

**Synthesis of complexes with tungsten–cobalt bonds  
via alkylidyne group coupling reactions;  
crystal structure of the compound  
[WCo{ $\mu$ -C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4)}(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] \***

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**Abstract**

Reactions between the compounds [WCo( $\equiv$ CR)(CO)<sub>8</sub>] and [W( $\equiv$ CR)(CO)<sub>2</sub>(L)] (R = C<sub>6</sub>H<sub>4</sub>Me-4, L =  $\eta$ -C<sub>5</sub>H<sub>5</sub> or  $\eta$ -C<sub>5</sub>Me<sub>5</sub>) afford chromatographically separable mixtures of the heterodinuclear compounds [WCo( $\mu$ -RC<sub>2</sub>R)(CO)<sub>5</sub>(L)] and [WCo{ $\mu$ -C(R)C(O)C(R)}(CO)<sub>5</sub>(L)]. In contrast, the reaction between [WCo( $\equiv$ CMe)(CO)<sub>8</sub>] and [W( $\equiv$ CMe)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] yields only the  $\mu$ -alkyne complex [WCo( $\mu$ -MeC<sub>2</sub>Me)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)], while that between [WCo( $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>8</sub>] and [W( $\equiv$ CMe)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] gives [WCo( $\mu$ -MeC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]. The molecular structure of [WCo{ $\mu$ -C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4)}(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] has been established by X-ray diffraction. The W–Co bond (2.669(1) Å) is spanned by the C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4) ligand, the terminal carbon atoms of which are  $\sigma$ -bonded to the tungsten and the cobalt atoms (W– $\mu$ -C 2.174(5) and 2.195(4), Co– $\mu$ -C 2.037(8) and 2.053(5) Å). Bonding between the tungsten or the cobalt atoms and the central carbon of the  $\mu$ -C<sub>3</sub> fragment, if present, must be weak (W  $\cdots$  C(O) 2.615(5), Co  $\cdots$  C(O) 2.517(5) Å). As expected, the tungsten atom is ligated by the  $\eta$ -C<sub>5</sub>H<sub>5</sub> group and two carbonyl ligands. The cobalt atom carries three terminal carbonyl groups. The reaction between [Mo( $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] and [WCo( $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>8</sub>] affords the dimolybdenum complex [Mo<sub>2</sub>( $\mu$ -C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4)}(CO)<sub>4</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], but the latter is more readily obtained by photolysis of the mononuclear molybdenum 4-tolylmethylidyne compound. Treatment of [WCo(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] with diphenylcyclopropenone or MeC $\equiv$ CPh gives, respectively, the bridged alkyne complexes [WCo( $\mu$ -RC<sub>2</sub>Ph)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (R = Ph or Me). The <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR data for the new compounds are reported and discussed.

\* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

## Introduction

We have recently shown [1,2] that the alkylidyne-dimetal complexes  $[\text{WM}(\equiv\text{CR})(\text{CO})_4(\text{L}_n)]$  (1,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{ML}_n = \text{Co}(\text{CO})_4$  or  $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ ;  $\text{R} = \text{Me}$ ,  $\text{ML}_n = \text{Co}(\text{CO})_4$ ) react with alkynes to afford products with a variety of different structures. These products result from a combination of coupling reactions between the alkynes and the alkylidyne groups, carbonyl insertion reactions, and also in some instances hydrogen migration processes. For example, depending on the temperature at which the reaction is carried out, but-2-yne reacts with 1c to afford either  $[\text{MoW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\}(\text{CO})_3(\eta\text{-MeC}_2\text{Me})_2(\eta\text{-C}_5\text{H}_5)]$  or  $[\text{MoW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{=CH}_2)\text{CH}(\text{Me})\text{C}(\text{O})\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$  [1]. Similarly, treatment of 1a with  $\text{MeC}\equiv\text{CMe}$  yields the complex  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\}(\text{CO})_7]$ , whereas the alkyne  $\text{C}_2(\text{C}_6\text{H}_4\text{Me-4})_2$  gives  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_7]$  [2]. These results, coupled with the isolobal relationship existing between the groups  $\text{CR}$  and  $\text{M}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) [3], have led us to investigate reactions of the dimetal complexes I with the mononuclear metal-alkylidyne compounds  $[\text{M}(\equiv\text{CR})(\text{CO})_2(\text{L})]$  ( $\text{I}$ ,  $\text{M} = \text{W}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$  or  $\text{Me}$ ,  $\text{L} = \eta\text{-C}_5\text{H}_5$ ;  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{L} = \eta\text{-C}_5\text{Me}_5$ ;  $\text{M} = \text{Mo}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ,  $\text{L} = \eta\text{-C}_5\text{H}_5$ ). The results of this work are described in this paper.

## Results and discussion

Compound 1a reacts at room temperature with 11a in light petroleum to give a mixture of the two complexes  $[\text{WCo}\{\mu\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIa) and  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IVa). Hexacarbonyltungsten(0) was observed as a major by-product. The two dimetal complexes were separated by column chromatography on alumina, and they were fully characterised by microanalysis and spectroscopic data (Tables 1 and 2). In addition, the structure of IVa was established by an X-ray diffraction study, the results of which are described later.

Compound IIIa exhibits seven terminal CO stretches in its IR spectrum between 2053 and 1923  $\text{cm}^{-1}$ . This property almost certainly reflects the presence in solution of two diastereoisomers, denoted as *cis* and *trans*. This type of isomerisation is not unusual, and has been previously observed in the family of trimetal compounds  $[\text{MCo}_2(\mu_3\text{-CR})(\text{CO})_8(\text{L})]$  ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$  or  $\text{W}$ ,  $\text{L} = \eta\text{-C}_5\text{H}_5$ ,  $\eta\text{-C}_5\text{Me}_5$  or  $\text{HB}(\text{pz})_3$

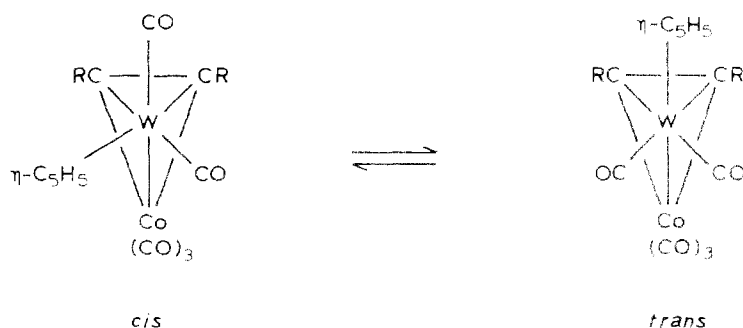


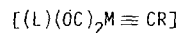
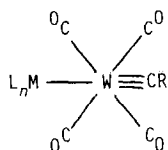
Table 1  
Analytical and other data

