Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 76.[1] Alkylidyne–Alkyne Coupling Reactions involving the Complexes [WCo(≡CR)(CO)$_8$] (R = Me or C$_6$H$_4$Me-4)

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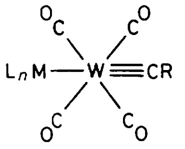
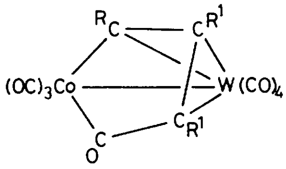
In light petroleum, at room temperature, the reaction between [WCo(≡CC$_6$H$_4$Me-4)(CO)$_8$] and the alkyne C$_2$(C$_6$H$_4$Me-4)$_2$ affords the complex [WCo{μ-C$_3$(C$_6$H$_4$Me-4)$_3$}(CO)$_7$]. The latter reacts reversibly with CO to give a product tentatively identified as [WCo{μ-C(C$_6$H$_4$Me-4)C(C$_6$H$_4$Me-4)C(C$_6$H$_4$Me-4)C(O)}(CO)$_7$]. Treatment of [WCo(≡CC$_6$H$_4$Me-4)(CO)$_8$] with PhC≡CPh affords a mixture of the isomeric compounds [WCo{μ-C(R^1)C(R^2)C(R^3)}(CO)$_7$] (R^1 = C$_6$H$_4$Me-4, R^2 = R^3 = Ph; R^2 = C$_6$H$_4$Me-4, R^1 = R^3 = Ph). With MeC≡CSiMe$_3$, the compounds [WCo(≡CR)(CO)$_8$] (R = C$_6$H$_4$Me-4 or Me) react to give the complexes [WCo{μ-C(R)C(Me)C(SiMe$_3$)C(O)}(CO)$_7$] which reversibly lose CO to yield the species [WCo{μ-C(R)C(Me)C(SiMe$_3$)}(CO)$_7$]. Both the former and the latter products on treatment with PPh$_3$ give the complexes [WCo{μ-C(R)C(Me)C(SiMe$_3$)C(O)}(CO)$_6$(PPh$_3$)] quantitatively. The compound [WCo(≡CMe)(CO)$_8$] reacts with EtC≡CEt to afford an inseparable mixture of three isomeric compounds [WCo{μ-C(R^1)C(R^2)C(R^3)C(O)}(CO)$_7$] (R^1 = R^2 = Et, R^3 = Me; R^1 = R^3 = Et, R^2 = Me; R^2 = R^3 = Et, R^1 = Me). The ^{1}H and ^{13}C-{^{1}H} n.m.r. data for the various tungsten–cobalt complexes are reported and discussed in the context of the structures proposed.

The reactivity of alkylidyne or alkylidene groups bridging di- or tri-metal centres is currently a topic of general interest.[2] In studies in this area we have focused on the reactivity of alkylidyne fragments spanning bonds between dissimilar transition elements.[3] Recently we reported[4,5] some reactions of alkynes with the compounds [WM(≡CR)(CO)$_4$(L$_n$)] [ML$_n$ = Co(CO)$_4$, R = C$_6$H$_4$Me-4 (**1a**) or Me (**1b**); ML$_n$ = Mo(CO)$_3$(η-C$_5$H$_5$), R = C$_6$H$_4$Me-4 (**1c**)]. In light petroleum at room temperature, (**1a**) reacts with MeC≡CMe or EtC≡CEt to give the complexes [WCo{μ-C(R)C(R^1)C(R^1)C(O)}(CO)$_7$] [R = C$_6$H$_4$Me-4; R^1 = Me (**2a**) or Et (**2b**)], whereas MeC≡CEt affords an inseparable mixture of the isomeric products [WCo{μ-C(R)C(R^1)C(R^2)C(O)}(CO)$_7$] [R = C$_6$H$_4$Me-4; R^1 = Me, R^2 = Et (**3a**) or R^1 = Et, R^2 = Me (**3b**)]. Reaction between (**1b**) and MeC≡CMe or MeC≡CPh yields the compounds [WCo{μ-C(R)C(Me)C(Me)C(O)}(CO)$_7$] [R = Me (**2c**) or Ph (**2d**)].[4] The nature of the products obtained by treating the molybdenum–tungsten compound (**1c**) with MeC≡CMe depends on the reaction conditions.[5] In thf (tetrahydrofuran) at reflux, the product is the species [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] (**4**), whereas at room temperature the complex [MoW{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)CH(Me)C(O)}(CO)$_6$(η-C$_5$H$_5$)] (**5**) is formed. Interestingly, the hydrogen migration reactions leading to (**5**) can be reversed, since when the latter is heated with MeC≡CMe complex (**4**) is produced.

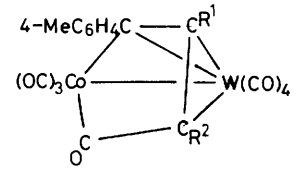
The complexes formed in these various reactions result from coupling of the alkylidyne groups present in (**1**) with



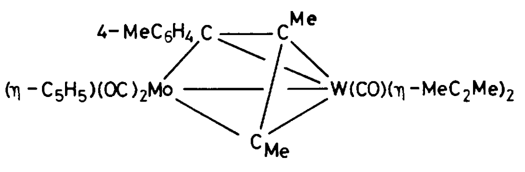
	ML$_n$	R
(**1a**)	Co(CO)$_4$	C$_6$H$_4$Me-4
(**1b**)	Co(CO)$_4$	Me
(**1c**)	Mo(CO)$_3$(η-C$_5$H$_5$)	C$_6$H$_4$Me-4



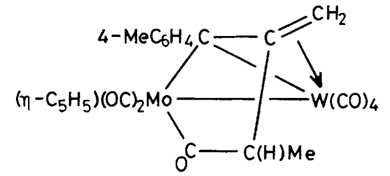
	R	R^1
(**2a**)	C$_6$H$_4$Me-4	Me
(**2b**)	C$_6$H$_4$Me-4	Et
(**2c**)	Me	Me
(**2d**)	Ph	Me
(**2e**)	C$_6$H$_4$Me-4	C$_6$H$_4$Me-4



	R^1	R^2
(**3a**)	Me	Et
(**3b**)	Et	Me



(**4**)



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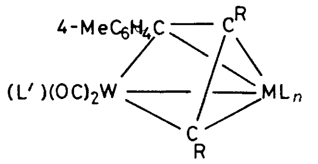
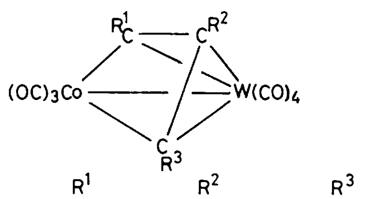
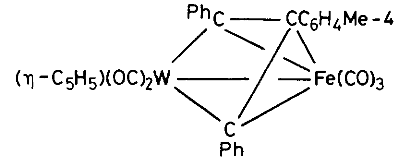


