph)], 136.4—126.5 (Ph), 119.6 [*C*(Me)C(Ph)], 98.3 [C(O)*C*(Me)], 18.3 [C(*Me*)C(Ph)], 15.0 [C(O)C(*Me*)]
(7)[h]	[e] 1.12, 1.20 [t × 2, 6 H, C(O)C(Me)C(CH_2*Me*) (**7a**), C(O)C(CH_2*Me*) (**7b**), *J*(HH) 7], 1.92 [m, 2 H, C(O)C(C*H*$_2$Me) (**7b**)], 2.05 [s, 3 H, C(O)C(Me) (**7a**)], 2.38 [s, 6 H, Me-4 (**7a**), (**7b**)], 2.40 [s, 3 H, C(O)C(Et)C(*Me*) (**7b**)], 2.50 [m, 2 H, C(O)C(Me)C(C*H*$_2$Me) (**7a**)], 7.20 [s, 8 H, C_6H_4 (**7a**), (**7b**)]	[e] 211.9 [W(CO), *J*(WC) 125, (**7a**)], 211.7 [W(CO), *J*(WC) 128, (**7b**)], 208.8 [*C*(O)C(Me) (**7a**), *C*(O)C(Et) (**7b**)], 176.8 [br, *C*(C_6H_4Me-4), (**7a**) and (**7b**)], 143.4 [C^1(C_6H_4), (**7a**) and (**7b**)], 137.6—129.3 [C_6H_4, (**7a**) and (**7b**)], 127.7 [*C*(Et), (**7a**)], 121.8 [*C*(Me), (**7b**)], 102.2 [*C*(Et), (**7b**)], 94.7 [*C*(Me), (**7a**)], 26.1 [C(*C*H$_2$Me), (**7a**)], 23.4 [C(*C*H$_2$Me), (**7b**)], 21.2 [Me-4, (**7a**) and (**7b**)], 18.3 [C(Me), (**7b**)], 15.8, 14.7, 13.9 [C(CH_2*Me*), (**7b**); C(*Me*)C(CH_2*Me*), (**7a**)]
(8a)	2.43, 2.50 [s × 2, 6 H, C(OH)C(*Me*)C(*Me*)], 2.70 [s, 3 H, C(Me)Co]	206.9 [W(CO), *J*(WC) 110], 205.2 [*C*(OH)], 197—185 [vbr, Co(CO)], 160.5 [br, *C*(Me)Co], 131.3 [C(OH)C(Me)*C*(Me)], 117.3 [C(OH)*C*(Me)], 30.1 [C(*Me*)Co], 16.4, 14.0 [C(OH)C(*Me*)C(*Me*)]
(8b)	1.76 [s, 3 H, C(OH)C(*Me*)], 2.10 [d, 3 H, C(Me)C(*Me*)C(Me), *J*(PH) 1], 2.41 [d, 3 H, C(Me)Co, *J*(PH) 2], 7.38—7.86 (m, 15 H, Ph), 8.50 (s, vbr, 1 H, OH)	[g] 208.0 [W(CO), *J*(WC), 118], 207.4 [br, *C*(OH)], 199.8, 196.7 [Co(CO)], 159.0 [br, *C*(Me)Co], 131.7—127.7 (Ph), 124.1 [C(OH)C(Me)*C*(Me)], 111.0 [C(OH)*C*(Me)], 28.3 [C(*Me*)Co], 15.1, 10.8 [C(OH)C(*Me*)C(*Me*)]
(8c)	2.05, 2.15 [s × 2, 6 H, C(OH)C(*Me*)C(*Me*)], 2.36 (s, 3 H, Me-4), 6.04 (s, br, 1 H, OH), 6.95—7.58 (m, 19 H, C_6H_4, Ph)	213.5 [br, *C*(OH)], 209.1 [W(CO), *J*(WC) 119], 199.5, 198.3 [br, Co(CO)], 164.3 [br, *C*(C_6H_4Me-4)], 142.1 [C^1(C_6H_4)], 139.5—128.9 (C_6H_4, Ph), 124.6 [*C*(Me)C(C_6H_4Me-4)], 111.2 [C(OH)*C*(Me)], 21.2 (Me-4), 18.9 [C(*Me*)C(C_6H_4Me-4)], 13.5 [C(OH)C(*Me*)]
(8d)	2.08, 2.14 [s × 2, 6 H, C(OH)C(*Me*)C(*Me*)], 6.07 (s, br, 1 H, OH), 6.78—7.51 (m, 20 H, Ph)	212.5 [C(OH)], 208.0 [W(CO), *J*(WC) 118], 198.2, 196.8 [Co(CO)], 162.3 [*C*(Ph)], 143.4 [C^1(Ph)], 133.3—127.0 (Ph), 123.1 [*C*(Me)C(Ph)], 109.4 [C(OH)*C*(Me)], 17.8 [C(*Me*)C(Ph)], 12.2 [C(OH)C(*Me*)]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature, unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$, with measurements in CD_2Cl_2—CH_2Cl_2. [d] Measured at −50 °C. [e] Measured in $CDCl_3$. [f] Measured at −60 °C. [g] Measured at −40 °C. [h] Mixture of isomers (**7a**) and (**7b**), see text.

spectrum of (**6c**) (Table 2). There is ^{31}P–^{1}H coupling between the Co(PPh_3) group and the protons of the methyl groups attached to the carbon atoms in α and β positions with respect to the cobalt atom.

The reaction between (**5c**) and bis(diphenylphosphino)methane (dppm) was investigated in an attempt to obtain a derivative of (**5c**) in which the Co–W bond would be bridged by the dppm ligand. The product, [WCo{μ-C(Me)C(Me)C(Me)C(O)}$(CO)_6$(dppm)] (**6d**), however, was one in which the dppm group is monodentate. This is clearly established from the ^{31}P-

Table 3. Phosphorus-31 n.m.r. data[a] for the tungsten–cobalt complexes

Compound	^{31}P (δ)[b]
(6a)	37.4 (s)
(6b)	36.4 (s)
(6c)	35.0 (s)
(6d)	[c]30.6 (s, Co*P*$Ph_2CH_2PPh_2$), −26.7 [d, $CoPPh_2CH_2$*P*Ph_2, *J*(PP) 100 Hz]
(6e)	37.5 (s)
(8b)	[d]30.0 (s)
(8c)	31.9 (s)
(8d)	32.0 (s)

[a] Chemical shifts (δ) in p.p.m. with positive values representing shifts to high frequency of 85% H_3PO_4 (external). [b] Hydrogen-1 decoupled, measured in CD_2Cl_2–CH_2Cl_2 at −40 °C, unless otherwise stated. All resonances for cobalt-ligated P nuclei are broad. [c] Measured at −50 °C. [d] Measured in $CDCl_3$.