Compound <sup>a</sup>	Colour	Yield (%)	$\tilde{\nu}_{\max}(\text{CO})^b$ (cm <sup>-1</sup> )	Analysis (Found (calcd)(%))	
				C	H
[WCo( $\mu$ -RC <sub>2</sub> R)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (IIIa)	Red	21	2053m, 2049m, 2004vs, 1988vs, 1977s, 1944m, 1937m	47.3 (47.7)	2.8 (2.9)
[WCo( $\mu$ -RC <sub>2</sub> Me)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (IIIb)	Red	20	2062m, 2000vs, 1983s, 1976s, 1936m	41.1 (41.6)	2.8 (2.6)
[WCo( $\mu$ -MeC <sub>2</sub> Me)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (IIIc)	Red	20	2047m, 1995vs, 1980s, 1972s, 1935m	33.7 (33.5)	2.6 (2.4)
[WCo( $\mu$ -RC <sub>2</sub> R)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> Me <sub>5</sub> )] (III d)	Orange	22	2040m, 1994s, 1977s 1961m, 1928w	50.6 (51.1)	3.7 (3.9)
[WCo( $\mu$ -PhC <sub>2</sub> Ph)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (IIIe)	Red	89	2054m, 2048s, 2006vs, 1989vs, 1979s, 1946m, 1940m	46.2 (46.0)	2.7 (2.4)
[WCo( $\mu$ -MeC <sub>2</sub> Ph)(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (III f)	Red	99	2051m, 2002vs, 1984s, 1976s, 1937m	40.7 (40.5)	2.3 (2.3)
[WCo( $\mu$ -C(R)C(O)C(R))(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (IVa)	Orange	13	2084vs, 2034vs, 1994m, 1942m, 1593m	47.3 (47.5)	2.8 (2.8)
[WCo( $\mu$ -C(R)C(O)C(R))(CO) <sub>5</sub> ( $\eta$ -C <sub>5</sub> Me <sub>5</sub> )] (IVb)	Orange	14	2076vs, 2026vs, 1978m, 1924m, 1584m	50.8 (51.1)	3.6 (3.9)
[Mo <sub>2</sub> ( $\mu$ -C(R)C(O)C(R))(CO) <sub>4</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ] (Vb)	Orange	25 <sup>c</sup>	2024vs, 1987s, 1943s, 1563m	55.5 (55.7)	4.0 (3.6)
[WCo( $\mu$ -RC <sub>2</sub> R)(CO) <sub>4</sub> (PPh <sub>3</sub> ) ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (VIa)	Red	88	1994s, 1956vs, 1930s, 1907m	57.2 (58.1)	3.6 (3.9)
[WCo( $\mu$ -MeC <sub>2</sub> Me)(CO) <sub>4</sub> (PPh <sub>3</sub> ) ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )] (VIb)	Red	95	1988m, 1954vs, 1926s, 1901s	50.7 (50.6)	3.0 (3.5)

<sup>a</sup> R = C<sub>6</sub>H<sub>4</sub>Me-4. <sup>b</sup> Compounds III in light petroleum, compounds IV-VI in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Yield is ca. 40% when prepared by irradiation of [Mo(≡CR)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)], see Experimental.

{hydrotris(pyrazol-1-yl)borate} [4]. In these species, the isolobal Co(CO)<sub>3</sub> fragment replaces a C(C<sub>6</sub>H<sub>4</sub>Me-4) group in IIIa.

The <sup>13</sup>C-<sup>1</sup>H NMR spectrum of IIIa, measured at -40 °C, exhibits resonances (Table 2) at  $\delta$  212.9 and 203.0 ppm attributable to the W(CO)<sub>2</sub> and Co(CO)<sub>3</sub>



	ML <sub>n</sub>	R		M	R	L
(Ia)	Co(CO) <sub>4</sub>	C <sub>6</sub> H <sub>4</sub> Me-4	(IIa)	W	C <sub>6</sub> H <sub>4</sub> Me-4	$\eta$ -C <sub>5</sub> H <sub>5</sub>
(Ib)	Co(CO) <sub>4</sub>	Me	(IIb)	W	Me	$\eta$ -C <sub>5</sub> H <sub>5</sub>
(Ic)	Mo(CO) <sub>3</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )	C <sub>6</sub> H <sub>4</sub> Me-4	(IIc)	W	C <sub>6</sub> H <sub>4</sub> Me-4	$\eta$ -C <sub>5</sub> Me <sub>5</sub>
			(IId)	Mo	C <sub>6</sub> H <sub>4</sub> Me-4	$\eta$ -C <sub>5</sub> H <sub>5</sub>

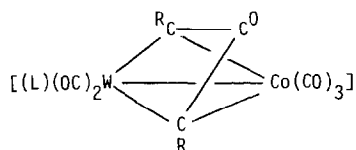
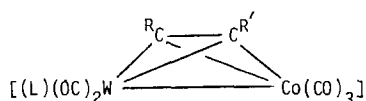
Table 2

NMR data <sup>a</sup>

Com-pound	$\delta(^1\text{H})^b$	$\delta(^{13}\text{C})^{c,d}$
IIIa	2.35 (s, 6H, Me-4), 5.51 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 7.09, 7.15 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 9)	<sup>e</sup> 212.9 (WCO, J(WC) 172), 203.0 (br. CoCO), 138.8, 137.1, 130.1, 129.2 (C <sub>6</sub> H <sub>4</sub> ), 92.1 ( $\mu$ -CR), 89.2 (C <sub>5</sub> H <sub>5</sub> ), 84.5 ( $\mu$ -CR), 21.3 (Me-4)
IIIb	2.34 (s, 3H, Me-4), 2.99 (s, 3H, Me), 5.47 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 7.11, 7.17 ((AB) <sub>2</sub> , 4H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8)	213.5 (WCO, J(WC) 166), 211.1 (WCO, J(WC) 170), 201.7 (CoCO), 139.5, 135.9, 128.8, 128.6 (C <sub>6</sub> H <sub>4</sub> ), 89.2 (C <sub>5</sub> H <sub>5</sub> ), 87.7, 81.8 ( $\mu$ -CMe and $\mu$ -CR), 21.1, 20.8 ( $\mu$ -CMe and Me-4)
IIIc	2.72 (s, 6H, Me), 5.42 (s, 5H, C <sub>5</sub> H <sub>5</sub> )	213.9 (WCO), 204.0 (CoCO), 92.9 ( $\mu$ -CMe), 89.5 (C <sub>5</sub> H <sub>5</sub> ), 86.4 ( $\mu$ -CMe), 20.3 (Me)
IIId	2.16 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 2.35 (s, 6H, Me-4), 7.07, 7.79 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8]	216.1 (WCO, J(WC) 166), 204.7 (br. CoCO), 138.0, 135.4, 129.2, 128.2 (C <sub>6</sub> H <sub>4</sub> ), 101.7 (C <sub>5</sub> Me <sub>5</sub> ), 87.9 ( $\mu$ -CR), 20.3 (Me-4), 10.2 (C <sub>5</sub> Me <sub>5</sub> )
IIIe	5.45 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 7.08–7.35 (m, 10H, Ph)	211.8 (WCO, J(WC) 169), 201.7 (CoCO), 142.1, 129.8, 128.2, 126.6 (Ph), 90.6 ( $\mu$ -CPh), 89.1 (C <sub>5</sub> H <sub>5</sub> ), 84.3 ( $\mu$ -CPh)
IIIf	2.98 (s, 3H, Me), 5.43 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 6.98–7.43 (m, 5H, Ph)	212.8, 210.2 (WCO), 202.1 (br. CoCO), 142.6, 128.3, 127.6, 125.5 (Ph), 88.6 (C <sub>5</sub> H <sub>5</sub> ), 88.2, 79.8 ( $\mu$ -CMe and $\mu$ -CPh), 20.3 (Me)
IVa	2.29 (s, 6H, Me-4), 5.26 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 7.29, 7.83 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8)	<sup>e</sup> 214.8 (WCO, J(WC) 142), 200.0 (br. CoCO), 177.1 ( $\mu$ -C(R)C(O)C(R)), 142.9, 137.2, 130.4, 129.5 (C <sub>6</sub> H <sub>4</sub> ), 106.2 (br. $\mu$ -CR), 21.5 (Me-4)
IVb	1.89 (s, 15H, C <sub>5</sub> Me <sub>5</sub> ), 2.28 (s, 6H, Me-4), 7.08, 7.78 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8)	<sup>f</sup> 218.8 (WCO), 177.0 ( $\mu$ -C(R)C(O)C(R)), 142.2, 135.8, 129.9, 128.6 (C <sub>6</sub> H <sub>4</sub> ), 106.1 (br. $\mu$ -CR), 100.3 (C <sub>5</sub> Me <sub>5</sub> ), 21.4 (Me-4), 9.2 (C <sub>5</sub> Me <sub>5</sub> )
Vb	2.32 (s, 6H, Me-4), 4.93 (s, 10H, C <sub>5</sub> H <sub>5</sub> ), 7.07, 7.58 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8)	227.5 (MoCO), 173.4 ( $\mu$ -C(R)C(O)C(R)), 148.7, 133.9, 128.6, 128.1 (C <sub>6</sub> H <sub>4</sub> ), 105.4 ( $\mu$ -CR), 93.7 (C <sub>5</sub> H <sub>5</sub> ), 21.5 (Me-4)
VIa	2.27 (s, 6H, Me-4), 5.22 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 6.48, 6.98 ((AB) <sub>2</sub> , 8H, C <sub>6</sub> H <sub>4</sub> , J(AB) 8), 7.10–7.34 (m, 15H, Ph)	217.0 (WCO), 208.5 (CoCO), 141.0 (C <sup>13</sup> C <sub>6</sub> H <sub>4</sub> ), 136.1–128.1 (C <sub>6</sub> H <sub>4</sub> and Ph), 90.6 (C <sub>5</sub> H <sub>5</sub> ), 89.6 ( $\mu$ -CR), 21.2 (Me-4)
VIb	2.09 (s, 6H, Me), 5.35 (s, 5H, C <sub>5</sub> H <sub>5</sub> ), 7.18–7.56 (m, 15H, Ph)	<sup>g</sup> 215.7 (WCO), 208.0 (CoCO), 136.3–127.3 (Ph), 88.3 ( $\mu$ -CMe), 87.8 (C <sub>5</sub> H <sub>5</sub> ), 18.9 (Me)