	R	ML_n	L′
(6a)	Me	$Fe(CO)_3$	η-C_5Me_5
(6b)	Ph	$Fe(CO)_3$	η-C_5Me_5
(6c)	Me	$Fe(CO)_3$	η-C_5H_5
(6d)	Ph	$Fe(CO)_3$	η-C_5H_5
(6e)	Me	$Co(\eta$-$C_5Me_5)$	η-C_5H_5
(6f)	Ph	$Co(\eta$-$C_5Me_5)$	η-C_5H_5
(6g)	Ph	$Rh(\eta$-$C_5Me_5)$	η-C_5H_5
(6h)	Me	$Rh(\eta^5$-$C_9H_7)$	η-C_5H_5
(6i)	Ph	$Rh(\eta^5$-$C_9H_7)$	η-C_5H_5



	R^1	R^2	R^3
(7a)	C_6H_4Me-4	C_6H_4Me-4	C_6H_4Me-4
(7b)	C_6H_4Me-4	Ph	Ph
(7c)	Ph	C_6H_4Me-4	Ph
(7d)	C_6H_4Me-4	Me	$SiMe_3$
(7e)	Me	Me	$SiMe_3$



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the alkynes. Moreover, except in the formation of (**4**), these reactions lead to products having a CO molecule incorporated into the bridging ligand. In contrast, in earlier studies[6] of reactions between the alkynes MeC≡CMe or PhC≡CPh and other tungsten-containing di- or tri-metal compounds with bridging *p*-tolylmethylidyne groups, we obtained the dimetal complexes $[WM\{\mu$-$C(C_6H_4Me$-$4)C(R)$-$C(R)\}(CO)_2(L_n)(L')]$ [(**6**), $ML_n = Fe(CO)_3$, $L' = \eta$-C_5Me_5 or η-C_5H_5, R = Me or Ph; $ML_n = Co(\eta$-$C_5Me_5)$ or $Rh(\eta^5$-$C_9H_7)$, $L' = \eta$-C_5H_5, R = Me or Ph; $ML_n = Rh(\eta$-$C_5Me_5)$, $L' = \eta$-C_5H_5, R = Ph]. In all these products the bridging μ-C_3 fragment is similar to that found in (**4**), and a CO insertion reaction does not occur.

In view of the variety of heterodinuclear metal compounds obtained in the above reactions, we have carried out further studies with the compounds (**1a**) and (**1b**) and alkynes, in order to gain a better understanding of the C–C bond forming processes that occur with these systems.

Results and Discussion

Treatment of (**1a**) with the alkyne $C_2(C_6H_4Me$-$4)_2$ in light petroleum at room temperature affords the orange complex $[WCo\{\mu$-$C_3(C_6H_4Me$-$4)_3\}(CO)_7]$ (**7a**) formed in *ca.* 70% yield. Due to the very high solubility of the compound, crystals could not be obtained, and it was isolated as an oil. Nevertheless, the spectroscopic data were in accord with the formulation. In the i.r. spectrum there were seven bands for terminal CO groups in the region 1 941—2 082 cm^{-1} (see Experimental section). There was no absorption attributable to an acyl group at *ca.* 1 650 cm^{-1}, as found in the spectra of the compounds (**2a**)—(**2d**).[4] The ^1H n.m.r. spectrum showed two singlet resonances at δ 2.25 and 2.29 (relative intensity 3:6) which may be assigned to the methyl groups of the C_6H_4Me-4 fragments attached to the central carbon and terminal carbons of the μ-C_3 ligand, respectively. Similarly, in the aromatic region there were two groups of signals (Table), one corresponding to four protons and the other to eight. The ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**7a**) was informative showing the expected signals for the carbonyl ligands at δ 217.6 p.p.m. [WCO, *J*(WC) 120 Hz] and 197.8 p.p.m. (CoCO). The latter resonance was broadened due to the ^{59}Co quadrupolar effect. The appearance of two peaks indicates that site exchange of the CO ligands occurs on the n.m.r. time-scale at each metal centre, but that no exchange takes place between the two metal centres. Peaks due to C_6H_4Me-4 groups in two different environments are clearly seen in the ratio 2:1. This is as expected, with the C_6H_4Me-4 fragments attached to the end carbon atoms of the μ-C_3 bridge being equivalent, and differing from that of the C_6H_4Me-4 group bonded to the central carbon. Significantly, there are two resonances at δ 125.1 and 120.6 p.p.m. (relative intensity *ca.* 1:2) attributable to the central and terminal carbon nuclei of the μ-C_3 group, respectively. The peak at 120.6 p.p.m. is somewhat broadened, due to the proximity of the cobalt nucleus. These signals are appreciably more deshielded than the corresponding peaks in the spectra of the compounds (**6**). Thus in the spectrum of (**6f**) the resonance for the central carbon of the bridge system is at δ 120.7 p.p.m., with those for the end carbon nuclei at δ 93.5 and 92.7 p.p.m.[6a] The difference in shifts may be due to the presence of the electron donating η-C_5H_5, η-C_5Me_5, or η^5-C_9H_7 groups in the complexes (**6**).

It is interesting to compare the formation of (**7a**) with the reactions of (**1a**) with MeC≡CMe or EtC≡CEt which yield, respectively, the species (**2a**) and (**2b**) containing acyl groups. We have suggested[4] that in the synthesis of (**2a**) and (**2b**), carbonyl 'insertion' to produce the CoC(O)C(alkyl) groups occurs as the last step in these reactions. We also showed that CO insertion is favoured at the end-carbon atom of the μ-C_3 group carrying an alkyl substituent. Thus the reaction between (**1b**) and MeC≡CPh afforded exclusively (**2d**). Hence it is not surprising that (**7a**) is formed in preference to $[WCo\{\mu$-$C(C_6H_4Me$-$4)C(C_6H_4Me$-$4)C(C_6H_4Me$-$4)C(O)\}(CO)_7]$ (**2e**) in the reaction between (**1a**) and $C_2(C_6H_4Me$-$4)_2$. However, prolonged treatment of light petroleum solutions of (**7a**) with CO gives rise to the appearance in the i.r. spectrum of new bands, including an absorption at 1 650 cm^{-1}, tentatively ascribed to (**2e**). Unfortunately, even after 2 d the uptake of CO by (**7a**) is only *ca.* 50% of that required for complete conversion (based on relative intensity of the i.r. bands). Moreover, if passage of CO is ceased, the mixture reverts rapidly to (**7a**). Consequently, it was not possible to obtain n.m.r. data for the transient species.

The reaction between (**1a**) and PhC≡CPh affords a mixture of the two isomeric compounds $[WCo\{\mu$-$C(R^1)C(R^2)C(R^3)\}$-$(CO)_7]$ [(**7b**), $R^1 = C_6H_4Me$-4, $R^2 = R^3 = Ph$; (**7c**), $R^2 = C_6H_4Me$-4, $R^1 = R^3 = Ph$]. Based on the relative intensity of the peaks in the n.m.r. spectra (Table), these species are produced in a (**7b**):(**7c**) ratio of *ca.* 2:1. The i.r. spectrum of the mixture in the carbonyl stretching region is virtually identical with that of (**7a**). The ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra of the mixture, when compared with that of (**7a**), provide good evidence for the formulations ascribed to the two isomers.