{^{1}H} n.m.r. spectrum (Table 3). There are two resonances, but none shows ^{183}W–^{31}P coupling, indicating that no P–W bond is present. The signal at δ 30.6 p.p.m. is broad, and its chemical shift corresponds to it being due to a $CoPPh_2$ group. The doublet resonance at δ −26.7 p.p.m. [*J*(PP) 100 Hz] corresponds to an unco-ordinated phosphorus nucleus of the dppm ligand. This conclusion is supported by data for the compound [WPt{μ-C(OMe)Me}(μ-dppm)$(CO)_4$(dppm)], in the ^{31}P-{^{1}H} n.m.r. spectrum of which the non-ligated phosphorus nucleus of the monodentate dppm group resonates at δ −22.3 p.p.m. [*J*(PP) 24 Hz].[13] Binding of the free PPh_2 group in **(6d)** to the tungsten centre evidently requires vigorous conditions, and we are unable to isolate a well defined μ-dppm complex by heating **(6d)**.

The reaction between **(1a)** and the unsymmetrical alkyne MeC≡CEt was also investigated and found to give a chromatographically inseparable mixture of the two isomers [WCo{μ-$C(C_6H_4Me$-4)C(R^1)C(R^2)C(O)}$(CO)_7$] [**(7a)**, R^1 = Et, R^2 = Me; **(7b)**, R^1 = Me, R^2 = Et]. By inspection of peak intensities in the ^{1}H n.m.r. spectrum, it was evident that the mixture consisted of *ca.* 30% of **(7a)** and *ca.* 70% of **(7b)**. The peak assignments in the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (Table 2) could be made by comparison with the resonances observed in the spectra of compounds **(5a)** and **(5b)**; products obtained from the symmetrical alkynes MeC≡CMe and EtC≡CEt, respectively.

With unsymmetrical alkynes the most revealing reaction studied was that between **(1b)** and MeC≡CPh. As discussed later, the result shed light on the pathway by which the alkyne, CR, and CO groups become linked in the products reported herein. Treatment of **(1b)** with MeC≡CPh in light petroleum at 0 °C afforded a single product [WCo{μ-C(Ph)C(Me)C(Me)C(O)}$(CO)_7$] **(5d)**. Examination of the ^{1}H and ^{13}C-{^{1}H} spectra of this complex revealed the absence of signals corresponding to the isomer [WCo{μ-C(Me)C(Me)C(Ph)C(O)}$(CO)_7$]. Compound **(5d)** is virtually identical with **(5a)**, the two species differing only by the presence of a CPh group in the former and a $C(C_6H_4Me$-4) group in the latter. The i.r. spectra of **(5a)** and **(5d)** in the carbonyl region are thus essentially the same (Table 1). Moreover, corresponding resonances in the ^{13}C-{^{1}H} n.m.r. spectra (Table 2) of the two compounds occur at closely similar chemical shifts. The correct assignment for the structure of **(5d)** was further established by an *X*-ray diffraction study on a derivative described below.

Treatment of **(5d)** with PPh_3 affords the complex [WCo{μ-C(Ph)C(Me)C(Me)C(O)}$(CO)_6(PPh_3)$] **(6e)**. The data for this product (Tables 1—3) leave no doubt of its formulation, and its close relationship with **(6a)**.

Protonation of **(5c)** with $HBF_4 \cdot Et_2O$ occurs at the acyl group oxygen atom to yield the salt [WCo{μ-C(Me)C(Me)C(Me)C(OH)}$(CO)_7$][BF_4] **(8a)**. Similarly, protonation of **(6c)** gives the closely related complex [WCo{μ-C(Me)C(Me)C(Me)C(OH)}$(CO)_6(PPh_3)$][BF_4] **(8b)**. The salts [WCo{μ-C(R)C(Me)C(Me)C(OH)}$(CO)_6(PPh_3)$][BF_4][**(8c)**, R = C_6H_4Me-4; **(8d)**, R = Ph] were similarly prepared from **(6a)** and **(6e)**, respectively. Data which characterise **(8a)**—**(8d)** are given in Tables 1—3. All four salts are formed in essentially quantitative yield. The structure of **(8d)** was established by *X*-ray diffraction. Selected parameters from this study are listed in Table 5, and the structure of the cation is shown in Figure 2.

The W–Co bond [2.660(1) Å] is bridged by the C(Ph)C(Me)C(Me)C(OH) group with C(1) and C(10) σ bonded to the cobalt atom [Co–C(1) 1.911(5), Co–C(10) 1.989(5) Å]. The W–C(1) distance [2.400(6) Å] indicates that C(1) ligates the tungsten atom, in contrast with C(1) in **(6a)** [W ··· C(1) 2.77 Å]. It is thus evident that **(8d)** can be formally regarded as a cobaltacyclopentadienyl complex of the cationic fragment $W(CO)_4^+$, since the $Co(CO)_2(PPh_3)$ group is isolobal with CH. However, this analogy must be viewed with caution since the separations between the tungsten atom and the atoms of the $\overline{\mathrm{CoC(1)C(8)C(9)C(10)}}$ ring are not equal. The W–Co distance is the longest [2.660(1) Å] as expected. The W–C(10) distance [2.267(4) Å] is the shortest, and the W–C(1), W–C(8), and W–C(9) separations (mean 2.375 Å) are very similar.

The C(1)–O(1) bond [1.347(7) Å] is longer than that in **(6a)** [1.227(8) Å], as a consequence of protonation at the oxygen atom of the acyl group in the former. A small peak of residual electron density was found near O(1) in **(8d)** and is tentatively assigned to the proton [O(1)–H(1) 1.06(7) Å]. The C(1)–C(8), C(8)–C(9), and C(9)–C(10) distances of 1.419(7), 1.435(8), and 1.401(6) Å, respectively, are all similar to the corresponding C–C distances in **(6a)**. As with the latter, the PPh_3 group [Co–P 2.261(1) Å] in **(8d)** is transoid to the metal–metal bond [P–Co–W 144.8(1)°].