<sup>a</sup> Chemical shifts in ppm, coupling constants in Hz, with measurements at room temperature, unless otherwise indicated. <sup>b</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe<sub>4</sub> (0.0 ppm), with measurements in CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> R = C<sub>6</sub>H<sub>4</sub>Me-4. <sup>e</sup> Measured at -40 °C. <sup>f</sup> CoCO signal not observed due to poor signal to noise and <sup>59</sup>Co quadrupolar effect. <sup>g</sup> Measured in CDCl<sub>3</sub>.

groups, respectively. The former signal shows <sup>183</sup>W satellite peaks, the latter resonance is broad due to the <sup>59</sup>Co quadrupolar effect. The most interesting feature of the spectrum is the two peaks at  $\delta$  92.1 and 84.5 ppm, attributable to the  $\mu$ -C<sub>2</sub> nuclei, the carbon atoms of which are inequivalent. Neither the <sup>1</sup>H nor the <sup>13</sup>C-{<sup>1</sup>H} spectra indicated inequivalent C<sub>6</sub>H<sub>4</sub>Me-4 groups, possibly due to coincident signals. The fact that there are two  $\mu$ -C resonances in a spectrum measured at -40 °C



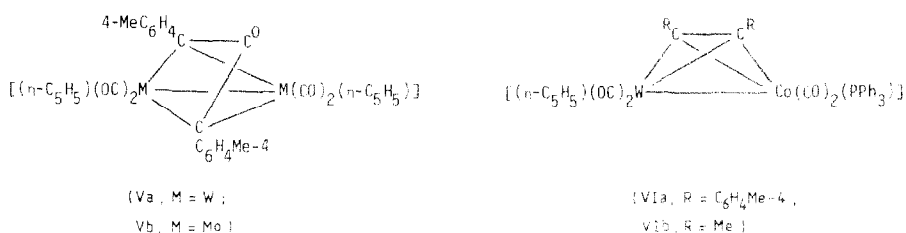
	R	R'	L
(IIIa)	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4	n-C <sub>5</sub> H <sub>5</sub>
(IIIb)	C <sub>6</sub> H <sub>4</sub> Me-4	Me	n-C <sub>5</sub> H <sub>5</sub>
(IIIc)	Me	Me	n-C <sub>5</sub> H <sub>5</sub>
(III d)	C <sub>6</sub> H <sub>4</sub> Me-4	C <sub>6</sub> H <sub>4</sub> Me-4	n-C <sub>5</sub> Me <sub>5</sub>
(IIIe)	Ph	Ph	n-C <sub>5</sub> H <sub>5</sub>
(III f)	Ph	Me	n-C <sub>5</sub> H <sub>5</sub>

	R	L
(IVa)	C <sub>6</sub> H <sub>4</sub> Me-4	n-C <sub>5</sub> H <sub>5</sub>
(IVb)	C <sub>6</sub> H <sub>4</sub> Me-4	n-C <sub>5</sub> Me <sub>5</sub>

suggests that the *cis* isomer may be the favoured form at this temperature. Presumably the observation of only one signal for the W(CO)<sub>2</sub> group, when two would have been expected for the *cis* isomer, reflects a fortuitous chemical shift equivalence of the two carbonyl ligands on tungsten.

A compound [MoCo{μ-C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>}(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)], similar to IIIa, has recently been reported [5], having been obtained from the reaction between [Co<sub>2</sub>{μ-C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>}(CO)<sub>6</sub>] and [Mo<sub>2</sub>(CO)<sub>6</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] in the presence of benzophenone ketyl or Na[Mo(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)]. Heterodinuclear metal-μ-alkyne complexes are not as common as the homodinuclear species, but include the compounds [MnCo(μ-RC<sub>2</sub>R')(CO)<sub>7</sub>] (R = R' = Et or Ph; R = Me, R' = Et; R = Me, R' = Ph) [6], [CoNi(μ-PhC<sub>2</sub>Ph)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] [7,8], [CoNi(μ-PhC<sub>2</sub>CO<sub>2</sub>Pr<sup>i</sup>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)], [MnNi(μ-PhC<sub>2</sub>CO<sub>2</sub>Pr<sup>i</sup>)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)], [MoNi(μ-PhC<sub>2</sub>CO<sub>2</sub>Pr<sup>i</sup>)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] [9] and [MoNi(μ-RC<sub>2</sub>R')(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (R = R' = Me; R = Me, R' = Et) [10]. These complexes have been prepared either by treating the appropriate heteronuclear dimetal compound, or by treating mixtures of two homonuclear dimetal compounds, with an alkyne. Unfortunately, <sup>13</sup>C-<sup>1</sup>H NMR data have only been reported [6] for the manganese-cobalt compounds. For the symmetrical alkyne species [MnCo(μ-RC<sub>2</sub>R')(CO)<sub>7</sub>] (R = R'), the resonances for the μ-C<sub>2</sub> nuclei occur as a single signal at δ 92.6 (R = Et) and 90.7 ppm (R = Ph), since in these species the CR fragments are in equivalent environments. Similarly, the dimolybdenum compounds [Mo<sub>2</sub>(μ-RC<sub>2</sub>R)(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (R = H or Me) show one resonance (δ 61.9 (H) and 82.6 ppm (Me)) for the μ-C nuclei [11].

