Heteronuclear Transition Metal–Alkyne Clusters. Part 1. Reactions of Tris(alkyne)monocarbonyltungsten Complexes with Octacarbonyldicobalt. Synthesis, *X*-Ray Crystal Structure, and Two-dimensional Nuclear Magnetic Resonance Studies of $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$†

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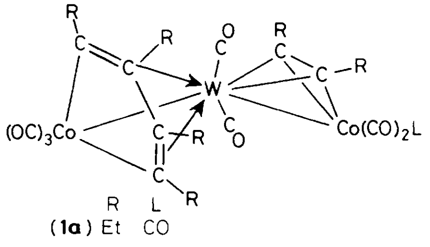
Reactions between the compounds $[W(C_2R_2)_3(CO)]$ (R = Et or Pr) and $[Co_2(CO)_8]$ afford the trinuclear metal complexes $[WCo_2(\mu\text{-}C_2R_2)(\mu\text{-}C_4R_4)(CO)_8]$. The molecular structure of $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ has been established by an *X*-ray diffraction study. The structure has a non-linear open chain of metal atoms [Co–W–Co 153.6(1)°] in which one tungsten–cobalt bond [2.732(1) Å] is bridged by a 3-hexyne ligand in a perpendicular co-ordination mode, while the second tungsten–cobalt bond [2.673(1) Å] is bridged by an alkyne-derived butadiene ligand, π-bound to tungsten and σ-bound to cobalt. The cobalt atoms are also ligated by three terminal carbonyl groups and the tungsten by two such groups. A full assignment of the ^1H and $^{13}C\text{-}\{^1H\}$ spectra of $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ using two-dimensional [^1H-^1H] and [^{13}C-^1H]-COSY n.m.r. spectroscopy reveals that alkyne rotation does not occur on the n.m.r. time-scale, although fluxional processes produce a mirror plane through the three metals. The complex $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ reacts with $P(OMe)_3$ to afford $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_7\{P(OMe)_3\}]$ in which carbonyl substitution at a cobalt centre has occurred.

Interest continues in the area of transition-metal cluster chemistry and in the reactivity of hydrocarbyl moieties ligated to such polynuclear metal systems.[1] Particular emphasis is being placed on the rational synthesis of clusters under mild conditions to facilitate the synthesis of clusters of a desired nuclearity and metal composition.[2] One strategy for promoting metal–metal bond formation is the incorporation of potentially bridging ligands into the cluster precursors as illustrated by the use of precursors containing phosphido or unidentate difunctional ligands such as bis(diphenylphosphino)methane.[3,4]

It has long been established that alkynes adopt one of a variety of bridging modes when co-ordinated to cluster complexes.[5] It would seem reasonable therefore to consider alkynes bound to a single metal centre as potential bridging ligands. The ability of a co-ordinated alkyne to ligate an incoming metal–ligand fragment has been demonstrated in a number of cases, possibly most clearly by the reaction of $[Pt(C_2Ph_2)_2]$ with $[Pt(C_2H_4)(PPh_3)_2]$ which affords $[Pt_2(\mu\text{-}C_2Ph_2)(C_2Ph_2)(PPh_3)_2]$ and $[Pt_3(\mu\text{-}C_2Ph_2)_2(PPh_3)_4]$ in which the polynuclear structures are held together by the bridging alkynes with negligible metal–metal bonding.[6] Another example is the formation of $[MCo(\mu\text{-}CF_3C_2CF_3)_2(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W) by the reaction of $[MCl(CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ with $[Co_2(CO)_8]$.[7] The binuclear complex is formed despite the fact that in the mononuclear precursor both sets of π orbitals on the alkynes are apparently involved in bonding to the metal.[8] Even alkynes functioning as four-electron donors to one or two metal centres can assist in the co-ordination of an incoming metal centre.[9–11]

In order to establish whether mononuclear alkyne complexes can serve as precursors to transition-metal clusters a class of complexes bearing more than one alkyne was chosen. The pseudo-tetrahedral molecules [W(alkyne)$_3$(CO)] contain three alkyne ligands each donating $3\frac{1}{3}$ electrons to the tungsten centre, since one symmetry combination of alkyne donor orbitals does not find a matching metal orbital.[12] It has been shown that this class of complex reacts with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ to give ditungsten species.[13] A preliminary account of some of the results described herein has been given.[14]



	R	L
(**1a**)	Et	CO
(**1b**)	Pr	CO
(**2**)	Et	P(OMe)$_3$

Results and Discussion

Reaction of the compounds $[W(C_2Et_2)_3(CO)]$ and $[W(C_2Pr_2)_3(CO)]$ with $[Co_2(CO)_8]$ in light petroleum at room temperature affords (**1a**) and (**1b**) respectively (see Experimental section). Analytical and spectroscopic data for the products are given in Tables 1 and 2. The isolation of $[W(C_2Pr_2)_3(CO)]$ as a slightly impure oil precluded the determination of a yield for (**1b**). The highest mass envelope in the fast-atom bombardment mass spectrum of compound (**1a**) was detected at *m/e* 716, corresponding to $[P - CO]^+$, and five successive carbonyl-loss peaks were also observed. Spectroscopic measurements

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† 1,1,1,2,2,3,3,3-Octacarbonyl-1,2-[μ-4′,5′-diethylocta-3′,5′-diene-3′,6′-diyl-$C^{3'}$(Co^{1}W)$C^{4',5'}$(W)$C^{6'}$(Co^{1}W)]-2,3-μ-[hex-3″-yne-$C^{3''}C^{4''}$-(Co^{2}W)]-1,3-dicobalt-2-tungsten(2*Co*–*W*).

