

# Octahedral Alkylidyne Complexes of Tungsten with Chelating Ligands as Precursors for Polynuclear Compounds. Crystal Structures of $[W(\equiv CR)(CO)_2(dmpe)(NCS)]$ and $[Co_2W(\mu_3-CR)(CO)_8(dmpe)Br]$ ( $R = C_6H_4Me-4$ , $dmpe = Me_2PCH_2CH_2PMe_2$ )<sup>†</sup>

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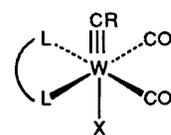
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The tungsten carbyne complexes  $[W(\equiv CR)(CO)_2(L-L)X]$  ( $R = C_6H_4Me-4$ ) where  $L-L = 2,2'$ -bipyridine (bipy), 1,2-bis(dimethylphosphino)ethane (dmpe), or 1,2-bis(diphenylphosphino)benzene (dppb), and  $X = Cl, Br$ , or  $NCS$  have been prepared and the structure of the  $N$ -bonded thiocyanate derivative  $[W(\equiv CR)(CO)_2(dmpe)(NCS)]$  determined by  $X$ -ray diffraction. The reaction of the octahedral carbynes with  $[AuCl(tht)]$  ( $tht =$  tetrahydrothiophene) gave the dimetallic species  $[AuW(\mu-CR)(CO)_2(L-L)X(Cl)]$ , which when  $X \neq Cl$  are mixtures due to an interchange of  $X$  and  $Cl$  between the  $Au$  and  $W$ . The carbynes also reacted with  $[Au(C_6F_5)(tht)]$  to give  $[AuW(\mu-CR)(CO)_2(L-L)(C_6F_5)X]$ , which for  $X = NCS$  are mixtures of two isomeric forms. The carbynes containing  $dmpe$  reacted with  $[Co_2(CO)_8]$  to give the trimetallic clusters  $[Co_2W(\mu_3-CR)(CO)_8(dmpe)X]$  ( $X = Cl$  or  $Br$ ) which in solution exist as a mixture of interconverting isomers. The  $X$ -ray crystal structure determination of the bromo derivative revealed that, in the solid, the stereochemistry of the  $W(CO)_2(dmpe)X$  fragment is different from that corresponding to the starting carbyne. The  $dmpe$  carbynes also reacted with  $[Fe_2(CO)_9]$  in toluene to afford the bimetallic compounds  $[FeW(\mu-CR)(CO)_6(dmpe)X]$  ( $X = Cl$  or  $Br$ ) having a  $Fe(CO)_4$  fragment co-ordinated to the  $W\equiv CR$  bond.

The neutral tungsten alkylidyne complexes of the general type  $[W(\equiv CR)(CO)_2L]^+$  ( $R =$  alkyl or aryl), where  $L = \eta^5-C_5H_5$ ,  $\eta^5-C_5Me_5$ , or  $HB(pz)_3$  ( $pz =$  pyrazol-1-yl), and the anionic  $[W(\equiv CR)(CO)_2(\eta^5-1,2-C_2B_9H_9Me_2)]^-$  have been extensively used as 'ligands' for the syntheses of polynuclear compounds with bonds between  $W$  and many other metals. By contrast, much less work of this sort has been done with octahedral carbynes of the general formula  $[W(\equiv CR)(CO)_nL_mX]$  where  $n + m = 4$ ,  $X =$  halogen or pseudo-halogen, and  $L_m$  are mono- and bi-dentate ligands. It has been reported that the tetracarbonyl  $[W(\equiv CR)(CO)_4Br]$  can be co-ordinated to  $PtL_2$  fragments ( $L = PMe_3$ ),<sup>3</sup> that the tricarbonyl  $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$ <sup>4</sup> has been co-ordinated to several metal-ligand fragments, and that the dicarbonyl  $[W(\equiv CR)(CO)_2(bipy)Br]$  ( $bipy = 2,2'$ -bipyridine) can be co-ordinated to  $AuCl$  and  $AuC_6F_5$  fragments.<sup>5</sup> The octahedral carbynes of the type  $[W(\equiv CR)(CO)_2(L-L)X]$ , where  $L-L$  is a chelating bidentate ligand,<sup>6</sup> may have various stereochemistries, although in the usual one the  $X$  is *trans* to the  $CR$  group and, therefore, the  $L-L$  ligand is *trans* to the two  $CO$ . Upon co-ordination of the  $W\equiv CR$  bond to a  $ML_n$  fragment, however, the changes in electron density at the metal centre and the steric effects may induce changes in the preferred stereochemistry. We, therefore, considered it of interest to study the reactivity of various carbynes of this type with several reagents that are sources of  $ML_n$  fragments. In this paper we describe the results obtained with  $[AuCl(tht)]$  ( $tht =$  tetrahydrothiophene),  $[Au(C_6F_5)(tht)]$ ,  $[Co_2(CO)_8]$ , and  $[Fe_2(CO)_9]$ .