The IR spectrum of IVa shows four terminal CO stretching bands between 2084 and 1942 cm<sup>-1</sup> (Table 1). There is also a peak at 1593 cm<sup>-1</sup> attributable to the acyl group in the μ-C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4) ligand. The <sup>1</sup>H NMR spectrum (Table 2) shows the expected signals for the η-C<sub>5</sub>H<sub>5</sub> ligand and the equivalent C<sub>6</sub>H<sub>4</sub>Me-4 groups. The <sup>13</sup>C-<sup>1</sup>H spectrum is more informative. Peaks at δ 214.8 and 200.0 ppm are assigned to the W(CO)<sub>2</sub> and Co(CO)<sub>3</sub> groups, respectively, since the former resonance has <sup>183</sup>W satellites, and the latter is broad due to the <sup>59</sup>Co quadrupolar effect. A signal at δ 177.1 ppm is assigned to the acyl carbonyl group.



The latter chemical shift may be compared with those observed for this moiety in the  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectra of the compounds  $[\text{W}_2(\mu\text{-C}\{\text{C}_6\text{H}_4\text{Me-4}\}\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}\text{(CO)}_4(\eta\text{-C}_5\text{H}_5)_2]$  (Va) ( $\delta$  177.3 ppm) [12,13] and  $[\text{Pt}_2\{\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\}\text{(CNBu}^t)_4]$  ( $\delta$  168.5 ppm) [14]. The  $\mu\text{-CC}_6\text{H}_4\text{Me-4}$  resonances in the  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum of IVa appear as one slightly broadened peak at  $\delta$  106.2 ppm. This is considerably more deshielded than the corresponding signals in the spectra of the aforementioned ditungsten and diplatinum compounds, which occur at  $\delta$  78.0 and 86.6 ppm, respectively.

The molecular structure of IVa is shown in Fig. 1, and selected bond distances and angles are given in Table 3. The W-Co bond length (2.669(1) Å) is longer than that in  $[\text{WCo}\{\mu\text{-}\sigma,\eta^3\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\text{H}\}\text{(}\mu\text{-CO)}\text{(CO)}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)\text{][BF}_4]$  (2.552(1) Å) [15], but the latter species is formally unsaturated (32 valence electron). A better comparison is made with the W-Co bond distances found in the complexes  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\text{C}(\text{O})\}\text{(CO)}_6(\text{PPh}_3)]$  (2.737(1) Å) and  $[\text{WCo}\{\mu\text{-C}(\text{Ph})\text{C}(\text{Me})\text{C}(\text{Me})\text{C}(\text{OH})\}\text{(CO)}_6(\text{PPh}_3)\text{][BF}_4]$  (2.660(1)

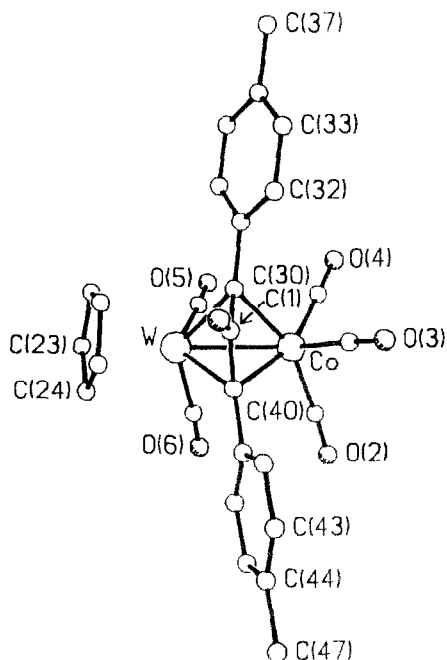


Fig. 1. Molecular structure of  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}\text{(CO)}_5(\eta\text{-C}_5\text{H}_5)]$  (IVa).

Table 3  
 Selected internuclear distances (Å) and angles (°) for [WCo( $\mu$ -C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4))(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (IVa)

W-Co	2.669(1)	W...C(1)	2.615(5)	W-C(5)	1.996(6)	W-C(6)	2.009(8)
W-C(30)	2.174(5)	W-C(40)	2.195(4)	Co-C(2)	1.823(9)	Co-C(3)	1.816(6)
Co-C(4)	1.833(5)	Co-C(30)	2.037(8)	Co-C(40)	2.053(5)	C(1)-O(1)	1.230(9)
C(1)-C(30)	1.486(6)	C(1)-C(40)	1.47(1)	C(2)-O(2)	1.13(1)	C(3)-O(3)	1.107(8)
C(4)-O(4)	1.123(6)	C(5)-O(5)	1.159(7)	C(6)-O(6)	1.13(1)	Co...C(1)	2.517(5)
range W-C( $\eta$ -C <sub>5</sub> H <sub>5</sub> )	2.34(1)-2.309(8)						
C(5)-W-C(6)	80.7(3)	C(2)-Co-C(3)	99.8(4)	C(2)-Co-C(4)	99.5(3)	C(3)-Co-C(4)	98.9(2)
W-C(1)-O(1)	140.9(4)	W-C(1)-C(30)	56.2(2)	O(1)-C(1)-C(30)	131.2(6)	W-C(1)-C(40)	57.0(2)
O(1)-C(1)-C(40)	131.6(4)	C(30)-C(1)-C(40)	96.8(5)	Co-C(2)-O(2)	176.1(6)	Co-C(3)-O(3)	175.3(7)
Co-C(4)-O(4)	176.0(7)	W-C(5)-O(5)	175.7(4)	W-C(6)-O(6)	174.8(5)	W-C(30)-Co	78.6(2)
W-C(30)-C(1)	89.2(3)	Co-C(30)-C(1)	89.8(4)	W-C(30)-C(31)	133.6(3)	Co-C(30)-C(31)	125.7(4)
C(1)-C(30)-C(31)	124.9(6)	W-C(40)-Co	77.8(1)	W-C(40)-C(1)	88.7(3)	Co-C(40)-C(1)	89.5(3)
W-C(40)-C(41)	135.8(3)	Co-C(40)-C(41)	123.9(5)	C(1)-C(40)-C(41)	125.3(5)		

Å) [2], both species being derived via reactions of alkynes with Ia or Ib. The Co–C(30) (2.037(8) Å) and Co–C(40) (2.053(5) Å) separations are similar to the Co– $\mu$ -C distances (av. 1.96 Å) in the  $\mu$ -alkyne complex  $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{CO})_6]$  [16]. Similarly, the W–C(30) (2.174(5) Å) and W–C(40) (2.195(4) Å) distances are very close to the W– $\mu$ -C(C<sub>6</sub>H<sub>4</sub>Me-4) separations (av. 2.22(1) Å) in the compound  $[\text{W}_2\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (Va) [13].

