

**The reactions of the alkylidyne complex
[W(\equiv CR)(CO)₂(η -C₅H₅)] with dicobaltatetrahedranes. Crystal
structure of [Co₂W(μ -₃-PhCCHCR)(μ -CO)(CO)₅(η -C₅H₅)]
· H₂O (R = C₆H₄Me-4)**

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Abstract

The alkylidyne complex [W(\equiv CR)(CO)₂(η -C₅H₅)] (I) (R = C₆H₄Me-4) reacts with [Co₂(CO)₆(μ - \perp -PhC₂H)] in refluxing hexane to give the trinuclear cluster [Co₂W(μ -₃-PhCCHCR)(μ -CO)(CO)₅(η -C₅H₅)] (II), which has been characterized by X-ray diffraction. By contrast, the reaction of I with [Co₂(CO)₆(μ - \perp -R'C₂R'')] (R' = R'' = Ph; R' = 'But, R'' = H) resulted, mainly, in the formation of the ditungstatetrahedrane complex [W₂(μ - \perp -C₂R₂)(CO)₄(η -C₅H₅)₂], and for R' = R'' = SiMe₃ this dimerization was found to be catalytic.

Introduction

The dicobaltatetrahedrane complexes of the type [Co₂(CO)₆(μ - \perp -R'C₂R'')] may react with alkynes in three ways, namely: (a) alkyne exchange [1] (b) alkyne coupling, to give coordinated open chain oligomers [1] (also with dimolybdenum complexes [2]); and (c) catalytic oligomerization of the alkyne [3]. Because of the analogy between alkynes and some alkylidynemetal complexes [4], it can be anticipated that the latter should react with acetylene-bridged dimetallic species in a similar way to the former, leading to C–C bond formation.

We describe below the results of the reactions of the tungsten carbyne complex [W(\equiv CR)(CO)₂(η -C₅H₅)] (R = C₆H₄Me-4) with some dicobaltaacetylene complexes.

Results and discussion

The complex $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (I), reacted readily with the compound $[\text{Co}_2(\text{CO})_6(\mu\text{-}\perp\text{-PhC}_2\text{H})]$ in refluxing hexane to give a red-black crystalline product in high yield. This was characterized as the trinuclear cluster $[\text{Co}_2\text{W}(\mu_3\text{-PhCCHCR})(\mu\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II) (reaction i in Scheme 1).

Although the spectroscopic data, specially the low-temperature ^{13}C NMR spectra, revealed the presence of the PhCCHCR ligand and a $\text{Co}_2(\text{CO})_4$ moiety with an additional bridging CO, it was not possible to establish the exact structure of II, and

Table 1

Atomic and thermal parameters for compound II

Atom	x	y	z	$U(\text{iso})^a$
W(1)	0.05687(6)	0.04361(4)	0.16031(8)	0.0396*
Co(1)	-0.0287(2)	0.1111(1)	0.3505(3)	0.0446*
Co(2)	0.1031(2)	0.1839(2)	0.2315(3)	0.0487*
O(1)	0.070(2)	-0.038(1)	0.394(1)	0.089(5)
O(2)	0.108(1)	0.1142(9)	0.556(2)	0.080(5)
O(3)	-0.223(1)	0.0994(9)	0.494(2)	0.078(5)
O(4)	0.267(2)	0.213(1)	0.411(2)	0.118(7)
O(5)	0.171(2)	0.314(1)	0.119(2)	0.094(6)
O(6)	-0.083(1)	0.2633(9)	0.333(2)	0.082(5)
O(7)	0.298(2)	0.083(1)	0.201(2)	0.116(7)
C(1)	0.056(2)	0.002(1)	0.319(2)	0.079(7)
C(2)	0.060(2)	0.114(1)	0.471(2)	0.066(6)
C(3)	-0.146(2)	0.102(1)	0.436(2)	0.052(6)
C(4)	0.200(2)	0.196(1)	0.338(3)	0.080(7)
C(5)	0.149(2)	0.259(1)	0.165(3)	0.082(7)
C(6)	-0.027(2)	0.212(1)	0.308(2)	0.066(7)
C(7)	-0.024(2)	-0.037(2)	0.029(2)	0.079(7)
C(8)	0.069(2)	-0.000(1)	-0.029(2)	0.064(6)
C(9)	0.162(2)	-0.019(1)	0.021(2)	0.066(7)
C(10)	0.139(2)	-0.064(1)	0.115(2)	0.065(7)
C(11)	0.020(2)	-0.074(1)	0.112(2)	0.080(8)
C(12)	0.022(2)	0.156(1)	0.095(2)	0.046(5)
C(13)	-0.086(2)	0.120(1)	0.111(2)	0.041(5)
C(14)	-0.109(1)	0.0872(9)	0.212(1)	0.027(4)
C(121)	0.040(2)	0.188(1)	-0.018(2)	0.049(5)
C(122)	0.143(2)	0.182(1)	-0.074(2)	0.068(7)
C(123)	0.159(2)	0.212(1)	-0.179(2)	0.073(7)
C(124)	0.076(2)	0.252(1)	-0.233(2)	0.069(7)
C(125)	-0.025(2)	0.263(1)	-0.176(2)	0.073(7)
C(126)	-0.040(2)	0.231(1)	-0.071(2)	0.055(6)
C(127)	0.094(2)	0.288(2)	-0.349(3)	0.098(9)
C(141)	-0.219(2)	0.049(1)	0.216(2)	0.041(5)
C(142)	-0.229(2)	-0.020(1)	0.272(2)	0.049(6)
C(143)	-0.330(2)	-0.057(1)	0.272(2)	0.066(6)
C(144)	-0.417(2)	-0.028(1)	0.218(2)	0.066(7)
C(145)	-0.409(2)	0.037(1)	0.158(2)	0.062(6)
C(146)	-0.312(2)	0.075(1)	0.163(2)	0.045(2)