## Results and Discussion

The tungsten carbyne complexes  $[W(\equiv CR)(CO)_2(L-L)X]$  (1)



$R = C_6H_4Me-4$

	X	L - L
(1a)	Cl	dmpe
(1b)	Br	dmpe
(1c)	NCS	dmpe
(1d)	Br	dppb
(1e)	Cl	bipy
(1f)	Br	bipy

( $R = C_6H_4Me-4$ ) were prepared by stirring a mixture of the bis(pyridine) derivatives  $[W(\equiv CR)(CO)_2(py)_2X]$  ( $X = Cl$  or  $Br$ ) and the appropriate ligand  $L-L$  in  $CH_2Cl_2$  at room temperature, as reported previously for analogous compounds.<sup>6</sup> The spectroscopic data (Table 2) were consistent with the expected stereochemistry shown, which was also confirmed by the results of an  $X$ -ray structure determination carried out on compound (1d).<sup>7</sup>

Although the chloro derivatives were accessible from the

<sup>†</sup> [1,2-Bis(dimethylphosphino)ethane- $\kappa^2 P, P'$ ]dicarbonylthiocyanato- $\kappa N$ (*p*-tolylmethylidyne)tungsten and [1,2-bis(dimethylphosphino)ethane-1 $\kappa^2 P, P'$ ]bromo-1 $\kappa Br$ -octacarbonyl-1 $\kappa^2 C, 2\kappa^3 C, 3\kappa^3 C$ - $\mu_3$ -*p*-tolylmethylidyne-dicobalt tungsten (*Co-Co, 2Co-W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix-xxii.