It is interesting to compare the W–C(1) separation (2.615(5) Å) in IVa with the corresponding distances in Va (av. 2.645(2) Å) [13] and in  $[\text{Pt}_2\{\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\}\text{(CNBu}^t)_4]$  (av. 2.50(2) Å) [14]. At issue is whether or not these parameters reflect weak metal–carbon bonding. Although in the diplatinum compound the Pt– $\mu$ -C(O) distance exceeds the sum of the covalent radii of the two atoms (C(*sp*<sup>2</sup>) 0.68, Pt 1.31 Å) involved, the observation of <sup>195</sup>Pt–<sup>13</sup>C coupling in the <sup>13</sup>C–{<sup>1</sup>H} NMR spectrum suggests the existence of some platinum–carbon bonding. This idea is further supported by the observed C–O separation (1.26(2) Å) in the acyl group, which is appreciably longer than that in cyclopropanone (1.18 Å). The marginally shorter acyl C–O bond lengths in IVa (1.230(9) Å) and Va (1.22(2) Å) suggest little or no distortion of the C=O bond, in turn implying the absence of any significant W– $\mu$ -C(O) interaction. This is supported by the tungsten–carbon distances listed above for these species. Indeed, the W–C(1) separation in IVa, although somewhat less than the sum of the covalent radii of the two atoms, is appreciably longer than generally observed for tungsten–carbon  $\sigma$ -bonds (ca. 2.1–2.4 Å) [17]. The Co...C(1) separation (2.517(5) Å) may be taken as non-bonding. For the three compounds, it appears that as the tungsten– $\mu$ -C(O) distance decreases, the C–O separation increases, perhaps reflecting the onset of weak metal–carbon bonding. In accord with the structural data, in the IR spectrum of the diplatinum compound the absorption for the acyl group (1556 cm<sup>–1</sup>) is appreciably lower in frequency than those for this group in the spectra of IVa (1593 cm<sup>–1</sup>) or Va (1586 cm<sup>–1</sup>).

The angle C(30)–C(1)–C(40) (96.8(5) Å) in IVa is similar to the corresponding angles in Va (98(1)°) and in  $[\text{Pt}_2\{\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\}\text{(CNBu}^t)_4]$  (99(1)°), and these parameters probably reflect the constraints imposed on the bridging ligand over the metal–metal bond. It is noteworthy that the smallest angle occurs in the complex with the shortest metal–metal bond. The C–C separations in the  $\mu$ -C<sub>3</sub> fragment of IVa (1.486(6) and 1.472(10) Å) are somewhat shorter than those in Va (1.52(2) and 1.53(2) Å), and slightly longer than those in the diplatinum compound (1.41(2) and 1.45(3) Å). Again these data seem to correlate with the degree of metal– $\mu$ -C(O) interaction decreasing in the order  $[\text{Pt}_2\{\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\}\text{(CNBu}^t)_4]$ , IVa and Va.

The reaction between Ia and IIb was next investigated, and found to afford the complex  $[\text{WCo}(\mu\text{-MeC}_2\text{C}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIb), characterised by the data given in Tables 1 and 2. Compound IIIb was also obtained as the product of the reaction between Ib and IIa. The IR spectrum of IIIb in the terminal CO stretching region shows only five bands, in contrast with the spectrum of IIIa. The fewer bands observed with IIIb probably indicates that this species in solution adopts a *cis* conformation with the  $\eta\text{-C}_5\text{H}_5$  ligand nearest the less bulky  $\mu\text{-CMe}$  group (see earlier Discussion of the *cis* and *trans* forms of IIIa). Indeed, in the solid state, the complex  $[\text{MoCo}(\text{CF}_3\text{C}_2\text{CF}_3)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  adopts a *cis* configuration [5].

As expected, due to the presence of the unsymmetrical alkyne ligand, the <sup>13</sup>C–{<sup>1</sup>H} NMR spectrum of IIIb shows two resonances for the  $\mu$ -C nuclei ( $\delta$  81.8



and 87.7 ppm). Other peaks in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum, and the signals in the  $^1\text{H}$  NMR spectrum, are in accord with the proposed structure.

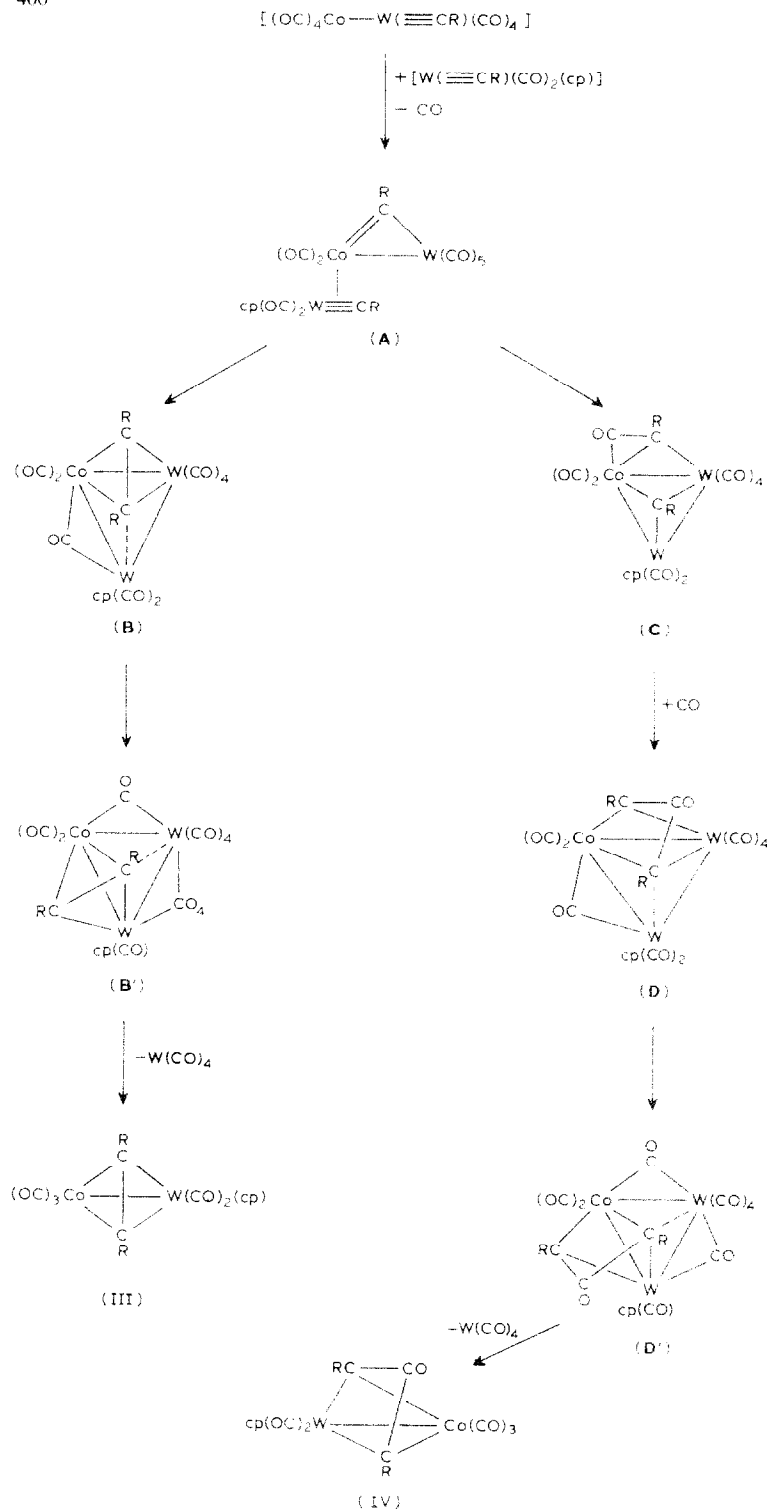
The reaction between Ib and IIb gives the compound  $[\text{WCo}(\mu\text{-MeC}_2\text{Me})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIc), data for which are given in Tables 1 and 2. The IR spectrum in the terminal CO stretching region again shows five bands, indicating that the *cis* configuration is probably favoured over the *trans* arrangement. This is supported by the fact that the room temperature  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum shows two signals ( $\delta$  86.4 and 92.9 ppm) for the  $\mu\text{-C}_2$  fragment. The *trans* isomer would have a plane of symmetry and hence make the  $\mu\text{-C}$  nuclei equivalent.