The ^{13}C-$\{^1H\}$ n.m.r. data reveal only one set of resonances for the carbonyl ligands [δ 216.4 (WCO) and 196.9 p.p.m. (CoCO)] and one peak for the Me-4 groups (δ 21.1 p.p.m.), indicating a

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

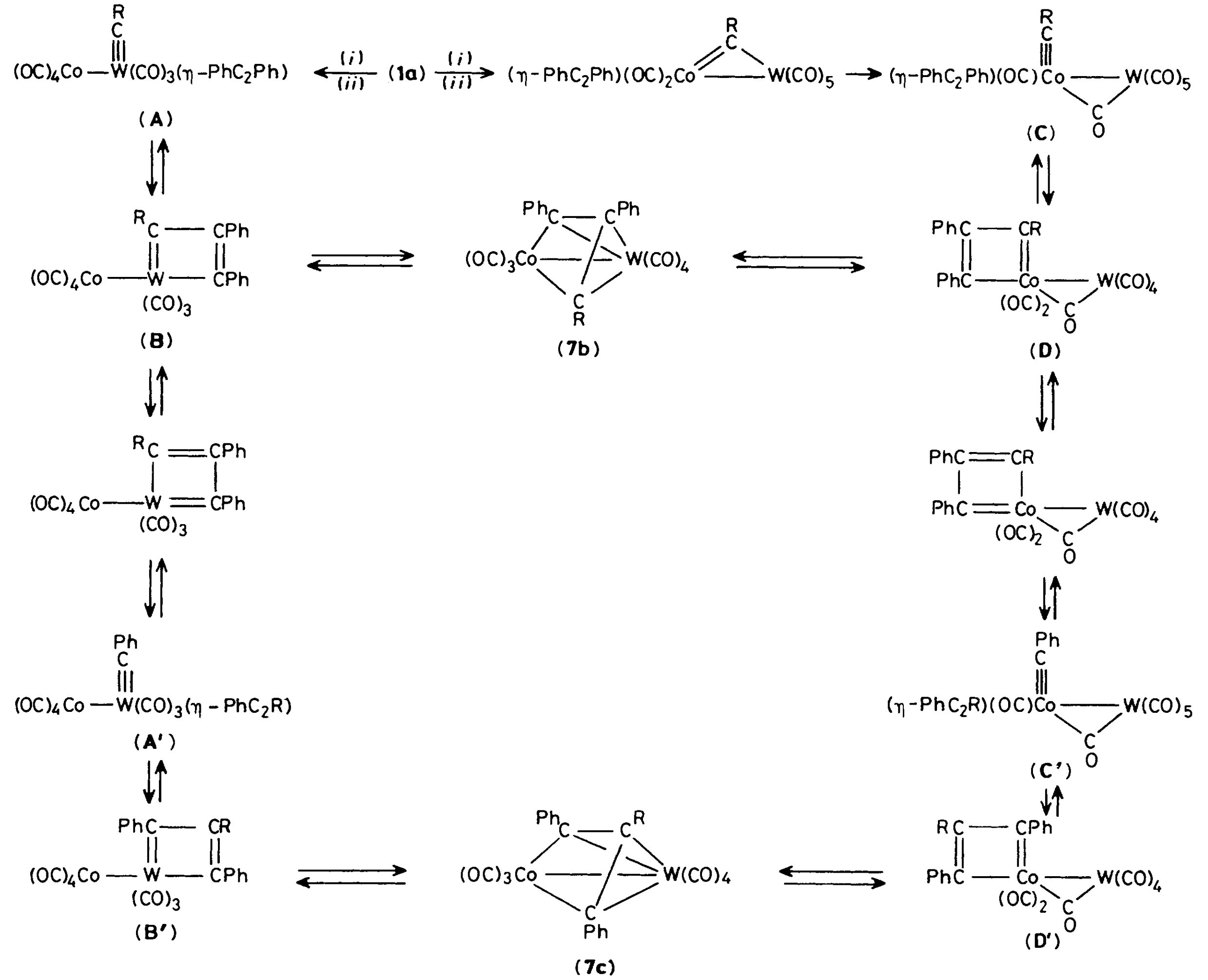
Compound	^{1}H(δ)[b]	^{13}C(δ)[c,d]
(**7a**)	2.25 (s, 3 H, Me-4), 2.29 (s, 6 H, Me-4), 6.81, 6.98 [(AB)$_2$ 4 H, C$_6$H$_4$, *J*(AB) 8], 7.08 (s, 8 H, C$_6$H$_4$)	217.6 [WCO, *J*(WC) 120], 197.8 (br, CoCO), 140.3 [2 C, C^1(C$_6$H$_4$), 138.7 [C^1(C$_6$H$_4$)], 137.7—129.2 (C$_6$H$_4$), 125.1 [C(R)*C*(R)C(R)], 120.6 [*C*(R)C(R)*C*(R)], 22.1 (Me-4), 22.0 (2 C, Me-4)
(**7b**) (**7c**)	2.33 [s, 3 H, Me-4 (**7c**)], 2.28 [s, 3 H, Me-4 (**7b**)], 6.72—7.68 (m, 28 H, C$_6$H$_4$ and Ph)	216.4 [WCO, *J*(WC) 120], 196.9 (br, CoCO), 142.3—126.7 (C$_6$H$_4$ and Ph), 124.6 [C(Ph)*C*(R)C(Ph)], 124.2 [C(R)*C*(Ph)C(Ph)], 119.7, 119.5, 119.2 [*C*(Ph)C(R)*C*(Ph), *C*(R)C(Ph)*C*(Ph)], 21.1 (Me-4)
(**7d**)	0.32 (s, 9 H, SiMe$_3$), 2.24 (s, 3 H, Me-4), 2.39 (s, 3 H, CMe), 7.21, 7.33 [(AB)$_2$, 4 H, C$_6$H$_4$, *J*(AB) 7]	[e] 218.5 [WCO, *J*(WC) 117], 201.4, 199.3, 194.3 (br, CoCO), 139.5 [C^1(C$_6$H$_4$)], 137.7, 130.8, 129.7 (C$_6$H$_4$), 126.9 (*C*Me), 121.7 (*C*R), 106.6 [*C*(SiMe$_3$)], 23.9 (C*Me*), 21.3 (Me-4), 2.2 (SiMe$_3$)
(**7e**)	0.20 (s, 9 H, SiMe$_3$), 2.00 [s, 3 H, C(*Me*)C(Me)C(SiMe$_3$)], 2.47 [s, 3 H, C(Me)C(*Me*)C(SiMe$_3$)]	[e] 219.1 [WCO, *J*(WC) 119], 131.2 [C(Me)*C*(Me)C(SiMe$_3$)], 120.2 [*C*(Me)C(Me)C(SiMe$_3$)], 107.3 [br, C(SiMe$_3$)], 24.3 [C(Me)C(*Me*)C(SiMe$_3$)], 21.3 [C(*Me*)C(Me)C(SiMe$_3$)], 1.8 (SiMe$_3$)
(**9a**)	0.32 (s, 9 H, SiMe$_3$), 2.42 (s, 3 H, Me-4), 2.49 (s, 3 H, CMe), 7.27 (s, 4 H, C$_6$H$_4$)	[e] 211.9 [WCO, *J*(WC) 127], 211.5 [br, *C*(O)C(SiMe$_3$)], 201.4—192.4 (vbr, CoCO), 186.7 (*C*R), 144.2 [C^1(C$_6$H$_4$)], 138.0, 132.0, 129.9, 128.1 (C$_6$H$_4$), 126.3 (*C*Me), 92.4 [C(SiMe$_3$), *J*(SiC) 55 Hz], 21.4 (Me-4), 19.4 (C*Me*), 0.0 (SiMe$_3$)
(**9b**)	0.24 (s, 9 H, SiMe$_3$), 2.52 [s, 3 H, C(O)C(SiMe$_3$)C(*Me*)], 3.10 [s, 3 H, C(Me)Co]	211.4 [WCO, *J*(WC) 126], 211.0 [br, *C*(O)C(SiMe$_3$)], 196.2 (br, CoCO), 182.1 [br, *C*(Me)Co], 126.8 [C(O)C(SiMe$_3$)*C*(Me)], 93.3 [*C*(SiMe$_3$)], 31.1 [C(*Me*)Co], 16.2 [C(O)C(SiMe$_3$)C(*Me*)], 1.0 (SiMe$_3$)
(**9c**) (**9d**) (**9e**)	1.04—1.54 [m, C(O)C(Me)C(CH$_2$*Me*) (**9c**), C(O)C(CH$_2$*Me*)C(Me) (**9d**), C(O)C(CH$_2$*Me*)C(CH$_2$*Me*) (**9e**)], 2.02 [s, CMe (**9c**)], 1.92—2.56 [m, C(O)C(Me)C(C*H*$_2$Me) (**9c**), C(O)C(C*H*$_2$Me)C(Me)C(CH$_2$Me) (**9d**), C(O)C(C*H*$_2$Me)C(C*H*$_2$Me) (**9e**)], 2.48 [s, CMe (**9d**)], 2.76—2.96, 3.08—3.40 [m × 2, C(C*H*$_2$Me)Co (**9c**), C(C*H*$_2$Me)Co (**9d**)], 3.21 [s, CMe (**9e**)]	212.2 [WCO, *J*(WC) 127 (**9c**)], 212.1 [WCO, *J*(WC) 127 (**9d**)], 211.9 [WCO, *J*(WC) 127 (**9e**)], 210.5, 210.4 [*C*(O)C(Et) (**9d**) and (**9e**), *C*(O)C(Me) (**9c**)], 200.8, 197.0, 193.2 (br, CoCO), 184.4 [C(Et)*C*(Et)Co (**9c**)], 183.6 [C(Me)*C*(Et)Co (**9d**)], 174.3 [*C*Me (**9e**)], 128.7 [C(O)C(Me)*C*(Et) (**9c**)], 128.2 [C(O)C(Et)*C*(Et) (**9e**)], 123.3 [C(O)C(Et)*C*(Me) (**9d**)], 103.8 [C(O)*C*(Et)C(Et) (**9e**)], 103.4 [C(O)*C*(Et)C(Me) (**9d**)], 96.5 [C(O)*C*(Me)C(Et) (**9c**)], 39.0 [C(Me)C(*C*H$_2$Me)Co (**9d**)], 38.7 [C(Et)C(*C*H$_2$Me)Co (**9c**)], 30.8 [C*Me* (**9e**)], 24.3, 24.2 [C(O)C(Me)C(*C*H$_2$Me) (**9c**) and C(O)C(Et)C(*C*H$_2$Me) (**9e**)], 23.9 [C(Me)C(CH$_2$*Me*)Co (**9d**)], 23.8, 23.7 [C(Et)C(CH$_2$*Me*)Co (**9c**) and C(O)C(*C*H$_2$Me)C(Et) (**9e**)], 21.8 [C(O)C(*C*H$_2$Me)C(Me) (**9d**)], 16.0 [C*Me* (**9d**)], 15.7, 15.6 [C(O)C(Me)C(CH$_2$*Me*) (**9c**) and C(O)C(Et)C(CH$_2$*Me*) (**9e**)], 15.3 [C*Me* (**9c**)], 14.7 [C(O)C(CH$_2$Me)C(Et) (**9e**)], 14.3 [C(O)C(CH$_2$*Me*)C(Me) (**9d**)]
(**10d**)	0.29 (s, 9 H, SiMe$_3$), 2.30, 2.35 (s × 2, 6 H, Me-4 and CMe), 6.87—6.96, 7.26—7.44 (m × 2, 19 H, C$_6$H$_4$ and Ph)	228.8 [br, *C*(O)C(SiMe$_3$)], 213.1 [WCO, *J*(WC) 127], 204.6, 199.3 (br, CoCO), 186.6 (*C*R), 146.0 [C^1(C$_6$H$_4$)], 137.8—128.3 (C$_6$H$_4$ and Ph), 124.2 (*C*Me), 94.6 [*C*(SiMe$_3$)], 21.1 (Me-4), 19.2 (C*Me*), 1.2 (SiMe$_3$)
(**10e**)	0.01 (s, 9 H, SiMe$_3$), 2.42 [s, 3 H, C(O)C(SiMe$_3$)C(*Me*)], 2.85 [d, 3 H, C(Me)Co, *J*(PH) 3], 7.36—7.47 (m, 15 H, Ph)	223.0 [br, *C*(O)C(SiMe$_3$)], 213.7 [WCO, *J*(WC) 127], 182.0 [br, *C*(Me)Co], 134.8—128.4 (Ph), 126.9 [C(O)C(SiMe$_3$)*C*(Me)], 95.1 [*C*(SiMe$_3$)], 32.2 [C(*Me*)Co], 16.8 [C(O)C(SiMe$_3$)C(*Me*)], 1.7 (SiMe$_3$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. [b] Measured in CD$_2$Cl$_2$. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$ (0.0 p.p.m.), with measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$. [d] R = C$_6$H$_4$Me-4. [e] Measured at −40 °C.

coincidence of the signals for these moieties for (**7b**) and (**7c**). In the aromatic region of the spectrum, however, there are too many peaks for the presence of just one isomer. The resonances at δ 124.2 and 124.6 p.p.m. are assigned to the centre μ-*C*Ph and μ-*C*C$_6$H$_4$Me-4 nuclei of (**7b**) and (**7c**), respectively. As mentioned above, the resonance in the spectrum of (**7a**) at δ 125.1 p.p.m. is due to the centre μ-*C*C$_6$H$_4$Me-4 group in this species. Peaks in the spectra of the isomeric mixture at δ 119.7, 119.5, and 119.2 p.p.m. may be attributed to the μ-*C*Ph and μ-*C*C$_6$H$_4$Me-4 nuclei bonded to the cobalt atom in (**7b**), and the μ-*C*Ph groups similarly bonded in (**7c**). However, specific assignments are not possible. In the ^{1}H n.m.r. spectrum of the isomeric mixture, signals for the Me-4 groups occur at δ 2.33 and 2.28. By comparison with the data for (**7a**) (Table), these resonances may be attributed to (**7c**) and (**7b**), respectively.