Supplementary data available: see ref. 14.

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

Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	Analysis (%) H	Analysis (%) Co
(**1a**) $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$	Orange	68	2 087s, 2 036vs, 2 029s, 1 990m, 1 970s, 1 959s, 1 948m	40.5 (40.4)	4.0 (4.0)	15.1 (15.3)
(**1b**) $[WCo_2(\mu\text{-}C_2Pr_2)(\mu\text{-}C_4Pr_4)(CO)_8]$	Orange		2 083s, 2 032vs, 2 026s, 1 985m, 1 965s, 1 954s, 1 943w	44.6 (44.9)	4.9 (5.0)	
(**2**) $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_7\{P(OMe)_3\}]$	Dark orange	88	2 079s, 2 027vs, 1 988w, 1 956s, 1 939m, 1 918w	38.8 (38.7)	4.8 (4.5)	

[a] Calculated values in parentheses. [b] In light petroleum.

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

Compound	$^1H(\delta)^b$	$^{13}C(\delta)^c$
(**1a**)	3.15—2.86 [m, 4 H, $(CH_2)_c$], 2.93 [q, 4 H, $(CH_2)_a$, J_{HH} 7], 2.53 [q, 4 H, $(CH_2)_b$, J_{HH} 7], 1.33 (t, 6 H, Me_a, J_{HH} 7), 1.24 (t, 6 H, Me_b, J_{HH} 7), 1.20 (t, 6 H, Me_c, J_{HH} 7)	210.9 (s, WCO, J_{WC} 152), 205.6, 198.9, 193.2 (3 × s, CoCO), 173.9 (s, C_a), 135.1 (s, C_b), 92.8 (s, C_c), 35.0 [s, $(CH_2)_a$], 26.7 [s, $(CH_2)_c$], 23.3 [s, $(CH_2)_b$], 21.0 (s, Me_a), 15.8 (s, Me_b), 14.6 (s, Me_c)
(**1b**)	2.98—2.70 (m, 8 H, CH_2), 2.42—2.39 (m, 4 H, CH_2), 1.64—1.37 (m, 12 H, CH_2), 1.05—0.83 (m, 18 H, CH_3)	211.8 (s, WCO, J_{WC} 153), 206.2, 199.6, 194.1 (3 × s, CoCO), 172.7 (s, C_a), 134.8 (s, C_b), 92.0 (s, C_c), 45.3, 36.7, 33.8, 31.3, 25.6, 24.7 (6 × s, CH_2), 15.2, 14.8 × 2 (3 × s, CH_3)
(**2**)	3.58 [d, 9 H, $P(OMe)_3$, J_{PH} 11], 2.98—2.92 (m, 8 H, CH_2), 2.61—2.56 (m, 4 H, CH_2), 1.33 (t, 6 H, CH_3, J_{HH} 7), 1.22 (t, 6 H, CH_3, J_{HH} 7), 1.12 (t, 6 H, CH_3, J_{HH} 7)	213.0 (s, WCO, J_{WC} 154), 208.5, 199.3, 193.1 (3 × s, CoCO), 173.9 (s, C_a), 133.3 (s, C_b), 87.2 (s, C_c), 50.4 [d, $P(OMe)_3$, J_{PC} 3], 34.5 (s, CH_2), 25.8 (d, CH_2, J_{PC} 4), 22.5 (s, CH_2), 20.7, 15.3, 13.8 (3 × s, CH_3)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled.

Table 3. Selected internuclear distances (Å) and angles (°) for $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1a**), with estimated standard deviations (e.s.d.s) in parentheses

W–Co(1)	2.732(1)	W–Co(2)	2.673(1)
W–C(1)	1.98(1)	Co(2)–C(11)	1.99(1)
W–C(2)	2.01(1)	Co(2)–C(14)	1.98(1)
W–C(11)	2.25(1)	W–C(21)	2.15(1)
W–C(12)	2.38(1)	W–C(22)	2.16(1)
W–C(13)	2.40(1)	Co(1)–C(21)	2.04(1)
W–C(14)	2.25(1)	Co(1)–C(22)	2.01(1)
C(11)–C(12)	1.40(1)		
C(12)–C(13)	1.43(1)	Carbonyl C–O (mean)	1.136(6)
C(13)–C(14)	1.40(1)		
C(21)–C(22)	1.36(2)	W–C(carbonyl) (mean)	1.99(1)
		Co–C(carbonyl) (mean)	1.78(1)
Co(1)–W–Co(2)	153.6(1)	C(22)–C(21)–C(211)	136(1)
C(111)–C(11)–C(12)	122.3(9)	C(21)–C(22)–C(221)	134(1)
C(11)–C(12)–C(13)	112.7(9)	C(21)–W–C(22)	36.8(5)
C(12)–C(13)–C(14)	115.6(9)	C(21)–Co(1)–C(22)	39.3(5)
Co(2)–C(11)–C(111)	120.5(8)		
Co(2)–C(14)–C(141)	121.8(7)		