**Table 1.** Analytical and physical data for the compounds<sup>a</sup>

Compound	Colour	$\nu_{\max}(\text{CO})^b/\text{cm}^{-1}$	Analysis (%) <sup>c</sup>		
			C	H	N
(1a) [W(=CR)(CO) <sub>2</sub> (dmpe)Cl]	Yellow	2 002s, 1 931s	36.7 (36.3)	4.2 (4.4)	
(1b) [W(=CR)(CO) <sub>2</sub> (dmpe)Br]	Yellow	2 005s, 1 932s	33.9 (33.5)	4.0 (4.0)	
(1c) [W(=CR)(CO) <sub>2</sub> (dmpe)(NCS)]	Orange	2 005s, 1 934s <sup>d</sup>	36.9 (37.0)	4.3 (4.2)	2.3 (2.5)
(1d) [W(=CR)(CO) <sub>2</sub> (dppb)Br]	Yellow	2 009s, 1 942s	54.9 (55.3)	3.6 (3.6)	
(1e) [W(=CR)(CO) <sub>2</sub> (bipy)Cl]	Red	1 984s, 1 897s	45.0 (44.9)	2.8 (2.8)	5.1 (5.2)
(1f) [W(=CR)(CO) <sub>2</sub> (bipy)Br]	Red	1 987s, 1 899s	41.7 (41.5)	2.5 (2.4)	5.0 (5.0)
(2a) [AuW(μ-CR)(CO) <sub>2</sub> (dmpe)(C <sub>6</sub> F <sub>5</sub> )Cl]	Orange	2 024s, 1 962s	29.9 (29.6)	2.3 (2.5)	
(2b) [AuW(μ-CR)(CO) <sub>2</sub> (dmpe)(C <sub>6</sub> F <sub>5</sub> )Br]	Orange	2 025s, 1 961s	29.7 (30.1)	2.7 (2.7)	
(2c) [AuW(μ-CR)(CO) <sub>2</sub> (dmpe)(C <sub>6</sub> F <sub>5</sub> )(NCS)] <sup>e</sup>	Orange	2 030s, 1 967s <sup>f</sup>	30.3 (30.2)	2.6 (2.5)	1.6 (1.5)
(4a) [AuW(μ-CR)(CO) <sub>2</sub> (dmpe)Cl <sub>2</sub> ]	Orange	2 025s, 1 961s	25.5 (25.3)	3.0 (3.0)	
(4e) [AuW(μ-CR)(CO) <sub>2</sub> (bipy)Cl <sub>2</sub> ]	Orange	2 016s, 1 939s	31.4 (31.3)	2.1 (2.0)	3.8 (3.7)
(4i) [AuW(μ-CR)(CO) <sub>2</sub> (dmpe)(NCS)Cl]	Orange	2 029s, 1 965s <sup>g</sup>	28.5 (28.4)	3.2 (3.2)	2.3 (1.7)
(5a) [Co <sub>2</sub> W(μ <sub>3</sub> -CR)(CO) <sub>8</sub> (dmpe)Cl]	Green	2 079s, 2 044vs, 2 025vs, 1 996w, <sup>h</sup> 1 941w, 1 901m, 1 855w, 1 821m	31.5 (32.4)	2.9 (2.9)	
(5b) [Co <sub>2</sub> W(μ <sub>3</sub> -CR)(CO) <sub>8</sub> (dmpe)Br]	Brown-green	2 080s, 2 045vs, 2 025vs, 1 992w, <sup>h</sup> 1 938w, 1 903m, 1 854w, 1 821m	31.1 (30.8)	2.9 (2.7) <sup>i</sup>	
(6a) [FeW(μ-CR)(CO) <sub>6</sub> (dmpe)Cl]	Red	2 060s, 2 008(sh), 1 995vs, <sup>h</sup> 1 982s, 1 870m	34.0 (34.5)	3.6 (3.3)	
(6b) [FeW(μ-CR)(CO) <sub>6</sub> (dmpe)Br]	Red	2 060s, 2 008(sh), 1 995vs, <sup>h</sup> 1 982s, 1 870m	33.1 (32.4)	3.2 (3.1)	

<sup>a</sup> R = C<sub>6</sub>H<sub>4</sub>Me-4. <sup>b</sup> Unless otherwise stated, in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Calculated values are given in parentheses. <sup>d</sup>  $\nu(\text{CN})$  2 067 cm<sup>-1</sup>. <sup>e</sup> Mixture of isomers (2c) and (3c). <sup>f</sup> For (3c): 2 006s and 1 927s cm<sup>-1</sup>.  $\nu(\text{CN})$  for (2c) and (3c): 2 065 cm<sup>-1</sup>. <sup>g</sup>  $\nu(\text{CN})$  2 065 cm<sup>-1</sup>. <sup>h</sup> In toluene. <sup>i</sup> The sample contained some compound (5c).