It is interesting to compare the structure of **(8d)** with that recently determined[14] for [WCo{μ-$C(C_6H_4Me$-4)C(Et)C(Et)C(OH)}$(CO)_4(\eta$-$C_5H_5)$]. Although the bridging ligand in this species is very similar to that in **(8d)**, there is a fundamental difference in bonding mode. In [WCo{μ-$C(C_6H_4Me$-4)C(Et)C(Et)C(OH)}$(CO)_4(\eta$-$C_5H_5)$] the cobalt atom carries two carbonyl groups and is η^4 co-ordinated by the μ-C_4 fragment, while the latter is σ bonded to the tungsten atom of the $W(CO)_2(\eta$-$C_5H_5)$ group *via* the terminal $C(C_6H_4Me$-4) and C(OH) groups. In contrast, in **(8d)** the reverse situation operates. The ligand is disposed such that it is the four carbon atoms of the μ_4-C bridge which ligate the tungsten atom, and the two carbon atoms at the ends of the C_4 chain are σ bonded to the $Co(CO)_2(PPh_3)$ group. It should be noted that the transformation in bridge bonding of the C_4 fragments is possible through the isolobal relationships shown below.

$$Co(CO)_2(PPh_3) \underset{o}{\longleftrightarrow} CH \underset{o}{\longleftrightarrow} W(CO)_2(\eta\text{-}C_5H_5)$$

$$Co(CO)_2 \underset{o}{\longleftrightarrow} W(CO)_4^+$$

The n.m.r. data for the salts **(8)** (Tables 2 and 3) are readily interpretable, following establishment of the structure of **(8d)**. Only the results for the latter are discussed and compared with those for **(5d)**. The ^{1}H n.m.r. spectrum of **(8d)** shows two singlet resonances for the methyl groups at δ 2.08 and 2.14, and a broad signal for the OH group at δ 6.07. The ^{31}P-{^{1}H} n.m.r. spectrum is as expected with a singlet peak at δ 32.0 p.p.m. The ^{13}C-{^{1}H} n.m.r. spectrum of **(8d)** is informative in the context of comparison with that of **(5a)**. The ligated carbon of the C(OH) group in **(8d)** has its resonance at δ 212.5 p.p.m., compared with the signal at δ 210.4 for the *C*(O)C(Me) nucleus in **(5d)**. In the spectrum of **(8d)**, the resonance for the carbonyl ligands of the $W(CO)_4$ group occurs at δ 208.0 p.p.m., whereas in the spectrum

Table 4. Selected internuclear separations (Å) and angles (°) for $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)C(O)\}(CO)_6(PPh_3)]$ **(6a)**

W–Co	2.737(1)	W–C(4)	2.055(8)	W–C(5)	2.001(7)	W–C(6)	2.007(8)
W–C(7)	1.991(7)	W–C(8)	2.381(7)	W–C(9)	2.291(6)	W–C(10)	2.219(6)
Co–P	2.237(2)	Co–C(1)	1.967(6)	Co–C(2)	1.802(7)	Co–C(3)	1.848(6)
Co–C(10)	1.996(6)	C(1)–O(1)	1.227(8)	C(1)–C(8)	1.467(9)	C(2)–O(2)	1.123(9)
C(3)–O(3)	1.104(8)	C(4)–O(4)	1.13(1)	C(5)–O(5)	1.136(9)	C(6)–O(6)	1.15(1)
C(7)–O(7)	1.159(9)	C(8)–C(9)	1.413(9)	C(8)–C(11)	1.529(8)	C(9)–C(10)	1.427(8)
C(9)–C(12)	1.523(9)	C(10)–C(21)	1.493(8)				

C(4)–W–C(5)	80.0(3)	C(4)–W–C(6)	146.1(3)	C(5)–W–C(6)	80.1(3)	C(4)–W–C(7)	83.7(3)
C(5)–W–C(7)	109.1(3)	C(6)–W–C(7)	77.3(3)	C(4)–W–C(8)	92.4(3)	C(5)–W–C(8)	88.1(3)
C(6)–W–C(8)	114.0(3)	C(7)–W–C(8)	161.3(3)	C(4)–W–C(9)	126.5(3)	C(5)–W–C(9)	101.4(3)
C(6)–W–C(9)	84.3(3)	C(7)–W–C(9)	140.7(2)	C(8)–W–C(9)	35.1(2)	C(4)–W–C(10)	136.9(3)
C(6)–W–C(10)	84.3(3)	C(7)–W–C(10)	106.2(2)	C(8)–W–C(10)	62.3(2)	C(9)–W–C(10)	36.8(2)
W–Co–P	146.4(1)	P–Co–C(1)	91.1(2)	P–Co–C(2)	101.1(2)	C(1)–Co–C(2)	85.1(3)
P–Co–C(3)	100.1(2)	C(1)–Co–C(3)	168.7(3)	C(2)–Co–C(3)	91.3(3)	P–Co–C(10)	98.7(2)
C(1)–Co–C(10)	83.9(3)	C(2)–Co–C(10)	157.5(3)	C(3)–Co–C(10)	95.8(3)	Co–C(1)–O(1)	126.4(5)
Co–C(1)–C(8)	111.0(4)	O(1)–C(1)–C(8)	122.5(5)	Co–C(2)–O(2)	178.1(7)	Co–C(3)–O(3)	173.6(6)
W–C(4)–O(4)	176.4(8)	W–C(5)–O(5)	174.9(8)	W–C(6)–O(6)	174.1(7)	W–C(7)–O(7)	176.1(6)
W–C(8)–C(1)	89.0(4)	W–C(8)–C(9)	69.0(4)	C(1)–C(8)–C(9)	114.6(5)	W–C(8)–C(11)	124.6(5)
C(1)–C(8)–C(11)	119.1(6)	C(9)–C(8)–C(11)	124.1(6)	W–C(9)–C(8)	75.9(4)	W–C(9)–C(10)	68.8(4)
C(8)–C(9)–C(10)	114.2(5)	W–C(9)–C(12)	126.2(5)	C(8)–C(9)–C(12)	120.0(5)	C(10)–C(9)–C(12)	125.7(5)
W–C(10)–Co	80.8(2)	W–C(10)–C(9)	74.4(3)	Co–C(10)–C(9)	112.7(4)	W–C(10)–C(21)	129.1(5)
Co–C(10)–C(21)	124.1(4)	C(9)–C(10)–C(21)	120.1(5)				

Table 5. Selected internuclear distances (Å) and angles (°) for $[WCo\{\mu\text{-}C(Ph)C(Me)C(Me)C(OH)\}(CO)_6(PPh_3)][BF_4]$ **(8d)**