^a U^* are U equiv.

Table 2
Selected bond lengths (Å) and angles (°) for compound II

<i>Distances</i>			
W(1)–Co(2)	2.787(3)	W(1)–Co(1)	2.758(3)
Co(2)–Co(1)	2.512(4)	W(1)–C(1)	2.02(3)
W(1)–C(7)	2.35(3)	W(1)–C(8)	2.37(2)
W(1)–C(9)	2.37(2)	W(1)–C(10)	2.29(2)
W(1)–C(11)	2.30(3)	W(1)–C(12)	2.26(2)
W(1)–C(13)	2.32(2)	W(1)–C(14)	2.25(2)
Co(1)–C(2)	1.77(3)	Co(1)–C(3)	1.74(2)
Co(1)–C(6)	1.94(2)	Co(1)–C(14)	1.95(2)
Co(1)–C(1)	2.29(3)	Co(2)–C(4)	1.73(3)
Co(2)–C(5)	1.69(3)	Co(2)–C(6)	1.89(2)
Co(2)–C(12)	1.95(2)	O(1)–C(1)	1.16(3)
O(2)–C(2)	1.16(3)	O(3)–C(3)	1.15(2)
O(4)–C(4)	1.22(3)	O(5)–C(5)	1.19(3)
O(6)–C(6)	1.20(2)	C(12)–C(13)	1.49(3)
C(12)–C(121)	1.47(3)	C(13)–C(14)	1.37(2)
C(14)–C(141)	1.51(3)	Co(2)–C(1)	3.57(3)
mean C–C in Cp	1.39(3)	mean C–C in Ph	1.39(3)
<i>Angles</i>			
Co(1)–W(1)–Co(2)	53.89(8)	Co(2)–Co(1)–W(1)	63.6(1)
Co(1)–Co(2)–W(1)	62.47(9)	C(1)–S(1)–Co(1)	54.8(7)
C(1)–W(1)–Co(2)	94.7(7)	C(12)–W(1)–Co(2)	43.8(5)
C(13)–W(1)–Co(1)	69.5(5)	C(13)–W(1)–Co(2)	70.0(5)
C(14)–W(1)–Co(1)	44.3(4)	C(13)–W(1)–C(12)	37.9(7)
C(14)–W(1)–C(12)	66.0(7)	C(14)–W(1)–C(13)	34.9(6)
C(2)–Co(1)–Co(2)	92.3(8)	C(3)–Co(1)–C(2)	92.2(10)
C(6)–Co(1)–C(2)	99.6(10)	C(6)–Co(1)–C(3)	104.2(10)
C(14)–Co(1)–C(2)	167.1(9)	C(14)–Co(1)–C(3)	92.9(9)
C(14)–Co(1)–Co(2)	88.7(5)	C(4)–Co(2)–Co(1)	95.7(10)
C(5)–Co(2)–Co(1)	155.2(9)	C(5)–Co(2)–C(4)	90.0(14)
C(6)–Co(2)–C(4)	100.6(11)	C(6)–Co(2)–C(5)	105.3(12)
C(12)–Co(2)–Co(1)	89.6(6)	C(12)–Co(2)–C(4)	166.2(11)
C(12)–Co(2)–C(5)	90.4(12)	Co(1)–C(1)–W(1)	79.3(9)
O(1)–C(1)–W(1)	160.2(22)	O(1)–C(1)–Co(1)	120.4(19)
O(2)–C(2)–Co(1)	172.8(22)	O(3)–C(3)–Co(1)	177.0(20)
O(4)–C(4)–Co(2)	172.7(25)	O(5)–C(5)–Co(2)	173.3(25)
Co(2)–C(6)–Co(1)	81.9(10)	O(6)–C(6)–Co(1)	134.1(19)
O(6)–C(6)–Co(2)	143.8(20)	Co(2)–C(12)–W(1)	82.7(7)
C(13)–C(12)–W(1)	73.2(10)	C(13)–C(12)–Co(2)	118.1(15)
C(121)–C(12)–W(1)	130.8(14)	C(121)–C(12)–Co(2)	123.7(15)
C(121)–C(12)–C(13)	114.9(18)	C(12)–C(13)–W(1)	68.9(10)
C(14)–C(13)–W(1)	70.1(11)	C(14)–C(13)–C(12)	118.6(17)
Co(1)–C(14)–W(1)	81.7(6)	C(13)–C(14)–W(1)	75.0(11)
C(13)–C(14)–Co(1)	121.9(13)	C(141)–C(14)–W(1)	128.5(13)
C(141)–C(14)–Co(1)	121.4(13)	C(141)–C(14)–C(13)	114.7(16)
mean C–C–C in Cp	108.0(2)	mean C–C–C in Ph	120.0(2)