**Table 2.** Proton, <sup>31</sup>P, and <sup>13</sup>C n.m.r. data<sup>a</sup> for the compounds

Compound	<sup>1</sup> H (δ)	<sup>13</sup> C (δ) <sup>b</sup>	<sup>31</sup> P (δ) <sup>c</sup>
(1a)	7.03, 6.76 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 1.94 (s, 3 H, Me-4), 1.40—0.80 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.32 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 9], 1.12 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8] <sup>d</sup>	268.0 [t, <i>J</i> (PC) 10.3, CR], 214.5 [dd, <i>J</i> (WC) 94, <i>J</i> (PC) 43 and 7, CO], 147.1 [ <i>J</i> (WC) 43, C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ], 137.4 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 128.8, 128.3 (C <sub>6</sub> H <sub>4</sub> ), 29.3 [dd, <i>J</i> (PC) 28 and 13, PCH <sub>2</sub> CH <sub>2</sub> P], 21.3 (Me-4), 18.0 [d, <i>J</i> (PC) 29, PMe <sub>2</sub> ], 11.8 [d, <i>J</i> (PC) 25, PMe <sub>2</sub> ] <sup>e</sup>	14.3 [ <i>J</i> (WP) 232] <sup>d</sup>
(1b)	7.05, 6.75 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 1.92 (s, 3 H, Me-4), 1.50—0.85 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.40 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8], 1.12 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8] <sup>d</sup>	267.1 [t, <i>J</i> (PC) 11.0, CR], 213.0 [dd, <i>J</i> (PC) 42 and 7, CO], 147.1 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 137.8 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.0, 128.7 (C <sub>6</sub> H <sub>4</sub> ), 30.1 [dd, <i>J</i> (PC) 28 and 13, PCH <sub>2</sub> CH <sub>2</sub> P], 21.7 (Me-4), 18.9 [d, <i>J</i> (PC) 28, PMe <sub>2</sub> ], 13.7 [d, <i>J</i> (PC) 26, PMe <sub>2</sub> ] <sup>e</sup>	9.01 [ <i>J</i> (WP) 231] <sup>d</sup>
(1c)	6.91, 6.72 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 1.91 (s, 3 H, Me-4), 0.88—0.85 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.22 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8], 1.01 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8] <sup>d</sup>	277.3 [t, <i>J</i> (PC) 11.0, CR], 213.0 [dd, <i>J</i> (PC) 40 and 7, CO], 147.4 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 137.8 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.1, 128.7 (C <sub>6</sub> H <sub>4</sub> ), 143.2 (SCN), 30.0 [dd, <i>J</i> (PC) 28 and 13, PCH <sub>2</sub> CH <sub>2</sub> P], 21.7 (Me-4), 18.3 [d, <i>J</i> (PC) 30, PMe <sub>2</sub> ], 13.5 [d, <i>J</i> (PC) 24, PMe <sub>2</sub> ] <sup>e</sup>	17.5 [ <i>J</i> (WP) 231] <sup>d</sup>
(1d)	7.4 (m, 24 H, C <sub>6</sub> H <sub>5</sub> ), 6.75, 6.33 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 2.16 (s, 3 H, Me-4) <sup>e</sup>	269.7 [t, <i>J</i> (PC) 9, CR], 211.0 [dd, <i>J</i> (PC) 44 and 8, CO], 146.0 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 138.3 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 143.5—127.9 (C <sub>6</sub> H <sub>4</sub> and C <sub>6</sub> H <sub>5</sub> ), 21.7 (Me-4) <sup>e</sup>	39.1 [ <i>J</i> (WP) 234] <sup>d</sup>