Formation of (**7c**) in the reaction between (**1a**) and PhC≡CPh implies cleavage of the alkyne into its constituent CPh fragments. This behaviour has precedent in the earlier observation[6a] that the reaction between the trimetal compound [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] and PhC≡CPh affords a mixture of the two complexes (**6d**) and (**8**). More recently Chisholm *et al.*[7] have observed similar reactions with the homodinuclear tungsten–alkylidyne species [W$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$]. For example, reaction with HC≡CH yields the two isomeric products [W$_2${μ-C(H)C(H)C(SiMe$_3$)}(μ-CSiMe$_3$)(CH$_2$SiMe$_3$)$_4$] and [W$_2${μ-C(H)C(SiMe$_3$)C(H)}(μ-CSiMe$_3$)(CH$_2$SiMe$_3$)$_4$]. Vollhardt and co-workers[8] have also observed the cleavage of alkynes and coupling of carbyne fragments in tricobalt clusters, and Chi and Shapley[9] have reported the conversion of the alkyne complex [OsW$_2${μ_3-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_7$(η-C$_5$H$_5$)$_2$] into the bis(alkylidyne) compound [OsW$_2$(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_5$(η-C$_5$H$_5$)$_2$]. Alkyne cleavage also occurs when the complex [RuW$_2${μ_3-C$_2$(C$_6$H$_4$Me-4)$_2$}(CO)$_7$(η-C$_5$H$_5$)$_2$] is heated, giving [RuW$_2$(μ-CC$_6$H$_4$Me-4)(μ_3-CC$_6$H$_4$Me-4)(CO)$_5$(η-C$_5$H$_5$)$_2$]. The latter with CO readily reverts to the μ_3-alkyne compound.[10] Relevant also is the synthesis of [FeW$_2$(μ_3-MeC$_2$C$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)$_2$] from the reaction between [W(≡CMe)(CO)$_2$(η-C$_5$H$_5$)] and [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)].[11]

Formation of the isomeric mixture of (**7b**) and (**7c**) may be rationalised according to one or other of the pathways shown in



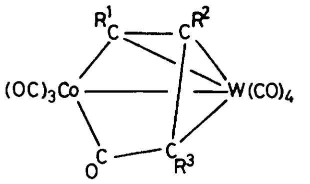
Scheme. R = C_6H_4Me-4, (*i*) +PhC≡CPh, (*ii*) -CO

the Scheme. As discussed earlier,[4] addition of an alkyne to (**1a**) might proceed either by attack at the alkylidyne–tungsten group, or at the cobalt centre. The well established lability of CO groups attached to cobalt, compared with tungsten, might favour the latter process in the initial step. In either pathway collapse of the metallacyclobutadiene intermediates (**B**) or (**D**) would yield (**7b**), the predominant isomer. It is noteworthy that the route to (**7b**) *via* (**D**) involves migration of the alkylidyne group from tungsten to cobalt for which there is precedent.[12] Moreover, the species (**B**) and (**D**) are structurally related to intermediates involved to account for alkyne metathesis at a mononuclear metal centre.[13–15] The Scheme also explains why there are two products (**7b**) and (**7c**) from this reaction. Thus (**B**) or (**D**) may not lead directly to (**7b**) but instead to the structurally related intermediates (**B′**) or (**D′**) *via* (**A′**) and (**C′**), respectively. If (**A**) and (**A′**) or (**C**) and (**C′**) were to establish an equilibrium, then one would expect an isomeric ratio of 2:1. That is (**A**) and (**C**) can only give (**7b**) whereas (**A′**) and (**C′**) have an equal probability of affording (**7b**) or (**7c**). Consequently it seems likely that (**7b**) and (**7c**) equilibrate. This same isomeric ratio (2:1) is also obtained when [$WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9(\eta\text{-}C_5H_5)$] is treated with PhC≡CPh to give (**6d**) and (**8**).[6a] However, the mechanism for this reaction must be complicated since an $Fe(CO)_4$ fragment is lost at some stage.

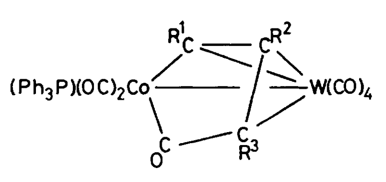
There may be pathways leading to (**7b**) and (**7c**) other than those shown in the Scheme. Thus we cannot rule out the possibility that intermediates (**A**) and (**A′**), or (**C**) and (**C′**), or species related to these, collapse directly to (**7b**) and (**7c**). However, in view of the work of Schrock and co-workers[15] on alkyne metathesis the metallacyclobutadiene intermediates shown in the Scheme might well play a role in the overall process.

The reaction between (**1a**) and the unsymmetrical alkyne $MeC{\equiv}CSiMe_3$ was next investigated. This was done with the object of comparing the results with the earlier study with MeC≡CEt, which had led to formation of the mixture of isomers (**3**).[4] At room temperature, in light petroleum, (**1a**) and $MeC{\equiv}CSiMe_3$ afforded a mixture of the two compounds [$WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(SiMe_3)\}(CO)_7$] (**7d**) and [$WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(SiMe_3)C(O)\}(CO)_7$] (**9a**), formed as an orange oil. Prolonged exposure of the mixture to vacuum results in decarbonylation of (**9a**) to yield microcrystals of (**7d**). This process is readily reversed since treatment of a light petroleum solution of the latter with CO for several minutes yields (**9a**) quantitatively. However, it proved impossible to isolate the latter species due to its facile loss of CO. Consequently, all spectroscopic measurements on (**9a**) were carried out on solutions saturated with carbon monoxide.

The i.r. spectrum of (**7d**) in the CO stretching region (see Experimental section) shows seven bands of similar pattern to those displayed by compounds (**7a**)—(**7c**). The ^1H n.m.r. spectrum (Table) has a singlet at δ 2.39 which may be ascribed to the μ-CMe group located in the central position in the $\mu\text{-}C_3$



	R^1	R^2	R^3
(9a)	C_6H_4Me-4	Me	$SiMe_3$
(9b)	Me	Me	$SiMe_3$
(9c)	Et	Et	Me
(9d)	Et	Me	Et
(9e)	Me	Et	Et



	R^1	R^2	R^3
(10a)	C_6H_4Me-4	Me	Me
(10b)	Me	Me	Me
(10c)	Ph	Me	Me
(10d)	C_6H_4Me-4	Me	$SiMe_3$
(10e)	Me	Me	$SiMe_3$

ligand. The assignment is made on the basis of the ^1H n.m.r. data for (**7e**), discussed below, and also by comparison with the previously reported spectra of (**6a**), (**6c**), (**6e**), and (**6h**).[6] In general, the signal for the Me substituent attached to the central carbon of the bridging ligand is more deshielded than one attached to a carbon at the ends of the μ-C_3 fragment. However, the resonance in (**7d**) is more shielded than those in the compounds containing the electron donating η-C_5Me_5, η-C_5H_5, or η^5-C_9H_7 groups.