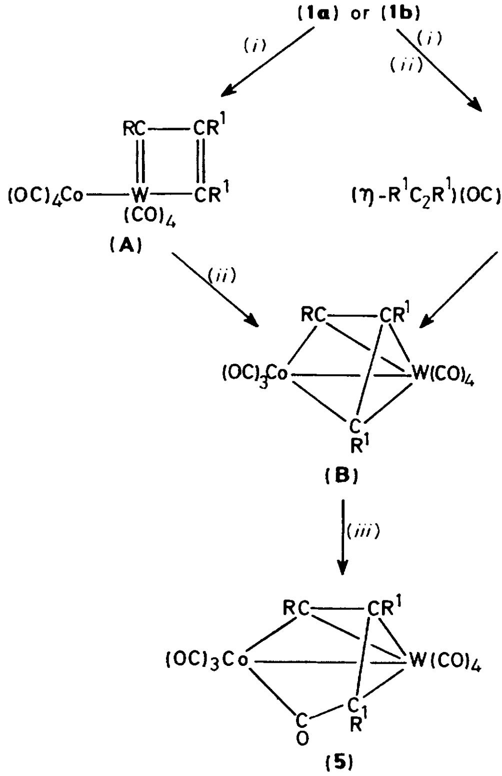
W–Co	2.660(1)	W–C(1)	2.400(6)	W–C(4)	2.030(6)	W–C(5)	1.999(9)
W–C(6)	2.023(7)	W–C(7)	2.028(7)	W–C(8)	2.370(5)	W–C(9)	2.354(4)
W–C(10)	2.267(4)	Co–P	2.261(1)	Co–C(1)	1.911(5)	Co–C(2)	1.819(6)
Co–C(3)	1.805(5)	Co–C(10)	1.989(5)	C(1)–O(1)	1.347(7)	C(1)–C(8)	1.419(7)
O(1)–H(1)	1.06(7)	C(2)–O(2)	1.115(8)	C(3)–O(3)	1.130(7)	C(4)–O(4)	1.121(8)
C(5)–O(5)	1.158(11)	C(6)–O(6)	1.139(8)	C(7)–O(7)	1.132(10)	C(8)–C(9)	1.435(8)
C(8)–C(11)	1.494(7)	C(9)–C(10)	1.401(6)	C(9)–C(12)	1.507(7)	C(10)–C(21)	1.499(7)
mean B–F	1.293						

Co–W–C(1)	44.0(1)	Co–W–C(4)	142.3(2)	C(1)–W–C(4)	99.6(3)	Co–W–C(5)	135.5(2)
C(1)–W–C(5)	143.1(2)	C(4)–W–C(5)	77.6(3)	Co–W–C(6)	89.7(2)	C(1)–W–C(6)	130.7(2)
C(4)–W–C(6)	119.1(3)	C(5)–W–C(6)	78.6(3)	Co–W–C(7)	89.6(2)	C(1)–W–C(7)	86.3(3)
C(4)–W–C(7)	76.2(3)	C(5)–W–C(7)	127.3(3)	C(6)–W–C(7)	75.6(3)	Co–W–C(8)	69.0(1)
C(1)–W–C(8)	34.6(2)	C(4)–W–C(8)	84.4(2)	C(5)–W–C(8)	109.4(2)	C(6)–W–C(8)	156.5(2)
C(7)–W–C(8)	112.6(3)	Co–W–C(9)	69.0(1)	C(1)–W–C(9)	59.5(2)	C(4)–W–C(9)	104.1(2)
C(5)–W–C(9)	85.1(2)	C(6)–W–C(9)	128.5(2)	C(7)–W–C(9)	145.6(3)	C(8)–W–C(9)	35.4(2)
Co–W–C(10)	46.8(1)	C(1)–W–C(10)	66.3(2)	C(4)–W–C(10)	139.2(2)	C(5)–W–C(10)	91.6(2)
C(6)–W–C(10)	96.4(2)	C(7)–W–C(10)	136.1(3)	C(8)–W–C(10)	62.0(2)	C(9)–W–C(10)	35.2(2)
W–Co–P	144.8(1)	W–Co–C(1)	60.7(2)	P–Co–C(1)	93.9(2)	W–Co–C(2)	103.7(2)
P–Co–C(2)	99.1(2)	C(1)–Co–C(2)	88.5(2)	W–Co–C(3)	106.3(2)	P–Co–C(3)	99.3(2)
C(1)–Co–C(3)	166.6(3)	C(2)–Co–C(3)	91.5(3)	W–Co–C(10)	56.2(1)	P–Co–C(10)	99.1(1)
C(1)–Co–C(10)	81.7(2)	C(2)–Co–C(10)	159.9(2)	C(3)–Co–C(10)	94.0(2)	W–C(1)–Co	75.3(2)
W–C(1)–O(1)	128.2(3)	Co–C(1)–O(1)	120.8(3)	W–C(1)–C(8)	71.5(3)	Co–C(1)–C(8)	117.4(4)
O(1)–C(1)–C(8)	121.6(4)	C(1)–O(1)–H(1)	131.0(32)	Co–C(2)–O(2)	175.5(6)	Co–C(3)–O(3)	177.6(5)
W–C(4)–O(4)	175.5(7)	W–C(5)–O(5)	178.9(6)	W–C(6)–O(6)	179.3(7)	W–C(7)–O(7)	179.0(5)
W–C(8)–C(1)	73.9(3)	W–C(8)–C(9)	71.7(3)	C(1)–C(8)–C(9)	111.7(4)	W–C(8)–C(11)	126.0(4)
C(1)–C(8)–C(11)	124.0(5)	C(9)–C(8)–C(11)	124.1(4)	W–C(9)–C(8)	72.9(3)	W–C(9)–C(10)	69.0(2)
C(8)–C(9)–C(10)	114.8(4)	W–C(9)–C(12)	126.9(4)	C(8)–C(9)–C(12)	119.7(4)	C(10)–C(9)–C(12)	125.4(5)
W–C(10)–Co	77.1(1)	W–C(10)–C(9)	75.8(3)	Co–C(10)–C(9)	113.4(4)	W–C(10)–C(21)	130.9(4)
Co–C(10)–C(21)	124.1(3)	C(9)–C(10)–C(21)	119.7(4)				

of **(5d)** the corresponding signal is at 211.6 p.p.m. The $Co(CO)_2(PPh_3)$ group in **(8d)** shows CO resonances at δ 198.2 and 196.8 p.p.m., and these signals are to be compared with those for the $Co(CO)_3$ fragment in **(5d)** at δ 199.0, 194.5, and 192.3 p.p.m. Thus whereas in **(5d)** and **(8d)** site exchange of the CO ligands attached to cobalt does not occur, the four carbonyl groups bonded to the tungsten in both compounds display an equivalence. This is as expected for rotation of the $W(CO)_4$ group in the manner discussed earlier for **(5a)**.