(1e)	9.33 (d, 2 H, H <sup>2,2'</sup> of bipy), 8.24 (d, 2 H, H <sup>5,5'</sup> of bipy), 8.07 (t, 2 H, H <sup>4,4'</sup> of bipy), 7.55 (t, 2 H, H <sup>3,3'</sup> of bipy), 7.11, 6.97 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 2.24 (s, 3 H, Me-4) <sup>e</sup>	266.6 (CR), 223.1 (CO), 155.5, 154.1, 139.8, 126.7, and 123.1 (bipy), 147.2 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 138.4 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.6, 128.5 (C <sub>6</sub> H <sub>4</sub> ), 21.4 (Me-4) <sup>e</sup>	—
(1f)	9.36 (d, 2 H, H <sup>2,2'</sup> of bipy), 8.25 (d, 2 H, H <sup>5,5'</sup> of bipy), 8.10 (t, 2 H, H <sup>4,4'</sup> of bipy), 7.60 (t, 2 H, H <sup>3,3'</sup> of bipy), 7.13, 6.97 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 2.24 (s, 3 H, Me-4) <sup>e</sup>	266.3 (CR), 222.4 (CO), 155.5, 154.3, 139.8, 126.7, and 123.1 (bipy), 146.7 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 138.5 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.5, 128.6 (C <sub>6</sub> H <sub>4</sub> ), 21.5 (Me-4) <sup>e</sup>	—
(2a) <sup>f</sup>	7.65, 6.81 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 8], 1.90 (s, 3 H, Me-4), 1.50—1.00 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.36 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 9], 1.20 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8] <sup>d</sup>	271.9 (μ-CR), 209.8 [dd, <i>J</i> (PC) 43 and 7, CO], 150.0—135.2 (m, br, C <sub>6</sub> F <sub>5</sub> ), 149.3 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 140.3 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.3, 129.1 (C <sub>6</sub> H <sub>4</sub> ), 28.1 [dd, <i>J</i> (PC) 29 and 10, PCH <sub>2</sub> CH <sub>2</sub> P], 21.3 (Me-4), 18.3 [d, <i>J</i> (PC) 30, PMe <sub>2</sub> ], 12.0 [d, <i>J</i> (PC) 29, PMe <sub>2</sub> ] <sup>d</sup>	10.9 [ <i>J</i> (WP) 211] (2a) 13.1, 8.7 (3a) <sup>d</sup>
(2b) <sup>f</sup>	7.72, 6.80 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , <i>J</i> (HH) 7], 1.86 (s, 3 H, Me-4), 1.36 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8], 1.26 [d, 6 H, PMe <sub>2</sub> , <i>J</i> (PH) 8] <sup>d</sup> , 1.23 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P)	273.5 [t, <i>J</i> (PC) 9, μ-CR], 208.3 [dd, <i>J</i> (PC) 40 and 7, CO], 151.0—135.8 (m, C <sub>6</sub> F <sub>5</sub> ), 149.5 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 141.0 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.9, 129.4 (C <sub>6</sub> H <sub>4</sub> ), 28.9 [dd, <i>J</i> (PC) 29 and 10, PCH <sub>2</sub> CH <sub>2</sub> P], 21.9 (Me-4), 19.3 [d, <i>J</i> (PC) 30, PMe <sub>2</sub> ], 14.2 [d, <i>J</i> (PC) 30, PMe <sub>2</sub> ] <sup>d</sup>	5.5 [ <i>J</i> (WP) 208] (2b) 10.6, 4.4 (3b) <sup>d</sup>