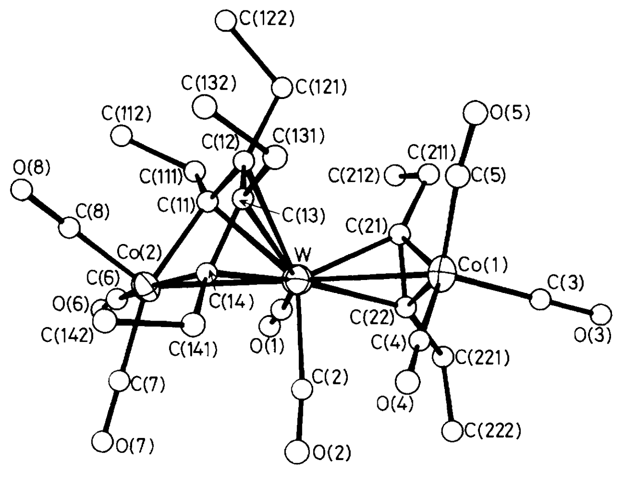

Figure 1. The molecular structure of $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1a**) showing the atom-labelling scheme

indicated that (**1a**) and (**1b**) were analogous, but discussion of these results will be deferred until after a description of the *X*-ray crystal structure of (**1a**) which established their formulation.

Selected structural parameters for compound (**1a**) are listed in Table 3 and the molecular structure is shown in Figure 1. The metal framework is a non-linear open chain [Co(1)–W–Co(2) 153.6(1)°], in which both tungsten–cobalt bonds are supported by organic moieties. The Co(1)–W bond [2.732(1) Å] is bridged by a 3-hexyne ligand in a perpendicular fashion [Co(1)–C(21) 2.04(1), Co(1)–C(22) 2.01(1), W–C(21) 2.15(1), and W–C(22) 2.16(1) Å]. The W–Co(2) bond [2.673(1) Å] is bridged by a butadiene ligand, derived from two 3-hexyne molecules, σ-bound to cobalt [Co(2)–C(11) 1.99(1), Co(2)–C(14) 1.98(1) Å] and π-bound to tungsten. The tungsten atom is closer to the terminal butadiene carbon atoms [2.25(1) Å] than the inner carbon atoms [W–C(12) 2.38(1), W–C(13) 2.40(1) Å]. Substantial tungsten–butadiene back donation is suggested by the similarity of the central [1.43(1) Å] and terminal [1.40(1) Å] butadiene bond lengths. Both cobalt atoms are also ligated by three terminal carbonyl groups and the tungsten by two, resulting in a cluster valence-electron count of 50, consistent with the open-chain structure.[5] The isolobal mapping $Co(CO)_3 \underset{\circ}{\longleftrightarrow} CH$ provides a formal relationship between (**1a**) and the binuclear complex $[MoCo\{\mu\text{-}C_2(CF_3)_2\}(CO)_5(\eta\text{-}C_5H_5)]$, by relating the metallocyclopentadienyl fragment, $Co(CO)_3C_4Et_4$, to C_5H_5.[15] A similar chain structure has been proposed for $[Ni_3\{\mu\text{-}C_2(CF_3)_2\}\{\mu\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_2]$[16] and the structure of $[Os_3(\mu\text{-}C_2Me_2)(\mu\text{-}C_4Me_4)(CO)_8]$[17] has been shown to contain a bent chain