The reaction between Ia and IIc was studied. It was hoped that the differing steric and electronic properties of the  $\eta\text{-C}_5\text{Me}_5$  group, compared with  $\eta\text{-C}_5\text{H}_5$ , would enable us to isolate a product, the nature of which would assist in elucidating the pathway followed in these evidently complicated processes. Unfortunately, in light petroleum at room temperature, the reaction of Ia with IIc is sluggish. On boiling the reactants in diethyl ether, the compounds  $[\text{W}(\text{CO})_6]$ ,  $[\text{WCo}\{\mu\text{-C}_2(\text{C}_6\text{H}_4\text{-Me-4})_2\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$  (IIIId), and  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$  (IVb) were isolated. Complexes IIIId and IVb are analogous to IIIa and IVa, respectively, except for the replacement of the  $\eta\text{-C}_5\text{H}_5$  ligand by the  $\eta\text{-C}_5\text{Me}_5$  moiety. Compound IIIId shows only five bands in the terminal CO region (Table 1) and only one  $\mu\text{-C}$  signal in its  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum (Table 2). This seems to imply that IIIId exists in a *trans* configuration; a most surprising result in view of the presence of the bulky  $\text{C}_6\text{H}_4\text{Me-4}$  substituents on the bridging carbon atoms.

Compound IVb has very similar spectroscopic properties to those of IVa. In the IR spectrum of the former, there is a band for the acyl carbonyl group ( $1584\text{ cm}^{-1}$ ) at slightly lower frequency than observed ( $1593\text{ cm}^{-1}$ ) in the spectrum of the latter. The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of IVb displays broad signals at  $\delta$  177.0 and 106.1 ppm, which may be assigned to the  $\text{C}(\text{R})\text{C}(\text{O})\text{C}(\text{R})$  and  $\text{C}(\text{R})\text{C}(\text{O})\text{C}(\text{R})$  ( $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ) nuclei, respectively. These peaks have virtually the same chemical shifts as those for the corresponding resonances in the spectrum of IVa.

An interesting feature of the above reactions is that those that occur between Ia and either IIa or IIc afford two types of product: those with bridging alkyne ligands as well as those with bridging  $\text{C}(\text{R})\text{C}(\text{O})\text{C}(\text{R})$  ( $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ) groups. In contrast, if the species Ib or IIb are used, formation of products in which a CO group is inserted between two alkyldiene fragments is suppressed. In our studies [2] on reactions of Ia and Ib with alkynes, we suggested that the initial step might involve the alkyne attacking either at the cobalt atom or at the  $\text{W}\equiv\text{CR}$  group. However, because of the facile displacement of CO groups from  $\text{Co}(\text{CO})_4$  by nucleophiles, we favoured the idea of alkyne attack at the cobalt centre with concomitant migration of the alkyldiene group from a terminal to a bridging position. In view of the isolobal mapping between CR ( $\text{R} = \text{Me}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ) and  $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{R}'_5)$  ( $\text{R}' = \text{H}$  or  $\text{Me}$ ) groups, a similar mechanism could be postulated to account for the formation of the products reported herein (Scheme 1). From the intermediate A, there are two competing pathways leading to the two types of product observed.

Conversion of A into B involves coupling of the alkyldiene groups on the trimetal cluster, a process which is well established [18–24]. The structure invoked for B is similar to that of the species  $[\text{M}_2\text{Fe}(\mu\text{-RC}_2\text{R})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ,  $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ) [19,22]. The alkyne adopts a  $\mu_3$  ( $\eta^2\text{-}\parallel$ ) bonding mode [25], bridging



Scheme 1. cp =  $\eta\text{-C}_5\text{H}_5$ , R =  $\text{C}_6\text{H}_4\text{Me-4}$  for both pathways. R = Me for pathway leading to  $\mu\text{-RC}_2\text{R}$  complex (see text).

one of the Fe–W edges of the metal triangle. Conversion of **B** into **B'** would result from a pivoting of the alkyne about the triply bridging carbon atom, with concomitant migration of CO groups. A similar process has been invoked to account for the dynamic behaviour of  $[\text{W}_2\text{Fe}(\mu\text{-RC}_2\text{R})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$  in solution, as revealed by NMR studies [19]. Release of a  $\text{W}(\text{CO})_4$  fragment from **B'** would afford products of type III. The  $\text{W}(\text{CO})_4$  group, via CO scavenging from the reactants or intermediates, would yield  $[\text{W}(\text{CO})_6]$ , as is observed. Moreover, this would account for the products being formed in only moderate yield.

The other pathway shown in Scheme 1 would lead to the alternative product IV. Formation of the intermediate **C** involves migration of a CO group so that a C–C bond is formed with the alkylidyne ligand. We have reported several examples of this process [21,26]. Coupling of the  $\eta^2\text{-C}(\text{R})\text{C}(\text{O})$  group in **C** with the  $\mu_3\text{-CR}$  fragment would generate the  $\text{C}(\text{R})\text{C}(\text{O})\text{C}(\text{R})$  ligand in **D**. Again a pivoting mechanism with CO migration would afford **D'**, from which release of a  $\text{W}(\text{CO})_4$  fragment would yield the products IV. Evidently this pathway is not favoured if one or other of the groups R in the reactants I or II is alkyl.

Treatment of compounds IIIa and IIIc with an excess of  $\text{PPh}_3$  produced the complexes  $[\text{WCo}(\mu\text{-RC}_2\text{R})(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$  ( $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$  (VIa) or Me (VIb)) in high yield. The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectra (in  $\text{CD}_2\text{Cl}_2$ ) of these species showed broad peaks at  $\delta$  39.5 (VIa) and 39.6 ppm (VIb), respectively (the chemical shifts being relative to 85%  $\text{H}_3\text{PO}_4$  (external)). The broadness of the signals, and the absence of  $^{183}\text{W}\text{-}^{31}\text{P}$  coupling, show that  $\text{PPh}_3$  substitution has occurred at the cobalt atoms. In the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectra (Table 2), the resonances for the  $\mu\text{-C}$  groups occur at  $\delta$  89.6 (VIa) and 83.3 ppm (VIb), respectively. Since only one signal for the  $\mu\text{-C}_2$  fragment is observed in each spectrum, the carbon atoms are equivalent, implying structures for these compounds having a plane of symmetry.

The reaction between Ia and IIc was also investigated. Surprisingly, apart from  $[\text{W}(\text{CO})_6]$ , the only product isolated in significant yield was the dimolybdenum compound  $[\text{Mo}_2\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  (Vb), the molybdenum analogue of Va. Data for Vb are given in Tables 1 and 2, and are in agreement with the structure shown. The pathway by which Vb is formed in the reaction is not apparent. It may be prepared in much better yield by photolysing IIc in the presence of CO; the method of choice to obtain Va from IIIa [13].