so it was determined by X-ray diffraction. The results are summarized in Tables 1 and 2, and the structure is shown in Fig. 1.

The structure consists essentially of a Co₂W triangle with a μ_3 - η^3 -C₆H₅CCHCC₆H₄Me-4 ligand having the three carbons bonded to the tungsten and

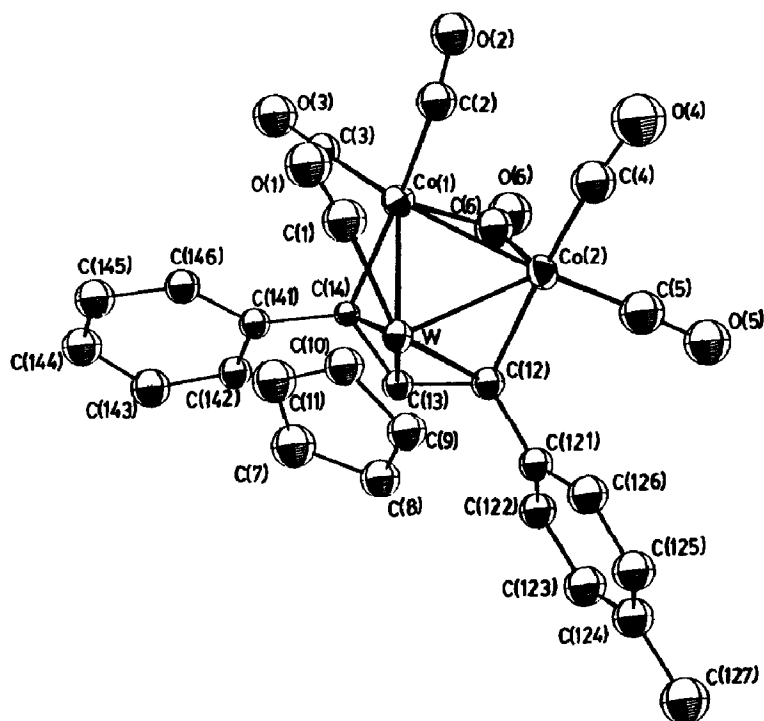


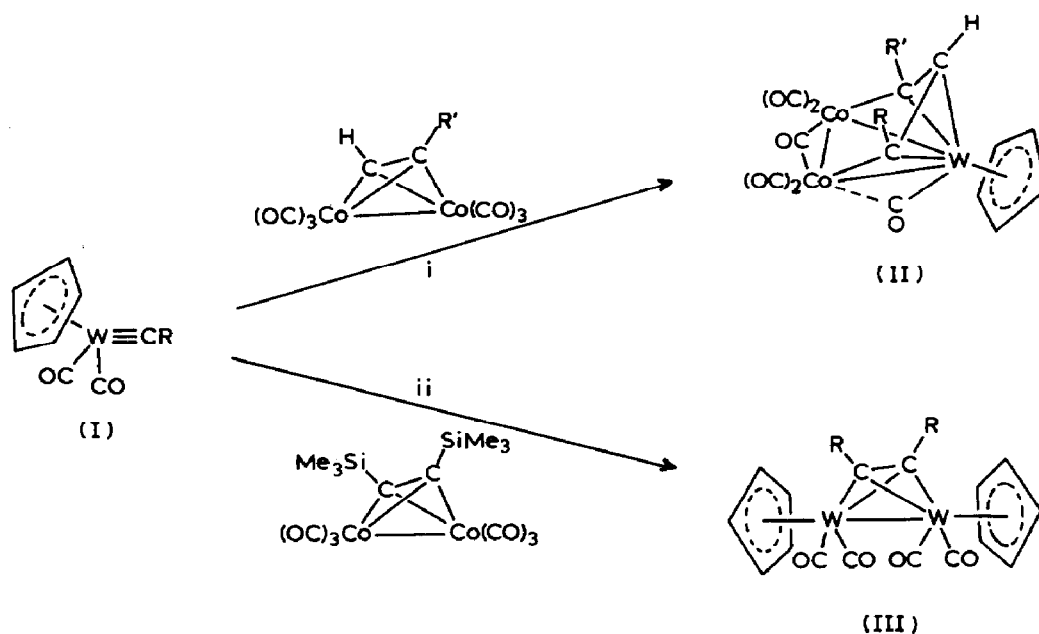
Fig. 1. The molecular structure of $[\text{Co}_2\text{W}(\mu_3\text{-PhCCHCR})(\mu\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II) ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$).

those bearing phenyl rings bridging the Co–W bonds. The two C–C bond distances are within the range normally found in other RCCRCR complexes [5,6], but the C(12)–C(13) (1.49(3) Å) distance is significantly larger than the C(13)–C(14) distance (1.37(2) Å). This effect is probably induced by the carbonyl ligand C(1)O(1), which is semi-bridging between W and Co(1) (C(1)Co(1) 2.29(3) Å, W–C(1)–O(1) 160(2)°). The Co(1)–Co(2)–C(12)–C(14) atoms are nearly in the same plane (the deviations in each case are < 0.014 Å) with the tungsten atom at 1.86 Å above, and the C(13) at 0.21 Å below that plane. This structure corresponds to the conformation depicted in Fig. 2, as found in other $\text{M}_3(\text{C}_3\text{R}_3)$ clusters [6], in accordance with theoretical predictions [7].

The molecule has a pseudomirror plane of symmetry which contains the tungsten and is perpendicular to the Co_2W triangle. However the semi-bridging C(1)O(1) carbonyl and the two inequivalent phenyl and tolyl groups induce enantiomerism in the molecule. The typical non-centrosymmetric $P2_12_12_1$ space group implies that



Fig. 2. Possible structures for the two isomers of compound II in solution.



Scheme 1. R = C₆H₄Me-4, R' = Ph.

the unit cell contains only one enantiomer. An attempt to determine the absolute configuration was frustrated by the effect of the presence of three heavy atoms.

In ¹³C NMR spectra at +20 and -50°C the signal corresponding to the C(1)O(1) semi-bridging carbonyl appeared as two very close peaks (232.9 and 233.0 ppm, *J*(WC) 150 Hz), indicating that, in solution, there is a mixture (ca. 50%) of the two isomers *a* and *b* shown in Fig. 2. The peaks at 156 and 157 ppm, that were much broader in the room temperature spectrum than that at -50°C, can be assigned to the C(12) and C(14) atoms of the PhCCHCR ligand.