Table 2 (continued)

Compound	$^1\text{H}$ ( $\delta$ )	$^{13}\text{C}$ ( $\delta$ ) <sup>b</sup>	$^{31}\text{P}$ ( $\delta$ ) <sup>c</sup>
(2c) <sup>f</sup>	7.66, 6.85 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 8], 1.92 (s, 3 H, Me-4), 1.50–1.00 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.33 [d, 6 H, PMe <sub>2</sub> , J(PH) 9], 1.13 [d, 6 H, PMe <sub>2</sub> , J(PH) 9] <sup>d</sup>	278.7 ( $\mu$ -CR), 207.7 [dd, J(PC) 38 and 7, CO], 148.8 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 142.1 (SCN), 141.1 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.3, 129.1 (C <sub>6</sub> H <sub>4</sub> ), 28.8 [dd, J(PC) 30 and 10, PCH <sub>2</sub> CH <sub>2</sub> P], 21.9 (Me-4), 19.1 [d, J(PC) 31, PMe <sub>2</sub> ], 13.9 [d, J(PC) 27, PMe <sub>2</sub> ] <sup>e</sup>	14.6 [J(WP) 207] <sup>d</sup> (2c) 8.39 [J(WP) 132], 16.6 [J(WP) 230] (3c) <sup>g</sup>
(4a)	7.81, 6.72 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 8], 1.85 (s, 3 H, Me-4), 1.80–1.00 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.55 [d, 6 H, PMe <sub>2</sub> , J(PH) 8], 1.08 [d, 6 H, PMe <sub>2</sub> , J(PH) 9] <sup>d</sup>	269.8 ( $\mu$ -CR), 210.0 [dd, J(PC) 43 and 7, CO], 147.6, (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 140.8 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 129.8, 129.4 (C <sub>6</sub> H <sub>4</sub> ), 28.4 [dd, J(PC) 29 and 10, PCH <sub>2</sub> CH <sub>2</sub> P], 21.3 (Me-4), 20.2 [d, J(PC) 30, PMe <sub>2</sub> ], 11.3 [d, J(PC) 32, PMe <sub>2</sub> ] <sup>d</sup>	9.44 [J(WP) 196] <sup>d</sup>
(4e)	9.13 (d, 2 H, H <sup>2,2'</sup> of bipy), 8.33 (d, 2 H, H <sup>5,5'</sup> of bipy), 8.20 (t, 2 H, H <sup>4,4'</sup> of bipy), 7.62 (t, 2 H, H <sup>3,3'</sup> of bipy), 7.60, 7.16 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 8], 2.37 (s, 3 H, Me-4) <sup>e</sup>	261.6 ( $\mu$ -CR), 215.9 (CO), 155.0, 154.3, 141.1, 127.4, 123.9 (bipy), 147.3 (C <sup>1</sup> of C <sub>6</sub> H <sub>4</sub> ), 141.2 (C <sup>4</sup> of C <sub>6</sub> H <sub>4</sub> ), 130.1, 129.3 (C <sub>6</sub> H <sub>4</sub> ), 21.5 (Me-4) <sup>e</sup>	—
(4i)	7.68, 6.71 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 8], 1.85 (s, 3 H, Me-4), 1.60–1.00 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.41 [d, 6 H, PMe <sub>2</sub> , J(PH) 8], 1.00 [d, 6 H, PMe <sub>2</sub> , J(PH) 9] <sup>e</sup>	<i>h</i>	13.4 [J(WP) 196] <sup>d</sup>
(5a)	7.70, 6.91 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 7], 2.12 (s, 3 H, Me-4), 1.05 [d, 12 H, PMe <sub>2</sub> , J(PH) 8], 1.04–0.65 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P) <sup>d</sup>	224.0 ( $\mu$ -CR), 199.4 (m, CO), 160.9–128.1 (C <sub>6</sub> H <sub>4</sub> ), 31.1–25.0 (m, PCH <sub>2</sub> CH <sub>2</sub> P), 21.0 (Me-4), 15.6–11.6 (m, PMe <sub>2</sub> ) <sup>d,i</sup>	12.0 [d, J(PP) 10, J(WP) 91], 8.35 (d, J(PP) 10, J(WP) 214) <sup>j,k</sup>
(5b)	7.71, 6.91 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 7], 2.11 (s, 3 H, Me-4), 1.08 [d, 12 H, PMe <sub>2</sub> , J(PH) 7], 1.05–0.70 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P) <sup>d</sup>	<i>i</i>	5.8 [d, J(PP) 9, J(WP) 88], 2.92 [d, J(PP) 9, J(WP) 217] <sup>j,l</sup>
(6b)	7.48, 7.08 [(AB) <sub>2</sub> , 4 H, C <sub>6</sub> H <sub>4</sub> , J(HH) 8], 2.20 (s, 3 H, Me-4), 1.58 [d, 6 H, PMe <sub>2</sub> , J(PH) 8], 1.52–0.80 (m, 4 H, PCH <sub>2</sub> CH <sub>2</sub> P), 1.15 [d, 6 H, PMe <sub>2</sub> , J(PH) 9] <sup>j</sup>	296.3, 296.1 [m, $\mu$ -CR), 220.6, 220.2 [m, W(CO) <sub>2</sub> ], 216.2, 212.1, 209.8, 209.3 [Fe(CO) <sub>4</sub> ], 163.4, 128.9 (C <sub>6</sub> H <sub>4</sub> ), 28.6, 28.1, 26.6, 26.1 (m, PCH <sub>2</sub> CH <sub>2</sub> P), 21.5 (Me-4), 13.8, 10.1 (m, PMe <sub>2</sub> ) <sup>j</sup>	17.6 [d, J(PP) 11, J(WP) 232], 5.14 [d, J(PP) 11, J(WP) 113] <sup>d,m</sup>