As expected, the i.r. spectrum of (**9a**) in the CO stretching region (see Experimental section) is very similar to that of (**2a**).[4] The ^1H n.m.r. spectrum (Table) showed four singlets at δ 0.32, 2.42, 2.49, and 7.27 of relative intensity 9:3:3:4 due to the $SiMe_3$, Me-4, CMe, and C_6H_4 protons, respectively. The resonance at δ 2.49 may be compared with that (δ 2.38) for the C(O)C(Me)C(*Me*) group in the spectrum of (**2a**). In the latter, the peak for the C(O)C(*Me*)C(Me) group is more shielded at δ 1.97. In accord with its formulation, the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**9a**) shows a signal at δ 19.4 p.p.m. which is very similar to the chemical shift (18.9 p.p.m.) observed for the C(O)C(Me)C(*Me*) group in (**2a**). Conclusive evidence for the structure of (**9a**) is provided by the resonances for the μ-C_3 group in the ^{13}C-$\{^1H\}$ n.m.r. spectrum. The resonances at δ 126.3 and 92.4 p.p.m. can be assigned to the *C*Me and *C*($SiMe_3$) groups, respectively, since the latter shows ^{29}Si satellite peaks [*J*(SiC) 55 Hz]. The coupling is assigned to ^{29}Si rather than ^{183}W since none of the previously characterised compounds of this structural type exhibited ^{183}W satellites. Moreover, the satellite intensity is much lower than one would expect for the ^{183}W nucleus and the coupling of 55 Hz is about what one might expect for a one bond C–Si coupling. Tetramethylsilane shows a ^{29}Si–^{13}C value of 50 Hz. The signal at δ 186.7 p.p.m. is due to the $\mathit{C}C_6H_4Me$-4 nucleus. In the spectrum of (**2a**) the resonances for the $\mathit{C}C_6H_4Me$-4 and *C*(Me)C(C_6H_4Me-4) nuclei occur at δ 175.6 and 123.0 p.p.m., respectively. The signals for the WCO, *C*(O)C(R) (R = Me or $SiMe_3$), and CoCO groups in the two compounds are also very similar. The chemical shifts are for (**2a**), δ 212.3 (WCO), 209.7 [*C*(O)C(Me)], 198.7 and 193.8 (br, CoCO), and for (**9a**), δ 211.9 (WCO), 211.5 [*C*(O)C($SiMe_3$)], and 201.4—192.4 p.p.m. (vbr, CoCO).

The reaction between (**1b**) and MeC≡C$SiMe_3$ is similar to that between (**1a**) and the alkyne, in that a mixture of two products is produced, these being [WCo{μ-C(Me)C(Me)C($SiMe_3$)}$(CO)_7$] (**7e**) and [WCo{μ-C(Me)C(Me)C($SiMe_3$)C(O)}$(CO)_7$] (**9b**). Unlike (**9a**), compound (**9b**) could not be completely decarbonylated *in vacuo*. However, prolonged storage under vacuum does increase the proportion of (**7e**). Solutions of the mixture treated with CO afford (**9b**) quantitatively. Consequently, spectral measurements on (**9b**) were carried out employing CO saturated solvents, while the data for (7e) were obtained from measurements on the mixture. Having identified the resonances due to (**9b**) from the CO saturated solutions, those of (**7e**) can be readily assigned.

Compound (**7e**) shows in its ^1H n.m.r. spectrum (Table) signals due to methyl groups at δ 0.20 ($SiMe_3$), 2.00 [C(*Me*)C(Me)C($SiMe_3$)], and 2.47 [C(Me)C(*Me*)C($SiMe_3$)]. Corresponding signals for these groups occur in the ^{13}C-$\{^1H\}$ n.m.r. spectrum at δ 1.8 ($SiMe_3$), 21.3 [C(*Me*)C(Me)C($SiMe_3$)], and 24.3 p.p.m. [C(Me)C(*Me*)C($SiMe_3$)]. These data preclude a structure containing a μ-C(Me)C($SiMe_3$)C(Me) group, since if the latter were present in (**7e**) the symmetry would result in a resonance for only one CMe group. The observation of three signals for the μ-C_3 fragment at δ 131.2, 120.2, and 107.3 p.p.m. also supports the formulation given.

The i.r. and n.m.r. data for (**9b**) are very similar to those of (**2c**).[4] Moreover, the data for (**9a**) are very similar to those of (**9b**), except for differences in the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra arising as a consequence of the CoC(C_6H_4Me-4) group in the former and the CoC(Me) group in the latter.

The ready interconversion between the species (**7d**) and (**9a**), and (**7e**) and (**9b**) is of interest. Although reversible uptake of carbon monoxide is a fairly common occurrence with organotransition metal complexes it is unusual to observe this phenomenon with co-ordinatively and electronically saturated species like (**7d**) and (**7e**). Moreover, although the reaction between (**1a**) and MeC≡CMe to produce (**2a**) probably proceeds *via* the intermediacy of a species [WCo{μ-C(C_6H_4Me-4)-C(Me)C(Me)}$(CO)_7$], no evidence for the latter was obtained.[4] Nor could its existence be demonstrated by decarbonylation of (**2a**). Similarly, the mixture of the two isomeric compounds (**3**) did not release CO to produce molecules structurally akin to (7).

Another interesting feature of the reactions between (**1a**) or (**1b**) and MeC≡C$SiMe_3$ is the absence of products containing the ligands μ-C(R)C($SiMe_3$)C(Me) and μ-C(R)C($SiMe_3$)C(Me)-C(O). Likewise it is surprising that (**7e**) does not insert CO into the CoC(Me) group to form a product [WCo{μ-C($SiMe_3$)C-(Me)C(Me)C(CO)}$(CO)_7$]. These various observations must relate to the electronic and steric properties of the $SiMe_3$ group in the alkyne MeC≡C$SiMe_3$, leading to somewhat different patterns in behaviour compared with those found in the reactions involving MeC≡CMe or MeC≡CEt and the alkylidyne tungsten–cobalt species.