In the mixture from reaction i (Scheme 1) a small amount of the known ditungstaacetylene complex [W₂(μ-⊥-C₂R₂)(CO)₄(η-C₅H₅)] (R = C₆H₄Me-4) (III) was detected (by IR), and so the main process was the coupling of the terminal CR group with the coordinated alkyne PhC₂H, to give the PhCCHCR ligand. The coupling between carbynes and two coordinated acetylenes, to give cyclopentadienyl derivatives, has been observed previously [8]. It is also known that open CRCRCR ligands can be formed by coupling of acetylenes with bridging or terminal carbyne ligands [5,9,10].

In contrast with the results obtained with reaction i (Scheme 1), the carbyne I reacted very slowly with the tetrahedrane [Co₂(CO)₆{C₂(SiMe₃)₂}] in refluxing hexane, but quickly in refluxing heptane, giving the ditungstaalkyne complex III catalytically (reaction ii in Scheme 1), although the decomposition of I and III under the reaction conditions prevented a high-yield conversion. Results similar to those observed for reaction ii were obtained for other dicobaltaacetylene complexes, such as [Co₂(CO)₆(C₂Ph₂)] and [Co₂(CO)₆(^tBuCCH)], although small amounts of other products could be detected. It is thus apparent that the reaction of I with acetylene-bridged dimetallic species depends on the alkyne.

The catalytic thermal conversion of I to III has been previously observed [11]. The mechanism proposed in the case of the catalyst [Cr₂(CO)₄(η-C₅H₅)₂] [11]