In the ^{13}C spectrum of **(8d)** the signals for the bridging carbon nuclei *C*Ph, *C*(Me)C(Ph), and C(OH)*C*(Me) occur at δ 162.3, 123.1, and 109.4 p.p.m., respectively, compared with those of **(5d)** at δ 175.0 (*C*Ph), 122.5 [*C*(Me)C(Ph)], and 96.3 p.p.m. [C(O)*C*(Me)]. Evidently protonation results in the greatest change in chemical shifts for the *C*Ph, and the C(OH)*C*(Me) and C(O)*C*(Me) groups.

It is interesting to consider possible pathways by which the compounds **(1a)** or **(1b)** react with alkynes to afford the products **(5)** and **(7)**. Previous work involving reactions of the tungsten–rhenium complex **(1d)** with hydride ion[2b] or PMe_3,[15] or with metal–ligand fragments,[2a,2c–e] suggests that attack by these species occurs initially at the carbyne-carbon atom. It has also been suggested that the synthesis of compounds **(2)** and **(3)** from **(1c)** and MeC≡CMe proceeds *via* attack of the alkyne at



Scheme 3. (*i*) $+ R^1C{\equiv}CR^1$, (*ii*) $-CO$, (*iii*) $+CO$

the $W{\equiv}CC_6H_4Me$-4 group, yielding initially a species containing a tungstacyclobutadiene fragment, *viz.* $(\eta$-$C_5H_5)(OC)_3$-Mo-W{=C(C_6H_4Me-4)C(Me)=C(Me)}$(CO)_4$. A similar pathway for attack of alkynes on (**1a**) or (**1b**) (Scheme 3) might lead *via* intermediates (**A**) and (**B**) to the compounds (**5**). There is clearly a close structural similarity between the postulated intermediate (**B**) and the previously isolated compounds (**2**) and (**4**). However, these species do not readily insert CO into the bridging C_3 fragment, as invoked for (**B**) in Scheme 3. Nevertheless, such a process might readily occur at a cobalt centre. This is because reactions involving intramolecular migration of a cobalt-ligated CO ligand to an adjacent Co–C σ bond to produce an acyl group CoC(O)C are known to be exceedingly facile. Clearly an unsymmetrical alkyne such as $MeC{\equiv}CEt$ could afford two isomers [(**7a**) or (**7b**)] depending on the direction of attack in the formation of (**A**). However, we believe that attack of alkynes on the dimetal compounds (**1**) may not occur at the W≡CR group. Alternatively, displacement of co-ordinated CO at the other metal centre by the alkyne ligand may occur initially. Some support for this idea comes from the observation that whereas (**1a**) and (**1b**) react with $MeC{\equiv}CMe$ at or below room temperatures, and (**1c**) reacts at room temperature, the tungsten–rhenium compound (**1d**) does not react with $MeC{\equiv}CMe$ even at elevated temperatures. It is well established that CO groups are more easily displaced from cobalt or molybdenum than from rhenium. Hence the inertness of (**1d**) compared with (**1a**)—(**1c**) towards $MeC{\equiv}CMe$ supports the idea that the first stage of reaction requires release of a CO group from the metal–ligand fragment σ bonded to the tungsten. Thus formation of the compounds (**5**) may proceed not *via* tungstacyclobutadiene intermediate (**A**) but *via* the dimetal species (**C**), with (**B**) being the common intermediate for both pathways.

With the unsymmetrical alkynes, there are two structures for intermediate (**B**) depending on whether a μ-C(R)C(R^1)C(R^2) or a μ-C(R)C(R^2)C(R^1) group is present. Formation of one or other of these fragments would depend on the mode of alkylidyne–alkyne coupling, occurring either during formation of a tungstacyclobutadiene ring as in intermediate (**A**), or in the transformation from (**C**) to (**B**). That isomeric μ-C_3 fragments can form by coupling of alkylidyne groups with unsymmetrical alkynes has been shown previously in the synthesis of a mixture of the two isomers [WCo{μ-C(C_6H_4Me-4)C(Ph)C(Me)}$(CO)_2$-$(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$] and [WCo{μ-C(C_6H_4Me-4)C(Me)C-(Ph)}$(CO)_2(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$] upon treatment of the dimetal compound [WCo(μ-CC_6H_4Me-4)$(CO)_3(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$] with $MeC{\equiv}CPh$.[4a]

The final step in the synthesis of the complexes (**5**) requires CO 'insertion' at the μ-C_3 fragment, a step which would involve CO attack at the cobalt centre, with concomitant migration of a terminal CR, CR^1, or CR^2 fragment to a cobalt-ligated carbonyl group to produce the acyl moiety. The carbon monoxide required for this process would arise from a dissociation step at an earlier stage in the reaction Scheme. Yields of products did not exceed 60% which is in accord with this premise. From the two fragments C(R)C(R^1)C(R^2) and C(R)C(R^2)C(R^1), with CO four stereoisomers are possible, depending on at which end of the chains insertion occurs. However, not all the possible isomers are formed. This is very probably because CO insertion occurs more readily with a Co–C(alkyl) group than with a Co–C(aryl) moiety. Thus the reaction between (**1a**) and $MeC{\equiv}CEt$ affords a mixture of (**7a**) and (**7b**) since formation of the other two possible isomers having the ring systems CoC(O)C(R)C(Et)C(Me) or CoC(O)C(R)C(Me)C(Et) would require rupture of a Co–C-(C_6H_4Me-4) bond, rather than Co–C(Me) or Co–C(Et) bonds. It is noteworthy that the synthesis of (**5c**) proceeds in significantly higher yield than those of (**5a**), (**5b**), (**5d**), or (**7**). This can be understood in terms of CO insertion being especially favoured when the carbon atoms at both ends of the μ-C_3 group in the intermediate (**B**) carry Me substituents.