We have previously reported[4] that the compounds (**2a**), (**2c**), and (**2d**) react with PPh_3 to afford the complexes [WCo{μ-C(R)C(Me)C(Me)C(O)}$(CO)_6(PPh_3)$] [R = C_6H_4Me-4 (**10a**), Me (**10b**), or Ph (**10c**)]. Similarly, treatment of (**9a**) and (**9b**) with PPh_3 yields the compounds [WCo{μ-C(R)C(Me)C($SiMe_3$)C-(O)}$(CO)_6(PPh_3)$] [R = C_6H_4Me-4 (**10d**) or Me (**10e**)] in essentially quantitative yield. These same two products are also obtained from reactions between PPh_3 and (**7d**) or (**7e**), respectively. Obviously the synthesis of (**10d**) and (**10e**) from

(**9a**) and (**9b**), respectively, involves a simple displacement of a cobalt ligated carbonyl group. Formation of the same products from (**7d**) and (**7e**) indicates that the $C(SiMe_3)$ fragment of the μ-C_3 group in these complexes migrates to a cobalt bound CO ligand leaving a vacant site on the metal for attachment of a PPh_3 molecule.

The spectroscopic data for (**10d**) and (**10e**) are, as expected, very similar to those of (**10a**) and (**10b**). The ^{31}P-$\{^1H\}$ n.m.r. spectra of the four compounds showed broad resonances at δ 37.4 (**10a**), 35.0 (**10b**), 36.7 (**10d**), and 34.6 p.p.m. (**10e**).

The last reaction to be studied was that between (**1b**) and EtC≡CEt. An isomeric mixture of the three compounds $[WCo\{\mu\text{-}C(R^1)C(R^2)C(R^3)C(O)\}(CO)_7]$ [$R^1 = R^2 = Et$, $R^3 = Me$ (**9c**); $R^1 = R^3 = Et$, $R^2 = Me$ (**9d**); $R^2 = R^3 = Et$, $R^1 = Me$ (**9e**)] was formed. The three isomers could not be separated by column chromatography, but relative peak intensities in the n.m.r. spectra (Table) revealed that they were produced in a (**9c**):(**9d**):(**9e**) ratio of *ca.* 6:2:7. It was not possible to assign all the multiplets in the ^1H n.m.r. spectrum of the isomeric mixture (Table), but the appearance of 15 resonances between δ 39.0 and 14.3 p.p.m. in the ^{13}C-$\{^1H\}$ n.m.r. spectrum indicated the presence of three isomers. Each isomer exhibits two CH_2 and three Me signals. In most cases these peaks have been definitively assigned to a given carbon nucleus in one or other isomer by comparison with the spectra of previously characterised compounds (**2a**)—(**2c**), (**3a**), and (**3b**).[4] The assignments were also aided by the fact that (**9d**) was the minor product. An interesting feature of the spectra is that the $CoC(CH_2Me)$ nuclei in (**9c**) and (**9d**) resonate at δ 38.7 and 39.0 p.p.m., respectively. These signals are relatively deshielded compared with those for CH_2 groups associated with other μ-C carbons, which occur generally in the region δ 21.8—24.3 p.p.m.

The formation of three isomers in the reaction between (**1b**) and EtC≡CEt can be readily understood *via* a similar Scheme to that shown for the formation of (**7b**) and (**7c**), with CO insertion occurring in the last step. Thus the precursor to (**9d**) would be a species $[WCo\{\mu\text{-}C(Et)C(Me)C(Et)\}(CO)_7]$. Complexes (**9c**) and (**9e**) would result from CO insertion at the terminal carbon atoms of the μ-C_3 fragment in an intermediate $[WCo\{\mu\text{-}C(Me)C(Et)C(Et)\}(CO)_7]$. If the CMe group migrates to cobalt, isomer (**9c**) would be produced, while a similar process at the terminal CEt group would afford (**9e**). As mentioned, (**9d**) was the minor product. This is as expected from the mechanism proposed. The linking of the CMe and CEt fragments, according to processes similar to those shown in the Scheme for the CC_6H_4Me-4 and CPh groups, is likely to be more facile for formation of an intermediate $[WCo\{\mu\text{-}C(Me)C(Et)C(Et)\}(CO)_7]$ than for $[WCo\{\mu\text{-}C(Et)C(Me)C(Et)\}(CO)_7]$. This explains why (**9c**) and (**9e**) predominate, since they are formed by CO insertion into the former. Many more steps are required for the formation of the $[WCo\{\mu\text{-}C(Et)C(Me)C(Et)\}(CO)_7]$, from which (**9d**) is derived. Moreover, higher concentrations of CO in solution would favour (**9c**) and (**9e**) since once formed these species do not decarbonylate.

The reactions described herein together with those reported earlier[4,5] demonstrate that the complexes (**1**) undergo a variety of C–C bond forming processes with alkynes under mild conditions. The nature of the products is markedly dependent on the substituents on the alkyne carbon atoms and whether tungsten–cobalt or tungsten–molybdenum species are involved.

Experimental

Experiments were carried out using Schlenk-tube techniques under dry oxygen-free nitrogen. Light petroleum refers to that fraction of b.p. 40—60 °C. Florisil (Fluka, 100—200 mesh) was used for chromatography columns. The instrumentation employed for spectroscopic measurements has been listed earlier.[6c] The compounds $[WCo(\equiv CR)(CO)_8]$ (**1**, R = C_6H_4Me-4[16] or Me[17]) were prepared as described previously. Infrared measurements were recorded in light petroleum unless otherwise stated. Phosphorus-31 proton-decoupled spectra were measured in CD_2Cl_2–CH_2Cl_2 at -40 °C, and chemical shifts (δ) are to high frequency of 85% H_3PO_4 (external).

Reactions of the Complex $[WCo(\equiv CC_6H_4Me\text{-}4)(CO)_8]$.—(*i*) A mixture of (**1a**) (0.57 g, 1.0 mmol) and $C_2(C_6H_4Me\text{-}4)_2$ (0.21 g, 1.0 mmol) in light petroleum (*ca.* 20 cm^3) was stirred at room temperature for 4 h. The solution was reduced in volume *in vacuo* to *ca.* 5 cm^3 and chromatographed (2 × 15 cm column). Elution with light petroleum removed successively small amounts of $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$ (identified by i.r.), followed by an orange eluate. Solvent was removed *in vacuo* giving $[WCo\{\mu\text{-}C_3(C_6H_4Me\text{-}4)_3\}(CO)_7]$ (**7a**) (0.51 g, 68%) as a non-crystallisable orange oil; $\nu_{max.}$(CO) at 2 082s, 2 049vs, 2 023s, 2 016s, 1 991m, 1 966s, and 1 941s cm^{-1}.

A sample (0.27 mmol) of (**7a**) in light petroleum (*ca.* 30 cm^3) was treated with a slow stream of CO for *ca.* 2 d. An i.r. spectrum revealed that *ca.* 50% of (**7a**) had been converted to the acyl complex $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)C(C_6H_4Me\text{-}4)C(O)\}(CO)_7]$ (**2e**); $\nu_{max.}$(CO) at 2 094s, 2 053s, 2 047vs, 2 033m, 2 000m, 1 965s, 1 946s, and 1 650m br cm^{-1}.