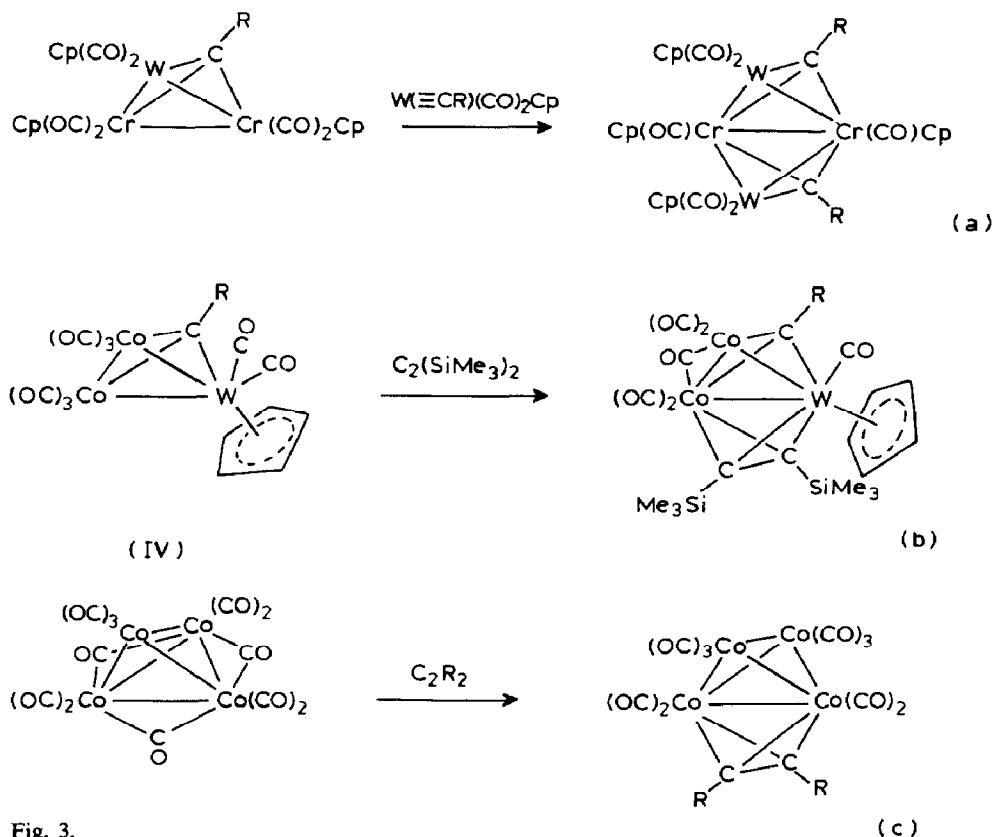


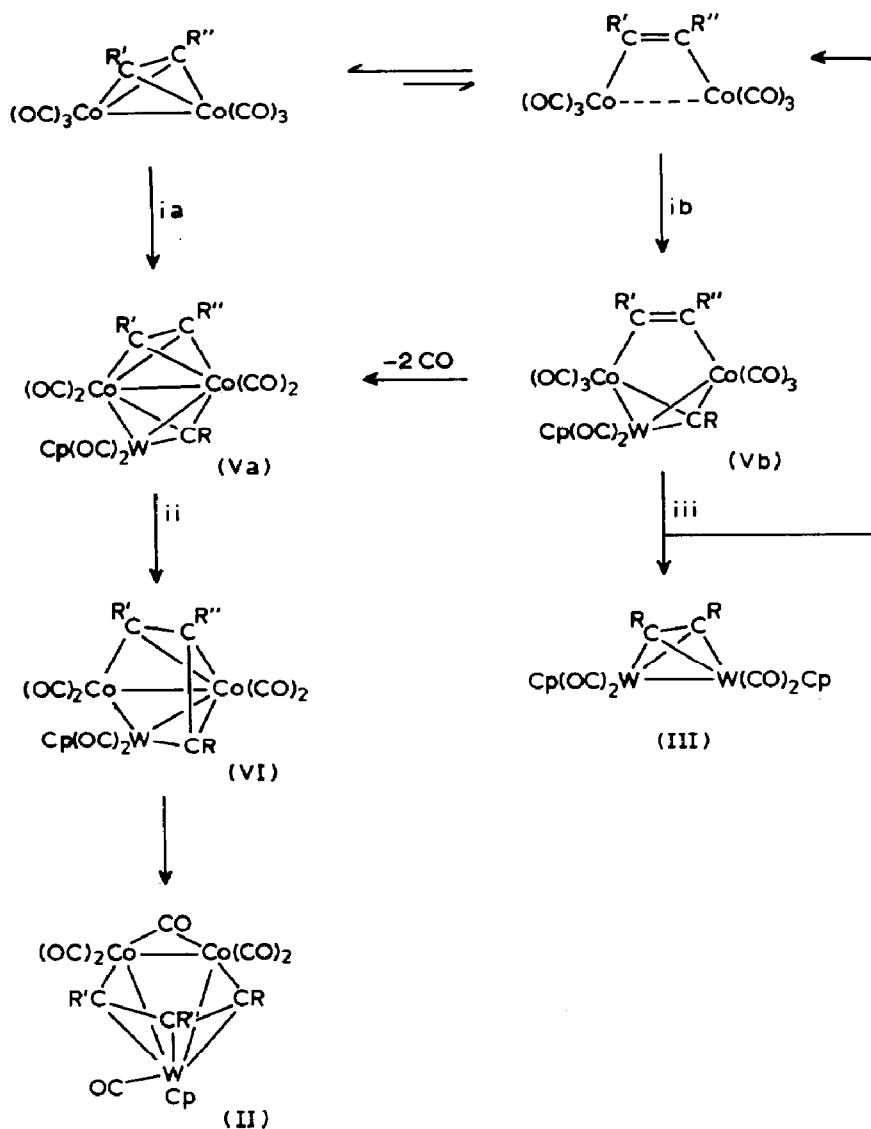
Fig. 3.

involves the addition of I to the dichromium compound, to give a trimetallic tetrahedrane intermediate, followed by the process shown in Fig. 3a. The latter process can be compared with the reaction of the cluster $[\text{Co}_2\text{W}(\mu\text{-CR})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (IV) with $[\text{C}_2(\text{SiMe}_3)_2]$ (Fig. 3b) [12] *, and of $[\text{Co}_4(\text{CO})_{12}]$ with acetylenes (Fig. 3c) [1]. Similarly, many homo- and hetero-nuclear tetrahedral clusters react with acetylenes to form analogous acetylene-bridged butterfly structures [13].

Heating of a solution of compound II in heptane results in decomposition to an unidentified black solid, but if the refluxing is carried out in the presence of I the dimer III is formed. We cannot, however conclude that an intermediate similar to II is involved in reaction ii (Scheme 1). The first step in the catalytic process ii could be either: (a) substitution of the acetylene for the carbyne I to give $[\text{Co}_2\text{W}(\mu\text{-CR})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (IV), or (b) addition of I to the dicobalttetrahedrane to give an expanded intermediate. Our data do not permit a choice between these two pathways.