Since the compounds IV are the first heterodinuclear metal complexes known containing the  $\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})$  ligand, we attempted a synthesis of a similar compound by treating  $[\text{WCo}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  with diphenylcyclopropenone. The platinum compound  $[\text{Pt}_2\{\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})\}(\text{CNBu}^t)_4]$  was prepared from  $[\text{Pt}_3(\text{CNBu}^t)_6]$  and diphenylcyclopropenone, the C=C double bond in the latter being cleaved [14]. However, reaction of the latter with  $[\text{WCo}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  afforded the bridged-alkyne complex  $[\text{WCo}(\mu\text{-PhC}_2\text{Ph})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIe), rather than the expected product in which a  $\mu\text{-C}(\text{Ph})\text{C}(\text{O})\text{C}(\text{Ph})$  moiety bridges a W–Co bond. Not surprisingly, IIIe has very similar spectroscopic properties to IIIa. The observation of seven terminal CO stretches in the IR spectrum (Table 1) probably indicates *cis-trans* isomers in equilibrium in solution, as discussed earlier for IIIa. Surprisingly, even at room temperature, the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectrum of IIIe exhibits two  $\mu\text{-C}$  resonances. This might have been expected at low temperatures where the *cis* isomer might be favoured, but not at higher temperatures where IR measurements indicate an isomeric mixture. Perhaps the absence of

more than two  $\mu$ -C signals in the  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum is due to poor resolution or coincidence of peaks of the *cis* and *trans* isomers.

Recently Chetcuti et al. [10] found that the heterodinuclear compound  $[\text{MoNi}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  reacted with various alkynes to give mixtures of the complexes  $[\text{MoNi}(\mu\text{-RC}_2\text{R})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$  and  $[\text{MoNi}\{\mu\text{-C}(\text{R})\text{C}(\text{R})\text{C}(\text{O})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ . The latter species readily decarbonylate to give the former. Moreover, for R = Me, bubbling CO through solutions of the former affords the latter. It is therefore likely that IIIe is formed via an intermediate in which the W-Co bond is bridged by a  $\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{O})$  group.

The alkyne  $\text{MeC}\equiv\text{CPh}$  also reacts with  $[\text{WCo}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  slowly at room temperature, but fairly rapidly in boiling light petroleum, to give  $[\text{WCo}(\mu\text{-MeC}_2\text{Ph})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (III f), data for which are given in Tables 1 and 2.

## Experimental

All experiments were carried out under nitrogen using Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60°C. The compounds Ia, Ib [27,28], II [29,30], and  $[\text{WCo}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  [31] were prepared by published procedures. NMR spectra were recorded with JEOL JNM FX90Q, GX270, and GX400 spectrometers, and IR spectra were measured with Nicolet MX5 and MX10 spectrophotometers.

### Reactions of $[\text{WCo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_8]$

(i) The complexes Ia (0.57 g, 1.0 mmol) and IIa (0.41 g, 1.0 mmol) were dissolved in light petroleum (ca. 50 cm<sup>3</sup>), and stirred at room temperature for ca. 1 h, during which period formation of  $[\text{W}(\text{CO})_6]$  was detected by IR spectroscopy. The mixture was reduced in volume in vacuo to ca. 20 cm<sup>3</sup>, and the suspension syringed onto the top of an alumina chromatography column (3 × 15 cm). Elution with light petroleum removed  $[\text{W}(\text{CO})_6]$  and a trace of  $[\text{Co}_3(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$  (identified by IR spectroscopy). Elution with  $\text{CH}_2\text{Cl}_2$ /light petroleum (10/1) removed traces of unidentified species, and a red fraction. The latter was collected, and solvent removed in vacuo affording an oil, which was dissolved in light petroleum (ca. 5 cm<sup>3</sup>) and cooled to -78°C. After several hours, removal of the supernatant liquid with a syringe yielded red microcrystals of  $[\text{WCo}\{\mu\text{-C}_2(\text{C}_6\text{H}_4\text{Me-4})_2\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIa) (0.14 g). Continued elution of the alumina column with tetrahydrofuran/ $\text{CH}_2\text{Cl}_2$  (1/20) gave orange microcrystals of  $[\text{WCo}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IVa) (0.09 g).

(ii) In a similar experiment, Ia (0.57 g, 1.0 mmol) and IIb (0.33 g, 1.0 mmol) in light petroleum (50 cm<sup>3</sup>) gave red microcrystals of  $[\text{WCo}(\mu\text{-MeC}_2\text{C}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$  (IIIb) (0.12 g).

(iii) The complexes Ia (0.29 g, 0.51 mmol) and IIc (0.24 g, 0.50 mmol) were heated under reflux in  $\text{Et}_2\text{O}$  (50 cm<sup>3</sup>) for ca. 2 h, during which period  $[\text{W}(\text{CO})_6]$  formed (IR), and some decomposition occurred. Solvent was removed in vacuo and the residue, suspended in light petroleum (ca. 20 cm<sup>3</sup>), was added to the top of an alumina chromatography column (3 × 15 cm). Elution with light petroleum removed  $[\text{W}(\text{CO})_6]$ , and a trace of  $[\text{Co}_3(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_9]$ . Elution with  $\text{CH}_2\text{Cl}_2$ /light petroleum (1/10) removed traces of unidentified species and one orange band. The latter was collected, solvent was removed in vacuo, and the residue was dissolved in

the minimum volume (ca. 5 cm<sup>3</sup>) of light petroleum. Cooling to -78 °C for several hours, and removal of supernatant liquid with a syringe, gave orange microcrystals of [WCo{μ-C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>}(CO)<sub>5</sub>(η-C<sub>5</sub>Me<sub>5</sub>)] (IIIId) (0.08 g). Continued elution of the column with tetrahydrofuran/CH<sub>2</sub>Cl<sub>2</sub> (1/20) yielded a second orange eluate. Removal of solvent in vacuo, and crystallisation of the residue from CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/5), afforded orange microcrystals of [WCo{μ-C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4)}(CO)<sub>5</sub>(η-C<sub>5</sub>Me<sub>5</sub>)] (IVb) (0.05 g).

(iv) The compounds Ia (0.57 g, 1.0 mmol) and IId (0.32 g, 1.0 mmol) were dissolved in light petroleum (50 cm<sup>3</sup>) and the mixture was stirred for 12 h at 0 °C, IR monitoring revealed the formation of [W(CO)<sub>6</sub>]. The volume was reduced in vacuo to ca. 20 cm<sup>3</sup>, and the suspension thereby obtained was chromatographed on alumina (3 × 15 cm column). Elution with light petroleum removed [W(CO)<sub>6</sub>] and traces of [Co<sub>3</sub>(μ<sub>3</sub>-CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>9</sub>]. Further elution with CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/9) removed small amounts of several unidentified compounds. Continued elution with tetrahydrofuran/CH<sub>2</sub>Cl<sub>2</sub> (1/5) gave an orange eluate. Removal of solvent in vacuo, and crystallisation of the residue from CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/4), yielded orange microcrystals of [Mo<sub>2</sub>{μ-C(C<sub>6</sub>H<sub>4</sub>Me-4)C(O)C(C<sub>6</sub>H<sub>4</sub>Me-4)}(CO)<sub>4</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (Vb) (0.08 g).

Compound Vb was prepared more rationally by dissolving IId (0.24 g, 0.67 mmol) in Et<sub>2</sub>O (ca. 50 cm<sup>3</sup>) and irradiating the CO saturated solution in a water-cooled quartz-jacketed Schlenk tube with a UV lamp for ca. 12 h. Solvent was removed in vacuo, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and chromatographed on alumina (2 × 15 cm column). Elution with tetrahydrofuran/CH<sub>2</sub>Cl<sub>2</sub> (1/1) gave an orange eluate. Removal of solvent in vacuo, and crystallisation of the residue from CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/10), afforded orange microcrystals of Vb (0.10 g).