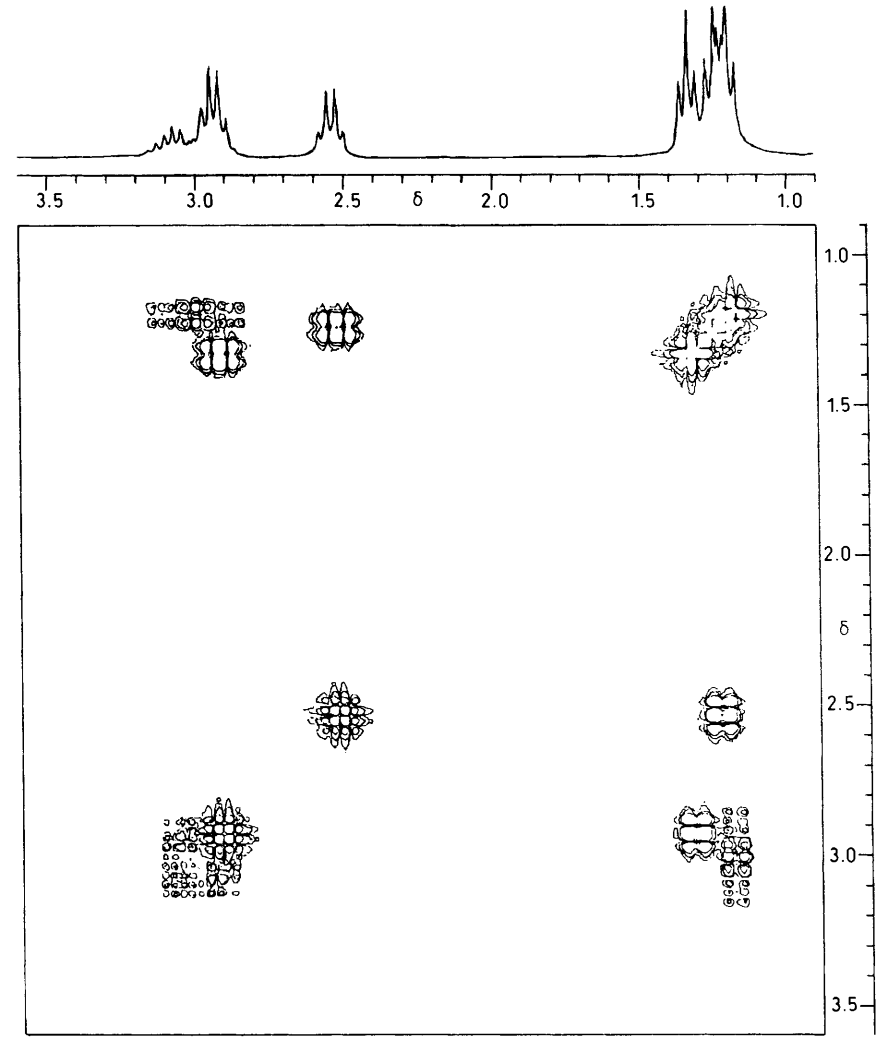

Figure 2. ^1H COSY-90 spectrum of $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1a**)

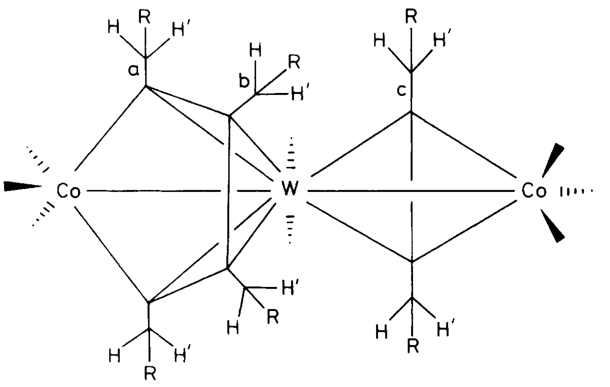

Figure 3. A schematic representation of the mirror plane for compounds (1)

[153.1(1)°], however in this case the butadiene fragment is π-bound to a terminal metal atom.

N.m.r. studies reveal that the complexes (**1a**) and (**1b**) undergo dynamic behaviour in solution. The ^1H n.m.r. spectrum of (**1a**) (see Figure 2) contains three triplets in the methyl region at δ 1.33, 1.24, and 1.20. Both halves of the butadiene and alkyne ligands are being rendered equivalent suggesting that the molecule twists through an intermediate with a mirror plane as illustrated in Figure 3. Similar behaviour has been observed for both $[Ni_3\{\mu\text{-}C_2(CF_3)_2\}\{\mu\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_2]$ and $[Os_3(\mu\text{-}C_2Me_2)(\mu\text{-}C_4Me_4)(CO)_8]$.[16,17] The methylene region of the spectrum is more complex consisting of two quartets and the partially obscured AB component of an ABX_3 multiplet. This is more clearly seen in the COSY-90 spectrum, also illustrated in Figure 2. This suggests that only one set of methylene groups is significantly diastereotopic. Rotation of the alkyne about W–Co(1) would equivalence the pairs H_C and H_C', but there is no obvious mechanism for equivalencing the pairs H_a,H_a' and H_b,H_b'. Good quality low-temperature ^1H n.m.r. spectra were difficult to obtain due to a consistent loss of resolution, but no change occurred down to 213 K. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum also shows equivalence of both sides of the molecule down to 193 K, the lowest temperature at which spectra were recorded, and hence three methylene and three methyl resonances are observed. Only one tungsten carbonyl resonance is observed (δ 210.9 p.p.m.) with ^{183}W satellite peaks (J_{WC} 152 Hz). Three broader signals are assigned to cobalt carbonyls at δ 205.6, 198.9, and 193.2 p.p.m. in the approximate ratio 2:3:1 suggesting that, while turnstile rotation occurs at about Co(1), rotation about Co(2) is hindered by the adjacent ethyl groups.[18] Peaks at δ 173.9 and 92.8 p.p.m. are assigned to the outer butadiene and alkyne carbons, respectively, while a sharper resonance at δ 135.1