A comparison of the reactions which afford compounds (**5a**) and (**5d**) is of interest in the context of the step from (**B**) to (**5**) in Scheme 3. In the preparation of (**5a**) from (**1a**) and $MeC{\equiv}CMe$ the *p*-tolyl substituent, as expected, is attached to the carbon atom σ bonded to the cobalt; CO insertion having occurred between cobalt and a CMe group. In the synthesis of (**5d**) from (**1b**) and $MeC{\equiv}CPh$, the aryl substituent is also attached to the carbon atom σ bonded to cobalt, while the two Me groups are attached to adjacent carbon atoms. This result suggests that a CMe to CoCO migration process is the last step in the reaction sequence, and that this step is favoured to the exclusion of CO insertion at the CoC(Ph) group; a result which would have led to the synthesis of [WCo{μ-C(Me)C(Me)C(Ph)C(O)}$(CO)_7$]. Interestingly, the reaction between (**1b**) and $MeC{\equiv}CPh$ might have afforded [WCo{μ-C(Me)C(Ph)C(Me)C(O)}$(CO)_7$], an isomer of (**5d**) derived by CO insertion into one or other of the Co–C(Me) groups in an intermediate [WCo{μ-C(Me)C(Ph)C-(Me)}$(CO)_7$]. No evidence for a complex of formulation [WCo{μ-C(Me)C(Ph)C(Me)C(O)}$(CO)_7$] was obtained, for reasons at present obscure.

The reactions described herein, and those reported previously,[3] show that the dimetal compounds (**1a**)—(**1c**) afford a variety of products with alkynes. The terminal alkylidyne groups in (**1a**)—(**1c**) readily form C–C bonds with the alkynes, suggesting that reactions of the dimetal compounds with other unsaturated compounds should be studied.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Light petroleum

Table 6. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**6a**), with estimated standard deviatons in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	252(1)	7 237(1)	5 265(1)	C(23)	−2 882(7)	9 963(5)	4 164(4)
Co	−1 935(1)	6 827(1)	5 257(1)	C(24)	−2 914(6)	9 813(5)	3 417(4)
P	−3 512(1)	7 224(1)	5 602(1)	C(25)	−2 397(7)	9 066(5)	3 236(4)
C(1)	−1 062(6)	6 927(4)	6 296(4)	C(26)	−1 853(6)	8 497(4)	3 790(4)
O(1)	−1 092(4)	6 425(3)	6 813(3)	C(27)	−3 516(8)	10 424(7)	2 809(5)
C(2)	−1 913(6)	5 673(5)	5 440(4)	C(31)	−3 469(6)	8 259(4)	6 114(3)
O(2)	−1 885(5)	4 949(3)	5 538(3)	C(32)	−4 165(7)	8 952(4)	5 858(4)
C(3)	−2 499(5)	6 641(4)	4 244(4)	C(33)	−4 082(8)	9 717(5)	6 259(5)
O(3)	−2 820(5)	6 452(4)	3 653(3)	C(34)	−3 318(8)	9 802(5)	6 929(5)
C(4)	548(7)	5 978(5)	5 640(4)	C(35)	−2 625(7)	9 115(5)	7 196(4)
O(4)	767(5)	5 291(4)	5 842(3)	C(36)	−2 689(6)	8 347(5)	6 796(4)
C(5)	1 856(6)	7 342(5)	5 826(4)	C(41)	−4 057(5)	6 438(4)	6 199(4)
O(5)	2 739(5)	7 440(5)	6 181(4)	C(42)	−4 257(6)	5 594(5)	5 947(4)
C(6)	756(6)	8 223(5)	4 698(4)	C(43)	−4 784(7)	5 002(5)	6 329(4)
O(6)	1 106(5)	8 736(4)	4 355(3)	C(44)	−5 089(7)	5 267(6)	6 969(5)
C(7)	206(6)	6 709(4)	4 265(4)	C(45)	−4 885(8)	6 078(6)	7 235(4)
O(7)	160(5)	6 447(4)	3 665(3)	C(46)	−4 357(7)	6 680(5)	6 855(4)
C(8)	−295(5)	7 675(4)	6 381(3)	C(51)	−4 758(6)	7 351(4)	4 831(3)
C(9)	−585(5)	8 315(4)	5 815(3)	C(52)	−5 795(5)	7 028(5)	4 866(4)
C(10)	−1 316(5)	8 011(4)	5 143(3)	C(53)	−6 715(7)	7 176(6)	4 280(5)
C(11)	521(6)	7 829(5)	7 135(4)	C(54)	−6 603(7)	7 665(6)	3 671(4)
C(12)	−162(6)	9 246(4)	5 965(4)	C(55)	−5 573(7)	7 983(5)	3 629(4)
C(21)	−1 829(6)	8 641(4)	4 541(4)	C(56)	−4 648(6)	7 833(4)	4 200(4)
C(22)	−2 369(5)	9 399(4)	4 714(4)				

Table 7. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**8d**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 846(1)	3 684(1)	1 209(1)	C(26)	5 890(5)	1 880(5)	1 563(4)
Co	2 985(1)	3 365(1)	2 937(1)	C(31)	3 065(5)	2 033(5)	4 690(4)
P	3 954(1)	2 029(1)	3 741(1)	C(32)	2 424(6)	1 138(5)	4 648(5)
C(1)	1 715(4)	2 430(4)	2 199(4)	C(33)	1 712(7)	1 251(6)	5 387(5)
O(1)	741(3)	2 364(4)	2 606(3)	C(34)	1 670(7)	2 229(7)	6 151(5)
C(2)	1 902(5)	4 150(5)	3 777(4)	C(35)	2 313(7)	3 114(6)	6 189(5)
O(2)	1 196(5)	4 660(5)	4 244(4)	C(36)	3 022(6)	3 019(5)	5 469(4)
C(3)	4 026(5)	4 459(4)	3 443(4)	C(41)	4 207(5)	520(4)	2 993(4)
O(3)	4 643(5)	5 171(4)	3 769(4)	C(42)	3 206(5)	−49(4)	2 467(4)
C(4)	292(6)	3 371(6)	207(5)	C(43)	3 394(6)	−1 177(5)	1 872(4)
O(4)	−607(5)	3 210(6)	−297(5)	C(44)	4 606(7)	−1 720(5)	1 782(5)
C(5)	2 390(7)	3 705(6)	−31(5)	C(45)	5 578(6)	−1 154(5)	2 315(5)
O(5)	2 719(7)	3 704(6)	−748(4)	C(46)	5 409(5)	−39(5)	2 922(4)
C(6)	2 419(6)	5 274(5)	1 591(5)	C(51)	5 507(5)	2 267(4)	4 436(4)
O(6)	2 752(5)	6 165(4)	1 812(5)	C(52)	5 913(5)	1 915(5)	5 287(4)
C(7)	472(6)	4 760(6)	1 882(6)	C(53)	7 113(6)	2 024(6)	5 778(5)
O(7)	−308(6)	5 354(6)	2 246(5)	C(54)	7 931(6)	2 457(6)	5 396(5)
C(8)	1 899(4)	1 734(4)	1 247(4)	C(55)	7 512(5)	2 819(6)	4 569(5)
C(9)	3 061(4)	1 859(4)	1 010(3)	C(56)	6 315(5)	2 724(5)	4 071(4)
C(10)	3 702(4)	2 725(4)	1 696(3)	B	−505(1)	−479(1)	2 464(1)
C(11)	1 041(5)	896(5)	607(4)	F(1)	−130(2)	227(2)	2 090(2)
C(12)	3 494(6)	1 093(5)	77(4)	F(2)	−1 106(2)	−1 223(2)	1 776(2)
C(21)	4 995(4)	2 839(4)	1 595(4)	F(3)	442(2)	−1 020(2)	2 903(2)
C(22)	5 366(5)	3 854(5)	1 567(5)	F(4)	−1 229(2)	100(1)	3 092(1)
C(23)	6 590(7)	3 922(7)	1 512(7)				
C(24)	7 469(7)	2 946(7)	1 491(7)				
C(25)	7 121(5)	1 943(7)	1 505(5)				