#### *Reaction of [W(≡CMe)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with [WCo(≡CMe)(CO)<sub>8</sub>]*

In a similar manner to the synthesis of IIIa, the compounds Ib (0.25 g, 0.50 mmol) and IIb (0.20 g, 0.49 mmol) were dissolved in light petroleum (ca. 50 cm<sup>3</sup>) and kept at ca. 4 °C (refrigerator) for 2 h, giving red microcrystals of [WCo(μ-MeC<sub>2</sub>Me)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (IIIc) (0.05 g).

#### *Triphenylphosphine reactions*

(i) Complex IIIa (0.05 g, 0.08 mmol) in light petroleum (20 cm<sup>3</sup>) was treated with PPh<sub>3</sub> (0.05 g, 0.19 mmol), and the solution was stirred at room temperature for 2 days. Solvent was removed in vacuo, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (2 cm<sup>3</sup>, 1/1) and chromatographed on alumina (1 × 15 cm column). Elution with CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/10) removed a trace of IIIa, followed by a red eluate when the CH<sub>2</sub>Cl<sub>2</sub> concentration was increased to 25%. Solvent was removed in vacuo from the red eluate, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>), and light petroleum (10 cm<sup>3</sup>) was added. Cooling to ca. -20 °C, and removal of the supernatant liquid with a syringe, yielded red microcrystals of [WCo{μ-C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>}(CO)<sub>4</sub>(PPh<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)] (VIa) (0.06 g).

(ii) In a similar experiment, IIIc (0.05 g, 1 mmol) in light petroleum (20 cm<sup>3</sup>) was treated with PPh<sub>3</sub> (0.05 g, 0.19 mmol) to give red microcrystals of [WCo(μ-MeC<sub>2</sub>Me)(CO)<sub>4</sub>(PPh<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)] (VIb) (0.07 g).

*Reactions of [WCo(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]*

(i) The compounds [WCo(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (0.10 g, 0.20 mmol) and diphenylcyclopropanone (0.06 g, 0.30 mmol) were dissolved in light petroleum (ca. 20 cm<sup>3</sup>) and heated under reflux for 2 h. The volume was reduced in vacuo to ca. 10 cm<sup>3</sup>, and the mixture was chromatographed on alumina (1 × 10 cm column). Elution with CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/10) afforded a red eluate, from which solvent was removed in vacuo. The residue was dissolved in light petroleum (5 cm<sup>3</sup>) and cooled to -78°C to give red microcrystals of [WCo( $\mu$ -PhC<sub>2</sub>Ph)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (IIIc) (0.11 g).

(ii) The compound [WCo(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (0.10 g, 0.20 mmol) in light petroleum (ca. 20 cm<sup>3</sup>) was treated with an excess of MeC≡CPh (ca. 0.2 cm<sup>3</sup>). The solution was heated under reflux for 1 h, and the volume was then reduced in vacuo to ca. 10

Table 4

Atomic positional parameters (fractional coordinates × 10<sup>4</sup>) for IVa

	x	y	z
W	3555(1)	6945(1)	6295(1)
Co	2456(1)	6082(1)	6721(1)
C(1)	5667(8)	6090(2)	6674(4)
O(1)	7212(6)	5911(1)	6726(3)
C(2)	2427(10)	6223(2)	7847(5)
O(2)	2542(9)	6313(2)	8581(4)
C(3)	3504(11)	5436(2)	7087(6)
O(3)	4284(10)	5054(2)	7343(6)
C(4)	-625(9)	5954(2)	5570(4)
O(4)	-2479(7)	5859(2)	4836(4)
C(5)	116(10)	6998(2)	5196(5)
O(5)	-1865(7)	7062(2)	4557(4)
C(6)	3105(9)	7235(2)	7319(4)
O(6)	2783(8)	7430(2)	7846(4)
C(21)	5373(12)	7077(2)	5569(7)
C(22)	3493(12)	7402(3)	5024(6)
C(23)	3936(14)	7740(2)	5831(7)
C(24)	6085(15)	7608(3)	6885(7)
C(25)	6927(11)	7197(3)	6688(6)
C(30)	3179(8)	6178(2)	5697(4)
C(31)	1876(8)	5952(2)	4561(4)
C(32)	2436(9)	5466(2)	4443(5)
C(33)	1189(10)	5244(2)	3386(5)
C(34)	-655(10)	5487(2)	2421(5)
C(35)	-1205(10)	5969(2)	2532(5)
C(36)	35(10)	6188(2)	3581(5)
C(37)	-2013(13)	5253(3)	1269(5)
C(40)	5728(8)	6344(2)	7526(4)
C(41)	7663(8)	6318(2)	8763(4)
C(42)	9358(10)	5951(2)	9205(5)
C(43)	11184(11)	5912(2)	10373(5)
C(44)	11351(9)	6230(2)	11127(4)
C(45)	9605(10)	6588(2)	10663(4)
C(46)	7820(9)	6636(2)	9509(4)
C(47)	13318(11)	6188(3)	12379(5)

cm<sup>3</sup>. Chromatography on alumina, eluting with CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/10), gave a red eluate. Solvent was removed in vacuo, and the residue was dissolved in light petroleum (ca. 5 m<sup>3</sup>) and cooled to -78°C. After removal of the supernatant liquid, red microcrystals of [WCo(μ-MeC<sub>2</sub>Ph)(CO)<sub>5</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (III<sub>f</sub>) (0.11 g) were obtained.

#### *Crystal structure determination*

Large rhombohedral orange crystals of IV<sub>a</sub> were grown from CH<sub>2</sub>Cl<sub>2</sub>/light petroleum (1/10). Diffracted intensities were recorded at 293 K from crystal of dimensions ca. 0.5 × 0.5 × 0.25 mm, cut from a larger crystal. Of the 4664 reflections ( $2\theta \leq 50^\circ$ ), measured on a Nicolet P2<sub>1</sub> diffractometer (Wyckoff ω-scans), 3443 had  $F \geq 5\sigma F$ , and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a semi-empirical method based on azimuthal scan data [32].

*Crystal data.* C<sub>27</sub>H<sub>19</sub>CoO<sub>6</sub>W,  $M = 682.3$ , monoclinic,  $a$  7.684(2),  $b$  26.470(6),  $c$  15.734(4) Å,  $\beta$  131.13(2)°,  $U$  2411(1) Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.88 g cm<sup>-3</sup>,  $F(000) = 1320$ , space group  $P2_1/c$ ,  $\mu(\text{Mo-K}\alpha)$  55.98 cm<sup>-1</sup>, Mo-K<sub>α</sub> X-radiation (graphite monochromator),  $\lambda$  0.71069 Å.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy atom and difference-Fourier methods. Aryl hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters ca. 1.2 times  $U$  (equivalent) of their parent carbon atoms. Methyl hydrogen atoms were included in calculated positions with a common isotropic thermal parameter. All remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares, with a weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.00019|F|^2]$ , converged at  $R = 0.026$  ( $R_w = 0.026$ ). The final electron-density difference synthesis showed no peaks  $\geq 0.4$  or  $\leq -0.9$  e Å<sup>-3</sup>. Scattering factors with corrections for the effects of anomalous dispersion were from ref. 33. All calculations were carried out on a Data General Eclipse computer with SHELXTL system of programs [32]. The atom coordinates are given in Table 4. Full listings of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

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