(*ii*) In a similar manner to the synthesis of (**7a**), the reaction between (**1a**) (0.57 g, 1.0 mmol) and PhC≡CPh (0.18 g, 1.0 mmol) in light petroleum (*ca.* 20 cm^3) yielded as an orange oil an inseparable isomeric mixture (*ca.* 2:1, as deduced from relative intensity of n.m.r. signals) of $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Ph)C(Ph)\}(CO)_7]$ (**7b**) and $[WCo\{\mu\text{-}C(Ph)C(C_6H_4Me\text{-}4)C(Ph)\}(CO)_7]$ (**7c**) (0.50 g, 69%); $\nu_{max.}$(CO) at 2 083s, 2050vs, 2 025s, 2 017s, 1 993m, 1 967s, and 1 943s cm^{-1}.

(*iii*) A mixture of (**1a**) (1.00 g, 1.75 mmol) and $MeC\equiv CSiMe_3$ (0.40 g, 3.50 mmol) was dissolved in light petroleum (*ca.* 60 cm^3) and stirred for 24 h at room temperature. The mixture was reduced in volume *in vacuo* to *ca.* 10 cm^3 and chromatographed. Elution with light petroleum removed trace amounts of $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$ (identified by i.r.). Elution with CH_2Cl_2 gave an orange solution from which solvent was removed *in vacuo* to afford an orange oil which proved to be a mixture of $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(SiMe_3)\}(CO)_7]$ (**7d**) and $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(SiMe)_3C(O)\}(CO)_7]$ (**9a**). Prolonged pumping *in vacuo* gave yellow *microcrystals* of (**7d**) (0.40 g, 35%) (Found: C, 38.2; H, 3.1. $C_{22}H_{19}CoO_8SiW$ requires C, 38.6; H, 2.9%); $\nu_{max.}$(CO) at 2 080m, 2 045vs, 2 022s, 2 014s, 1 980s, 1 969m, and 1 950 cm^{-1}. For (**9a**), $\nu_{max.}$(CO) at 2 095s, 2 052s, 2 046vs, 2 033m, 2 000m, 1 967s, 1 941s, and 1 641br cm^{-1}.

A pure sample of (**9a**) could not be obtained in crystalline form. However, exposure of a solution of (**7d**) in light petroleum to CO gas rapidly (*ca.* 10 min) afforded (**9a**) quantitatively (i.r.).

Reactions of the Complex $[WCo(\equiv CMe)(CO)_8]$.—(*i*) A mixture of (**1b**) (0.50 g, 1.0 mmol) and $MeC\equiv CSiMe_3$ (0.20 g, 1.8 mmol) was dissolved in light petroleum (*ca.* 50 cm^3) and placed in a refrigerator (*ca.* 4 °C) for 24 h. The mixture was reduced in volume *in vacuo* to *ca.* 5 cm^3 and chromatographed. Elution with light petroleum removed traces of $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (identified by i.r.). Elution with CH_2Cl_2 gave an orange eluate. Solvent was removed *in vacuo* to yield an orange oil (0.45 g) which proved to be a mixture of $[WCo\{\mu\text{-}C(Me)C(Me)C(SiMe_3)\}(CO)_7]$ (**7e**) and $[WCo\{\mu\text{-}C(Me)C(Me)C(SiMe_3)C(O)\}(CO)_7]$ (**9b**). Treatment of solutions of the mixture with CO resulted in quantitative conversion to (**9b**) [$\nu_{max.}$(CO) at 2 093s, 2 050vs, 2 042vs, 2 031m, 2 002m, 1 961s, 1 942s, and 1 641m br cm^{-1}]. For (**7e**), $\nu_{max.}$(CO) at 2 080m, 2 043vs, 2 017s, and 1981s cm^{-1} with other bands obscured by those due to (**9b**).

(*ii*) The complex (**1b**) (0.50 g, 1.0 mmol) was dissolved in light petroleum (*ca.* 60 cm^3) and treated with EtC≡CEt (0.20 g, 2.43 mmol) at *ca.* 4 °C (refrigerator) for 24 h. After reducing the volume to *ca.* 5 cm^3, chromatography, eluting with light petroleum, removed traces of $[W(CO)_6]$ and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$. Elution with CH_2Cl_2 gave an orange solution. Removal of solvent *in vacuo* and crystallisation from light petroleum (*ca.* 5 cm^3) at −78 °C yielded orange *microcrystals* of a mixture of $[WCo\{\mu\text{-}C(Et)C(Et)C(Me)C(O)\}(CO)_7]$ (**9c**), $[WCo\{\mu\text{-}C(Et)C(Me)C(Et)C(O)\}(CO)_7]$ (**9d**), and $[WCo\{\mu\text{-}C(Me)C(Et)C(Et)C(O)\}(CO)_7]$ (**9e**) (0.36 g, 62%) (Found: C, 33.2; H, 2.0. $C_{16}H_{13}CoO_8W$ requires C, 33.4; H, 2.3%); $\nu_{max.}(CO)$ at 2 094s, 2 051vs, 2 041s, 2 030s, 2 003s, 1 962s, 1 942s, and 1 647m br cm^{-1}.

Reactions with Triphenylphosphine.—(*i*) A solution of (**9a**) was prepared by bubbling CO through a light petroleum (10 cm^3) solution of (**7d**) (0.20 g, 0.29 mmol) for 10 min. The mixture was treated with PPh_3 (0.10 g, 0.38 mmol) with stirring for 20 min. The supernatant solvent was removed from a red precipitate and the latter was washed with light petroleum (2 × 20 cm^3) to give red *microcrystals* of $[WCo\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(SiMe_3)C(O)\}(CO)_6(PPh_3)]$ (**10d**) (0.27 g, 100%) (Found: C, 51.1; H, 3.8. $C_{39}H_{34}CoO_7PSiW$ requires C, 51.1; H, 3.7%); $\nu_{max.}(CO)$ at 2 062vs, 2 021s, 2 004(sh), 1 951s, 1 921s, and 1 594m br cm^{-1}.

Subsequently, it was found that (**9a**) could also be obtained quantitatively by treating light petroleum solutions of (**7d**) with PPh_3.

(*ii*) A mixture (0.20 g, 0.33 mmol) of (**7e**) and (**9b**) in light petroleum (10 cm^3) was treated with PPh_3 (0.09 g, 0.34 mmol) for *ca.* 20 min. The solution was then reduced in volume to *ca.* 2 cm^3 and cooled to −78 °C to afford red *microcrystals of* $[WCo\{\mu\text{-}C(Me)C(Me)C(SiMe_3)C(O)\}(CO)_6(PPh_3)]$ (**10e**) (0.27 g, 95%) (Found: C, 46.5; H, 4.2. $C_{33}H_{30}CoO_7PSiW$ requires C, 47.2; H, 3.7%); $\nu_{max.}(CO)$ at 2 064vs, 2 020s, 2 006s, 1 987m, 1 948s, 1 929s, and 1 598m br cm^{-1}.

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