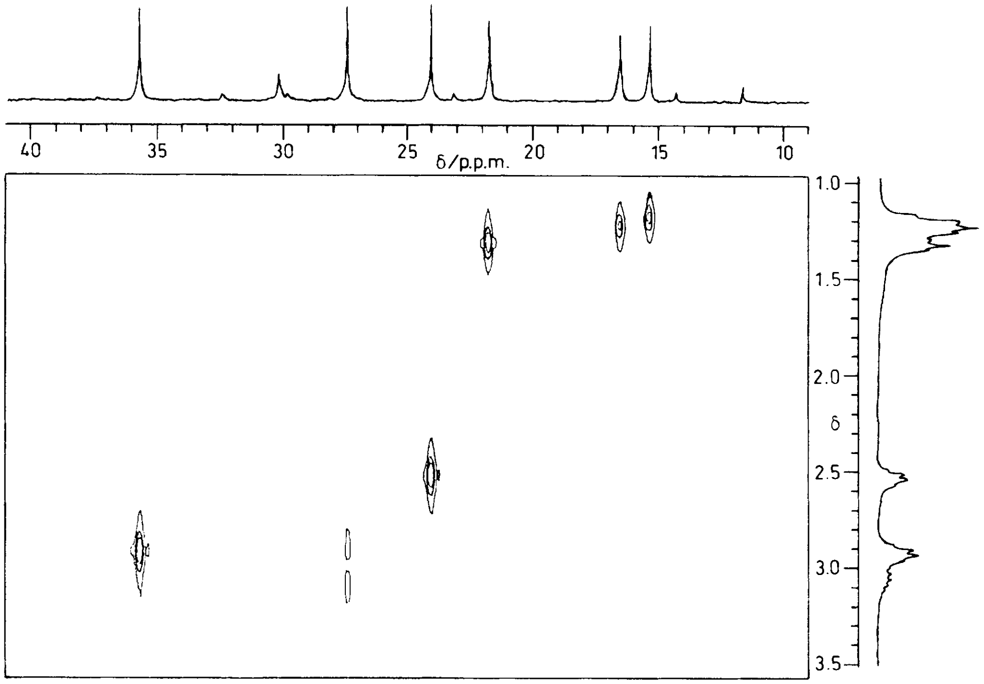

Figure 4. [^{13}C-^{1}H]-COSY Spectrum of [$WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8$] (**1a**)

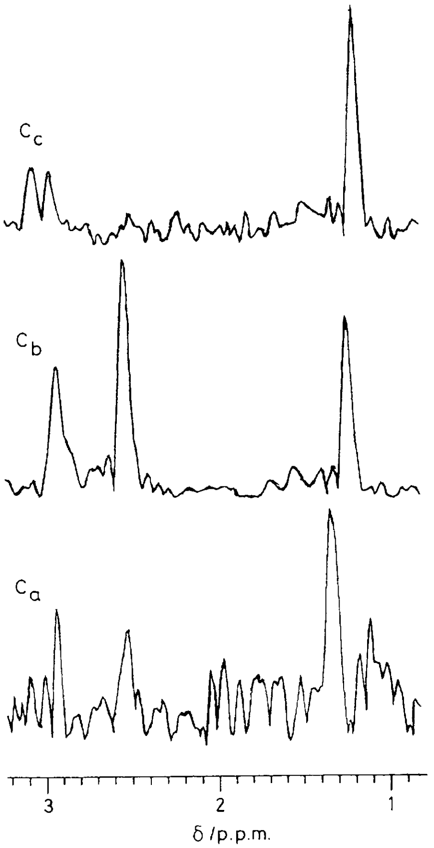

Figure 5. Cross-sections through the long-range [^{13}C-^{1}H]-COSY spectrum of [$WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8$] (**1a**)

p.p.m. is assigned to the inner butadiene carbons which are not ligated to cobalt. These assignments are in accord with those made for a variety of [$Fe_2(\mu\text{-}C_4R_4)(CO)_6$] and [$Co_2(\mu\text{-}C_2R_2)(CO)_6$] complexes.[19] Similar n.m.r. properties are displayed by (**1b**).

In order to gain further insight into the ^{1}H n.m.r. spectrum of compound (**1a**) a series of experiments designed fully to assign the ^{1}H and ^{13}C spectra were undertaken.The two-dimensional COSY-90 (Figure 2) allowed the methyl triplets in the ^{1}H n.m.r. spectrum to be assigned to their methylene partners. Thus the diastereotopic methylene resonance was correlated with the methyl signal at δ 1.2. From these proton assignments the methyl and methylene signals in the ^{13}C spectrum were also identified from the [^{13}C-^{1}H] COSY (Figure 4) experiment. The remaining problem was to assign the three types of ethyl groups to the three types of ligated carbon which were assigned above. This was accomplished through a [^{13}C-^{1}H] COSY using a long-range coupling constant of $^{n}J_{CH}$ *ca.* 6 Hz. Cross-sections of this spectrum at the three ligated ^{13}C shift positions (Figure 5) show unequivocally that C_c exhibits cross-peaks with both diastereotopic protons H_c and H_c', while C_a and C_b show cross-peaks with both $(CH_2)_a$ and $(CH_2)_b$ corresponding to two- and three-bond coupling. Carbons C_a, C_b, and C_c also show cross-peaks *via* three-bond couplings ($^{3}J_{CH}$) to Me_a, Me_b, and Me_c respectively. These results prove that the AB part of the ABX_3 pattern in the ^{1}H n.m.r. spectrum of (**1a**) is due to the alkyne protons, $(CH_2)_c$, and therefore the alkyne cannot be rotating relative to the W–Co(1) bond on the n.m.r. time-scale.