refers to that fraction of b.p. 40—60 °C. Florisil (Fluka, 100—200 mesh) was used for chromatography columns. The instrumentation used for spectroscopic studies has been mentioned previously.[1] The compounds [$WCo(\equiv CR)(CO)_8$] were prepared as described earlier.[2e] Aldrich $HBF_4{\cdot}Et_2O$ was used for the protonation of complexes.

Reactions of [$WCo(\equiv CR)(CO)_8$] ($R = C_6H_4Me$-4 *or* Me) *with Alkynes.*—(*i*) A mixture of compounds (**1a**) (1.00 g, 1.75 mmol) and $MeC\equiv CMe$ (0.25 cm^3, 3.2 mmol) in light petroleum (*ca.* 20 cm^3) was stirred at room temperature for 24 h. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2-light petroleum (10 cm^3, 1 : 3) and chromatographed (15 × 2 cm column). Elution with the same solvent mixture, gradually increasing the concentration of CH_2Cl_2 to 100%, removed successively eluates containing [$W(CO)_6$] and [$Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9$] (identified by i.r.), traces of unidentified complexes, and a bright orange product. Removal of solvent from the latter afforded an oily residue, which was dissolved in the minimum of light petroleum (*ca.* 5 cm^3) and cooled to −78 °C.

The supernatant liquid was removed with a syringe to give orange *microcrystals* of [WCo{μ-C(C_6H_4Me-4)C(Me)C(Me)-C(O)}$(CO)_7$] (**5a**) (0.45 g).

(*ii*) In a similar manner to the synthesis of (**5a**), the reaction between EtC≡CEt (0.15 g, 1.32 mmol) and (**1a**) (0.50 g, 0.88 mmol) in light petroleum (10 cm^3) yielded orange *microcrystals* of [WCo{μ-C(C_6H_4Me-4)C(Et)C(Et)C(O)}$(CO)_7$] (**5b**) (0.23 g).

(*iii*) A mixture of (**1b**) (0.25 g, 0.50 mmol) and MeC≡CMe (0.10 cm^3, 1.20 mmol) in light petroleum (50 cm^3) was stirred at 0 °C for 24 h. Volatile material was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2—light petroleum (5 cm^3, 1:4) and chromatographed (20 × 2 cm column). Elution with the same solvent mixture, gradually increasing the CH_2Cl_2 concentration to 100% gave initially a mixture of [$W(CO)_6$] and [$Co_3(\mu_3$-CMe)$(CO)_9$] (identified by i.r.), followed by an orange eluate. Removal of solvent *in vacuo* from the latter, followed by crystallisation of the residues from light petroleum (*ca.* 5 cm^3) at −78 °C gave orange *microcrystals* of [WCo{μ-C(Me)C(Me)C-(Me)C(O)}$(CO)_7$] (**5c**) (0.17 g).

(*iv*) In a manner similar to the synthesis of (**5c**), a mixture of (**1b**) (0.50 g, 1.0 mmol) and MeC≡CPh (0.20 g, 1.72 mmol) in light petroleum (40 cm^3) afforded orange *microcrystals* of [WCo{μ-C(Ph)C(Me)C(Me)C(O)}$(CO)_7$] (**5d**) (0.25 g).

(*v*) In a synthesis similar to that which gave complex (**5a**), a mixture of (**1a**) (0.30 g, 0.53 mmol) and MeC≡CEt (0.10 g, 1.47 mmol) in light petroleum (20 cm^3) gave orange *microcrystals* (0.13 g) of an isomeric mixture (*ca.* 3:7 by n.m.r. peak intensities) of [WCo{μ-C(C_6H_4Me-4)C(Et)C(Me)C(O)}-$(CO)_7$] (**7a**) and [WCo{μ-C(C_6H_4Me-4)C(Me)C(Et)C(O)}-$(CO)_7$] (**7b**), respectively.

Reactions with PPh_3 *or* $Ph_2PCH_2PPh_2$.—(*i*) A light petroleum (30 cm^3) solution of (**5a**) (0.31 g, 0.50 mmol) was treated with PPh_3 (0.20 g, 0.76 mmol), and the mixture stirred for 20 min. The supernatant liquid was removed with a syringe, and the orange-red precipitate was washed with light petroleum (2 × 10 cm^3) to afford red *microcrystals* of [WCo{μ-C(C_6H_4-Me-4)C(Me)C(Me)C(O)}$(CO)_6(PPh_3)$] (**6a**) (0.41 g).

(*ii*) Similarly, treatment of (**5b**) (0.33 g, 0.50 mmol) in light petroleum (40 cm^3) with PPh_3 (0.20 g, 0.76 mmol) gave red-orange *microcrystals* of [WCo{μ-C(C_6H_4Me-4)C(Et)C(Et)-C(O)}$(CO)_6(PPh_3)$] (**6b**) (0.42 g).