Thus we found that the cluster IV reacted with I in refluxing heptane to give III (as detected by IR spectroscopy), although concomitant decomposition prevented the recovery of IV. Compound IV also reacted with I in the presence of $[\text{C}_2(\text{SiMe}_3)_2]$, under the same conditions to give III, but the process is not catalytic owing to the

* It is interesting to compare the result of the reaction of Fig. 3b with that of reaction ii in Scheme 1; a clear relation is evident.



Scheme 2. i: $+[\text{W}(\equiv\text{CR})(\text{CO})_2\text{Cp}]$; ii: $\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$; iii: $+[\text{W}(\equiv\text{CR})(\text{CO})_2\text{Cp}]$, $\text{R}' = \text{R}'' = \text{SiMe}_3$.

formation of the known green cluster $[\text{Co}_2\text{W}(\mu_3\text{-CR})\{\text{C}_2(\text{SiMe}_3)_2\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ [12]*.

The addition of I to the dicobaltacylene complex (path b) could occur with loss of CO, as in the analogous reaction of Fig. 3a, giving an intermediate Va (see path ia in Scheme 2). But it is interesting to speculate on the possibility that the addition occurs in a different manner to give another intermediate, Vb (see step ib in Scheme 2). It has recently been shown that the perpendicular (tetrahedrane) into parallel (dimetallated olefin) interconversion in $[\text{Co}_2(\text{CO})_6(\text{C}_2\text{R}'\text{R}'')]$ species can account for aspects of their reactions [14].

* We checked that heating I in refluxing heptane alone or with $[\text{C}_2(\text{SiMe}_3)_2]$ did not result in the formation of III.

The intermediate V (a or b) could react with more I to give a cluster of higher nuclearity, (perhaps similar to the $[\text{Co}_2(\text{CO})_4(\text{R}'\text{C}_2\text{R}'')]_3$ [1] or the known tris-acetylene-dimolybdenum species [2]), that is unstable, decomposing to III and regenerating the dicobaltaacetylene complex. This process (iii in Scheme 2) would be predominant in the case of $\text{R}' = \text{R}'' = \text{SiMe}_3$, accounting for occurrence of reaction i in Scheme 1.

However, for $\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$ and other alkynes, the intermediate Va could undergo a reductive elimination, with C–C coupling to form the kinetic product VI, which could rearrange to the thermodynamically more stable observed structure II (Scheme 2). The necessary rearrangement involves the rotation of the $\text{PhCCHCC}_6\text{H}_4\text{Me}$ ligand on the Co_2W triangle (Fig. 2) [7] with concomitant transfer of CO from W to Co.

Experimental

All reactions were carried out under nitrogen in purified solvents. IR spectra were recorded with a Perkin–Elmer 298 spectrophotometer and calibrated against the 1901.4 cm^{-1} polystyrene absorption. NMR spectra were measured with a Bruker AC-300 instrument. ^1H and ^{13}C NMR spectra are reported in ppm relevant to internal TMS. The compounds $[\text{Co}_2(\text{CO})_2(\text{C}_2\text{R}'\text{R}'')]$ [15] and $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) [16] were prepared by published methods.

Preparation of $[\text{Co}_2\text{W}(\mu_3\text{-PhCCHC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II)