Variable-temperature experiments using the isopropyl group as an n.m.r. probe in the compound [$CoNi(\mu\text{-}PhC_2Pr^i)(CO)_3(\eta\text{-}C_5H_5)$] have shown that the barrier to the formal relative rotation of the C–C and Co–Ni bond vectors is *ca.* 86 kJ mol^{-1}.[20] The alkyne-bridged compound [$WNi(\mu\text{-}MeC_2Et)(CO)_2(\eta\text{-}C_5H_4Me)(\eta\text{-}C_5H_5)$] has also been studied *via* variable-temperature ^{1}H n.m.r. spectroscopy in which the ethyl group appears as an ABX_3 pattern even up to 368 K indicating a lack of rotation on the n.m.r. time-scale.[21] Thermal instability of (**1a**) precluded the recording of spectra significantly above room temperature and $(CH_2)_c$ was also observed as an ABX_3 pattern at the lower field of 60 MHz. The chemical shift separation of H_c and H_c' indicates that the barrier to rotation must be in excess of 66 kJ mol^{-1}. Theoretical calculations of acetylene rotation in

$[Co_2(\mu\text{-}C_2H_2)(CO)_6]$ have also indicated a relatively high activation energy.[22,23]

It is noteworthy that both $(CH_2)_a$ and $(CH_2)_b$ appear as simple quartets. It is possible that their environments are not sufficiently asymmetric to render the methylenic protons non-equivalent in the n.m.r. experiment. This is rather surprising in view of the marked non-equivalence of H_c and H_c' and the non-equivalence of methylenic protons in similar systems.[24] High-energy fluxional processes have been observed in $[Fe_2(\mu\text{-}C_4R_4)(CO)_6]$[25] and $[Co_2(\mu\text{-}C_4R_4)(\eta\text{-}C_5H_5)_2]$[26] in which the two metal centres are rendered equivalent by an interchange of the σ- and π-bonded metal atoms. Such a process will not equivalence the methylenic protons in a heteronuclear system such as (**1a**) and a mechanism by which the methylenic carbons pass through the mirror plane of the three metal atoms would have to be postulated.

The reactions of the compounds $[W(C_2Ph_2)_3(CO)]$ and $[W(MeC_2Ph)_3(CO)]$ with $[Co_2(CO)_8]$ were also investigated. The diphenylacetylene derivative reacts to form a mixture of two products which are orange and brown. Separation can be achieved by column chromatography using a Florisil support, but characterisation was hampered by the conversion in solution of the orange into the brown compound followed by decomposition of the brown material. Products of greater stability were obtained from the reaction of $[W(MeC_2Ph)_3(CO)]$ with $[Co_2(CO)_8]$. Again orange and brown products were obtained, with conversion of the orange into the brown in solution. Mass spectral analysis of the brown material showed an envelope at *m/e* 847 with seven carbonyl-loss peaks suggesting a composition of $[WCo_2(\mu\text{-}MeC_2Ph)(\mu\text{-}C_4Me_2Ph_2)(CO)_8]$ with $[P - CO]^+$ as the highest ion observed in a similar fashion to (**1a**). Also observed was an unidentified impurity with an isotope envelope centred at *m/e* 859 with associated CO loss peaks. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum also supported a formulation analogous to compounds (**1a**) and (**1b**), but the brown product was never isolated in a pure form. It is possible that the orange intermediates contain uncoupled alkyne ligands as is observed in the formation of $[MCo\{\mu\text{-}C_4(CF_3)_4\}(CO)_4(\eta\text{-}C_5H_5)]$ (M = Mo or W).[8]