(*iii*) Similarly, [WCo{μ-C(Me)C(Me)C(Me)C(O)}$(CO)_6$-(PPh_3)] (**6c**) (0.37 g) was obtained as red *microcrystals* from (**5c**) (0.27 g, 0.50 mmol) and PPh_3 (0.20 g, 0.76 mmol) in light petroleum (40 cm^3).

(*iv*) Treatment of (**5c**) (0.11 g, 0.20 mmol) with dppm (0.08 g, 0.20 mmol) in light petroleum (20 cm^3) afforded orange *microcrystals* of [WCo{μ-C(Me)C(Me)C(Me)C(O)}$(CO)_6$-(dppm)] (**6d**) (0.17 g).

(*v*) Similarly, red-orange *microcrystals* of [WCo{μ-C(Ph)C-(Me)C(Me)C(O)}$(CO)_6(PPh_3)$] (**6e**) (0.41 g) were prepared from (**5d**) (0.30 g, 0.50 mmol) and PPh_3 (0.20 g, 0.76 mmol) in light petroleum (40 cm^3).

Protonation Studies.—(*i*) A CH_2Cl_2 (10 cm^3) solution of (**5c**) (0.14 g, 0.25 mmol) was treated with HBF_4·Et_2O (0.25 mmol), the colour changing immediately from orange to yellow. Addition of light petroleum (40 cm^3) gave a yellow precipitate. Solvent was removed with a syringe and the precipitate washed with light petroleum (3 × 10 cm^3) to give yellow *microcrystals* of [WCo{μ-C(Me)C(Me)C(Me)C(OH)}$(CO)_7$][BF_4] (**8a**) (0.15 g).

(*ii*) A suspension of (**6c**) (0.21 g, 0.25 mmol) in Et_2O (30 cm^3) was treated with an excess (2—3 drops) of HBF_4·Et_2O. The red suspension dissolved rapidly precipitating yellow microcrystals. Removal of the supernatant ligand with a syringe and washing the residue with Et_2O (2 × 10 cm^3) gave yellow *microcrystals* of [WCo{μ-C(Me)C(Me)C(Me)C(OH)}$(CO)_6(PPh_3)$][BF_4] (**8b**) (0.16 g).

(*iii*) In a synthesis similar to that of (**8b**), the compound (**6a**) (0.10 g, 0.12 mmol) was suspended in Et_2O (25 cm^3) and treated with HBF_4·Et_2O (2—3 drops). After removal of solvent *in vacuo*, and washing the residue with Et_2O (2 × 10 cm^3) yellow *microcrystals* of [WCo{μ-C(C_6H_4Me-4)C(Me)C(Me)C(OH)}-$(CO)_6(PPh_3)$][BF_4] (**8c**) (0.11 g) were obtained.

(*iv*) A suspension of (**6e**) (0.21 g, 0.25 mmol) in Et_2O (30 cm^3) was treated with HBF_4·Et_2O (2—3 drops) affording yellow *microcrystals* of [WCo{μ-C(Ph)C(Me)C(Me)C(OH)}$(CO)_6$-(PPh_3)][BF_4] (**8d**).

Crystal Structure Determination of (**6a**).—Crystals of (**6a**) were grown from CH_2Cl_2–Et_2O as dark red rhombs. Diffracted intensities were collected (ω—2θ scans) at room temperature from a crystal of dimensions *ca.* 0.35 × 0.25 × 0.20 mm on a Nicolet *P*3*m* four-circle diffractometer. Of the 5 524 intensities measured (2θ ⩽ 50°), 4 014 had $F \geqslant 5.0\sigma(F)$, and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption. The latter was based on a semi-empirical method using azimuthal scan data.[16]

Crystal data. $C_{37}H_{28}CoO_7PW$, $M = 858.4$, monoclinic, $a = 12.191(8)$, $b = 15.34(1)$, $c = 18.30(1)$ Å, $\beta = 102.90(5)°$, $U = 3\,335(4)$ Å^3, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 1\,688$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 41.1 cm^{-1}.

The structure was solved by conventional heavy-atom and difference-Fourier methods, and refined by blocked-cascade least squares. All non-hydrogen atoms were given anisotropic thermal parameters, with the hydrogen atoms included at calculated positions. Refinement converged at $R = 0.033$ ($R' = 0.037$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.000\,80|F_o|^2]$ gave a satisfactory weight analysis. The final electron density maps showed no peaks ⩾0.97 or ⩽ −1.55 e Å^{-3}.

Crystal Structure Determination of (**8d**).—Orange crystals of (**8d**) were grown from CH_2Cl_2–light petroleum (*ca.* 1:10), and that rhomb chosen for study was *ca.* 0.35 × 0.40 × 0.50 mm. Diffracted intensities (ω − 2θ scans) were collected at room temperature. Of the total of 6 992 intensities (2θ ⩽ 50°), 5 687 with $F \geqslant 5.0\sigma(F)$ were used in structure solution and refinement after corrections for Lorentz, polarisation, and *X*-ray absorption effects.[16]

Crystal data. $C_{36}H_{27}BCoF_4O_7PW$, $M = 932.2$, triclinic, $a = 11.060(3)$, $b = 12.124(3)$, $c = 14.387(4)$ Å, $\alpha = 106.78(2)$, $\beta = 101.24(2)$, $\gamma = 80.09(2)°$, $U = 1\,798(3)$ Å^3, $Z = 2$, $D_c = 1.72$ g cm^{-3}, $F(000) = 912$, space group $P\bar{1}$, μ(Mo-K_α) = 38.36 cm^{-1}.

The structure was solved by the usual heavy-atom and difference-Fourier methods. Refinement was by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom on O(1) was located and refined with an isotropic thermal parameter *ca.* 1.2 × U_{iso} of the parent oxygen atom. Aromatic and methyl hydrogen atoms were included at calculated positions (C–H 0.960 Å) with fixed isotropic thermal parameters 1.2 times U_{equiv} of their parent carbon atoms. The BF_4 anion showed some signs of positional disorder but was adequately modelled as a rigid tetrahedral group. Refinement with the weighting scheme $w^{-1} = [\sigma^2(F_o) + 0.000\,36|F_o|^2]$ converged at $R = 0.036$ ($R' = 0.039$). The final electron density maps showed no peaks ⩾ 1.13 or ⩽ −0.85 e Å^{-3}.

For both structures all calculations were performed using the SHELXTL system of programs,[16] with scattering factors and corrections for anomalous dispersion taken from ref. 17. The atom co-ordinates for (**6a**) and (**8d**) are listed in Tables 6 and 7, respectively.

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

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