A mixture of $[\text{Co}_2(\text{CO})_8]$ (0.34 g, 1 mmol) and $\text{PhC}\equiv\text{CH}$ (0.12 g, 1.2 mmol) in hexane (10 ml) was stirred for 2 h at room temperature. After filtration the volatiles were removed in vacuo during 2 h. The oily residue was dissolved in hexane (20 ml) and the complex $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) (0.5 g, 1.22 mmol) was added. The mixture was refluxed for 15 min then allowed to cool to room temperature. The liquids were decanted off, and the precipitate was washed with hexane (2×20 ml), then dissolved in CH_2Cl_2 (15 ml). The extract was filtered, hexane (15 ml) was added, and the mixture was concentrated in vacuo to give black microcrystals of II (0.65 g, 72%). M.p. 180°C dec. Analysis, found: C, 43.5; H, 2.40. $\text{Co}_2\text{WC}_{27}\text{H}_{18}\text{O}_6$ calcd.: C, 43.8; H, 2.43%. IR (cm^{-1} , in CH_2Cl_2): $\nu_{\text{max}}(\text{CO})$ 2059s, 2024s, 2004m, 1987sh, 1862m(br), 1807m(br). ^1H NMR: 2.32(s, 3H, Me-4), 4.79(s, 5H, C_5H_5), 5.65(s, 1H, CH), 7.2(AB q, J 7.5 Hz, 4H, C_6H_4). ^{13}C NMR (20°C): 233.0, 232.9 (WCO) $J(\text{WC})$ 150 Hz), 210 (br). $[\text{Co}_2(\text{CO})_5]$, 156.8, 156.0 ($\text{C-C}_6\text{H}_5$, $\text{C-C}_6\text{H}_4\text{Me-4}$), 154.6, 151.6 (C_1 C_6H_5 , $\text{C}_6\text{H}_4\text{Me-4}$), 137.4 (C_4 , $\text{C}_6\text{H}_4\text{Me-4}$), 129.2, 128.6, 128.2, 128.0, 127.2 (C_6H_5 , $\text{C}_6\text{H}_4\text{Me-4}$), 102.7 (CH), 93.6 (C_6H_5), 21.0 (Me-4). At -50°C the main differences are: 230.9 ($\mu\text{-CO}$), 201.5 $[\text{Co}_2(\text{CO})_4]$, 131.0, 129.7, 129.0, 128.4, 128.0, 127.5, 127.2, 125.3, 124.7 (C_2 , C_3 , C_6H_5 , $\text{C}_6\text{H}_4\text{Me-4}$ and $\text{C}_4\text{-C}_6\text{H}_5$).

Reaction of $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Co}_2(\text{CO})_6\{\text{C}_2(\text{SiMe}_3)_2\}]$

A mixture of $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (I) (0.2 g, 0.49 mmol) and $[\text{Co}_2(\text{CO})_6\{\text{C}_2(\text{SiMe}_3)_2\}]$ (0.2 g, 0.44 mmol) in hexane (20 ml) was stirred at room temperature for 15 h then refluxed for 2.5 h. IR spectroscopy showed little change. The solvent was evaporated and replaced by heptane (20 ml). After 1 h refluxing all the I had disappeared, giving the dimer $[\text{W}_2\{-\text{C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$

(III). More I (0.15 g, 0.37 mmol) was added, and after 1 h it had been converted into III without detectable consumption of the dicobalta-acetylene product. Chromatography on alumina separated $[\text{Co}_2(\text{CO})_6\{\text{C}_2(\text{SiMe}_3)_2\}]$ (0.14 g, 70%) and III (0.14 g, 40%).

Crystal structure determination of II

Crystal data and data collection. $\text{C}_{27}\text{H}_{20}\text{Co}_2\text{O}_7\text{W}$. $M = 758.2$. Orthorhombic, a 12.094(4) Å, b 18.533(5) Å, c 11.720(1) Å, V 2626(2) Å³. Cell dimensions obtained from least squares refinement of 25 reflections in the 12–15° range. Space group $P2_12_12_1$. $Z = 4$. $d(\text{calc.})$ 1.92 g cm⁻³. $F(000) = 1464$. Crystal of approximate dimensions 0.045–0.030–0.015 cm. μ 59.7 cm⁻¹. Philips PW1100. ω -28 mode. Mo- K_α radiation and graphite monochromator. Recording θ range 1–20°. 1387 reflections were measured at room temperature, and 1276 with $F > 3\sigma(F)$ used for refinements. Two standard reflections measured every 2 h, showed no change. Empirical absorption correction using the ψ scan of one reflection were applied; the minimum–maximum transmission factors were 1.00 and 1.43.

Structure analysis and refinement. The tungsten atom was located on a Patterson map and all other atoms found in subsequent Fourier maps. Least squares refinements were carried out in three blocks (167 parameters). Only cobalt and tungsten atoms were anisotropically refined because of the small number of observed reflections. A difference map revealed one water molecule. Except for those of the water molecule, which were not introduced, the hydrogen atoms were placed in calculated positions and not refined. R 4.27%, R_2 4.66% (the R values for the appropriate absolute configuration, R 4.30%, R_w 4.68% were not significantly different). The weighting scheme was $w = 1/\sum_{r=1,3} A_r T_r(X)$ with three coefficients: 2.12, -0.80, 1.04 for a Chebyshev series in which X is $F_0/F_0(\text{max})$. The final positional parameters and thermal parameters are shown in Table 1; and selected bond lengths and bond angles in Table 2. Fig. 1 shows a perspective view of the molecule with the numbering scheme and thermal ellipsoids at a 20% probability level.

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