Attempts to expel a carbonyl ligand from compound (**1a**) either thermally or photochemically to produce a triangular 48-electron cluster were unsuccessful. Reaction of (**1a**) with an excess of $P(OMe)_3$ results in carbonyl substitution to afford $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_7\{P(OMe)_3\}]$ (**2**) and can be monitored by a shift of carbonyl absorption peaks to lower frequency (see Table 1). In the absence of an excess of phosphite (**2**) slowly decomposes in solution (days) to produce (**1a**) as the only identified product. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of compound (**2**) contains a single broad resonance a δ 162 p.p.m. to low field of 85% H_3PO_4 (external) with no evidence of ^{183}W satellites indicating that the phosphite is ligated to a cobalt centre. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is similar to those of compounds (**1a**) and (**1b**) and again there is equivalence through the centre of the molecule. Compared to (**1a**) the butadiene resonances are in a very similar position, δ 173.9 and 133.3 compared to δ 173.9 and 135.1 p.p.m. for (**1a**). The 3-hexyne resonance at δ 87.2 p.p.m. shows a larger change from that of (**1a**) at δ 92.8 p.p.m. and indicates that the phosphite is ligated to Co(1). The 3-hexyne methylene resonance at δ 25.8 p.p.m., assigned by comparison with the spectrum of (**1a**), displays phosphorus coupling of 4 Hz. Similar reactivity has been observed for the isolobally related complex $[MoCo\{\mu\text{-}C_2(CF_3)_2\}(CO)_5(\eta\text{-}C_5H_5)]$ which undergoes carbonyl substitution at the cobalt centre.[15]

Triphenyl phosphite also reacts with compound (**1a**) but the product decomposes rapidly in the absence of an excess of phosphite. Similar results were obtained with the phosphines PPh_3, PMe_3, and PMe_2Ph, triphenylphosphine producing the least-stable adduct suggesting steric rather than electronic reasons for instability. Mass spectral and i.r. evidence was obtained for products of a second carbonyl substitution but they could not be isolated. Compounds (**1a**) and (**1b**) react with the alkynes C_2Ph_2, C_2Et_2, and C_2Pr_2 at 60 °C but again no products could be isolated.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents used were pre-dried and deoxygenated. In particular, diethyl ether and tetrahydrofuran (thf) were distilled over sodium–benzophenone, dichloromethane over CaH_2, and light petroleum (b.p. 40—60 °C) over Na/K alloy. Brockman activity I alumina was used for chromatography. Analytical and other data for the new compounds are given in Tables 1 and 2. The i.r. spectra were measured with a Perkin-Elmer 683 spectrophotometer and n.m.r. spectra with a JEOL GX 270 instrument. The fast-atom bombardment mass spectra were recorded by the S.E.R.C. mass spectra service at Swansea using a VG ZAB-E instrument. The compounds $[W(C_2R^1R^2)_3(CO)]$ ($R^1 = R^2$ = Et or Ph; R^1 = Me, R^2 = Ph) were prepared by literature methods.[27] The procedure described for the preparation of $[W(C_2Et_2)_3(CO)]$ was used to prepare $[W(C_2Pr_2)_3(CO)]$.[27] The compound $[Co_2(CO)_8]$ was purchased from Strem.

Synthesis of the Compounds $[WCo_2(\mu\text{-}C_2R_2)(\mu\text{-}C_4R_4)(CO)_8]$ (R = Et *or* Pr).—(*i*) A mixture of $[W(C_2Et_2)_3(CO)]$ (0.30 g, 0.66 mmol) and $[Co_2(CO)_8]$ (0.23 g, 0.66 mmol) in light petroleum (20 cm^3) was stirred for 20 h. Filtration of the solution through an alumina pad (1.5 × 5 cm) and removal of the solvent *in vacuo* afforded $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1a**) (0.35 g, 0.45 mmol).

(*ii*) An oil of $[W(C_2Pr_2)_3(CO)]$ was stirred with an excess of $[Co_2(CO)_8]$ in light petroleum for 3 h. Work-up as for (**1a**) afforded $[WCo_2(\mu\text{-}C_2Pr_2)(\mu\text{-}C_4Pr_4)(CO)_8]$ (**1b**).

Reaction of the Compound $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ *with* $P(OMe)_3$.—To a solution of compound (**1a**) (0.10 g, 0.130 mmol) in light petroleum (20 cm^3) was added six drops of $P(OMe)_3$. After stirring for 36 h the solution was filtered through a Celite pad and removal of the solvent *in vacuo* afforded $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_7\{P(OMe)_3\}]$ (0.10 g, 0.115 mmol).

Crystal Structure Determination.—Crystals of compound (**1a**) were grown from 2-propanol–light petroleum at −20 °C. A dark red prismatic crystal *ca.* 0.6 × 0.5 × 0.4 mm was mounted in a general position on an Enraf-Nonius CAD4F diffractometer. Unit-cell dimensions were determined from a least-squares fit to the setting angles of 25 reflections ($\theta \geqslant 12°$). Data were collected at ambient temperatures in the range $2 < \theta < 30°$ using the θ—2θ scan mode. The intensities of two standard reflections $\bar{3}\,4\,\bar{4}$ and $\bar{2}\,\bar{4}\,5$ showed no significant change during data collection. Data were corrected for Lorentz/polarisation effects and for absorption using the method of Walker and Stuart.[28] A unique quadrant of data (*h*, 0 to 13, *k*, 0 to 20, *l*, −14 to +14) totalling 4 563 observations were collected, yielding 4 331 independent reflections. Of these 2 981 having $I > 2.5(\sigma)I$ were deemed observable and used for structure solution and refinement.

Crystal data. $C_{26}H_{30}Co_2O_8W$, *M* = 772.24, monoclinic, space group $P2_1$ (no. 4, C_2^2), $a = 9.372(3)$, $b = 14.547(3)$, $c = 10.525(2)$ Å, $\beta = 89.95(2)°$, $U = 1\,434.9(6)$ Å^3, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000) = 756$, Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 52.7$ cm^{-1}.

Systematic absences were consistent with the space groups

Table 4. Atomic positional (fractional co-ordinates) parameters with e.s.d.s in parentheses for the complex $[WCo_2(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	−0.237 44(3)	0.000 00	0.220 08(3)	C(11)	−0.415 7(9)	−0.064 7(7)	0.107 6(9)
Co(1)	−0.154 27(12)	0.003 95(22)	0.468 77(10)	C(12)	−0.406 9(10)	−0.122 1(7)	0.213 8(9)
Co(2)	−0.251 54(14)	−0.075 23(10)	−0.011 29(12)	C(13)	−0.269 2(10)	−0.163 9(7)	0.227 4(9)
O(1)	−0.341 5(10)	0.172 4(6)	0.068 9(9)	C(14)	−0.165 6(10)	−0.135 5(7)	0.139 4(9)
O(2)	0.076 9(9)	0.056 1(7)	0.153 8(9)	C(21)	−0.331 3(11)	0.059 2(7)	0.387 0(9)
O(3)	−0.085 0(11)	0.126 6(7)	0.675 6(9)	C(22)	−0.213 5(12)	0.109 3(7)	0.357 3(10)
O(4)	0.124 1(12)	−0.075 2(11)	0.413 7(11)	C(111)	−0.556 7(11)	−0.022 4(8)	0.063 3(12)
O(5)	−0.321 9(14)	−0.129 4(7)	0.615 6(10)	C(112)	−0.633 4(13)	−0.083 0(11)	−0.037 9(14)
O(6)	−0.379 2(11)	0.051 7(7)	−0.195 7(9)	C(121)	−0.530 9(12)	−0.139 0(7)	0.306 2(11)
O(7)	0.021 7(10)	−0.040 3(8)	−0.133 5(10)	C(122)	−0.624 6(13)	−0.219 1(9)	0.264 4(14)
O(8)	−0.342 3(12)	−0.257 7(7)	−0.098 2(10)	C(131)	−0.242 7(13)	−0.236 6(7)	0.328 9(11)
C(1)	−0.302 6(11)	0.110 3(7)	0.126 5(10)	C(132)	−0.271 1(14)	−0.332 9(8)	0.279 9(13)
C(2)	−0.036 6(13)	0.039 5(8)	0.183 1(11)	C(141)	−0.019 0(11)	−0.178 7(7)	0.134 5(10)
C(3)	−0.110 2(13)	0.078 8(8)	0.596 3(10)	C(142)	0.002 4(15)	−0.258 2(10)	0.043 7(11)
C(4)	0.017 7(14)	−0.042 9(10)	0.432 1(13)	C(211)	−0.469 8(13)	0.077 9(9)	0.452 8(10)
C(5)	−0.254 3(16)	−0.081 4(9)	0.552 5(11)	C(212)	−0.565 7(18)	0.137 5(12)	0.371 9(14)
C(6)	−0.331 4(11)	−0.000 8(17)	−0.123 0(10)	C(221)	−0.175 4(18)	0.210 1(9)	0.369 1(12)
C(7)	−0.082 4(12)	−0.055 8(9)	−0.085 3(10)	C(222)	−0.021(2)	0.233(1)	0.355(2)
C(8)	−0.307 9(13)	−0.186 2(8)	−0.068 7(11)				

$P2_1$ or $P2_1/m$. Analysis of E statistics indicated the non-centrosymmetric $P2_1$ and analysis was initiated in this space group. This choice was subsequently confirmed by successful solution and refinement of the structure. The metal atom positions were determined using the direct methods program MITHRIL[29] and subsequent Fourier difference series revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were included at calculated positions (C–H 1.073 Å) and refined with fixed thermal (U = 0.05 $Å^2$) and positional parameters. All non-hydrogen atoms were allowed anisotropic thermal motion. Refinement was by full-matrix least squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma^2(F)$ used and judged satisfactory. Final discrepancy indices R, R' were 0.031, 0.035 respectively where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. A final Fourier difference synthesis showed no peaks >0.96 or < −0.93 e $Å^{-3}$ the largest features being in the vicinity of the W atom. The correctness of the chosen enantiomer was confirmed by refinement of the eta parameter, the coefficient of the imaginary component of the anomalous scattering factor.[30] In addition, refinement using the inverted configuration converged at $R(R')$ = 0.036 (0.042) with significantly higher discrepancy indices.

Scattering factors were taken from ref. 31, with corrections for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini computer using the GX suite of programs.[32] Atom co-ordinates are listed in Table 4.

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Received 26*th October* 1988; *Paper* 8/04266G