<sup>a</sup> Chemical shifts ( $\delta$ ) in p.p.m., coupling constants in Hz. <sup>b</sup> Hydrogen-1 decoupled,  $\delta$  positive to high frequency of SiMe<sub>4</sub>. <sup>c</sup> Hydrogen-1 decoupled,  $\delta$  positive to high frequency of external 85% H<sub>3</sub>PO<sub>4</sub>. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>e</sup> In CDCl<sub>3</sub>. <sup>f</sup> <sup>19</sup>F N.m.r.: -116, -159, and -163 p.p.m., with reference to internal CFCl<sub>3</sub>. <sup>g</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup> Due to low solubility and instability in solution, no good spectra were obtained. <sup>i</sup> Very broad signals. <sup>j</sup> In [2H<sub>6</sub>] toluene at -50 °C. <sup>k</sup> Other isomer: 17.3 and 5.06; at room temperature (r.t.) ca. 10 (vbr) p.p.m. <sup>l</sup> Other isomer: 12.2 and -0.57; at r.t. ca. 3.0 (vbr) p.p.m. <sup>m</sup> For (6a): 22.7 [d, J(PP) 12, J(WP) 232] and 8.64 p.p.m. [d, J(PP) 12, J(WP) 115 Hz].

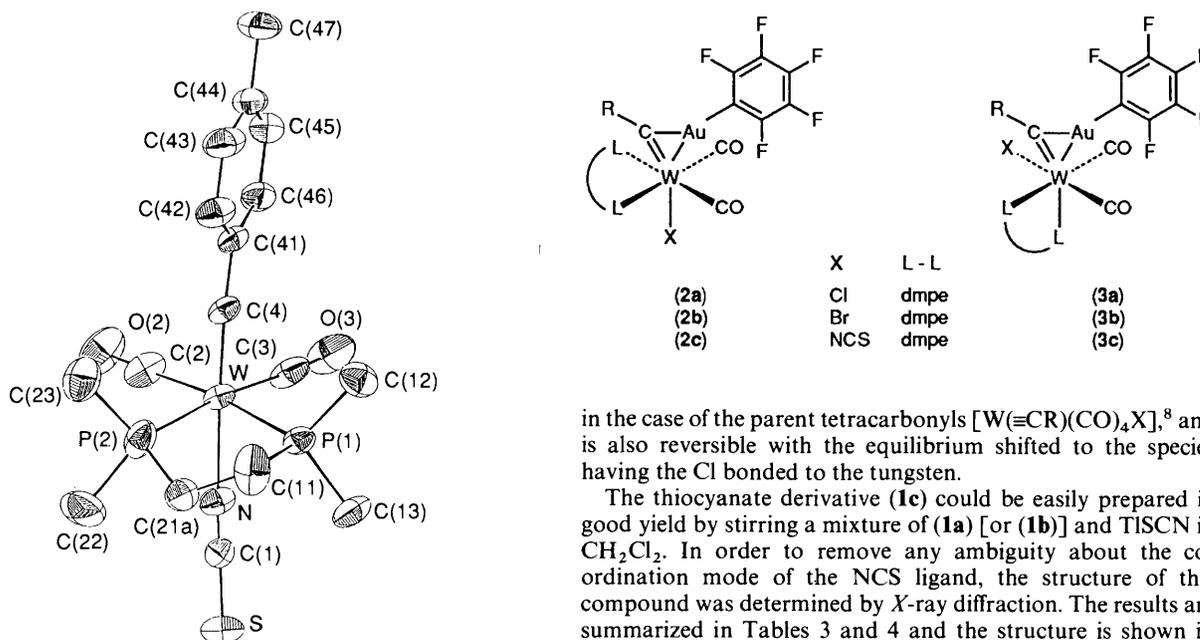


Figure 1. A view of the molecular structure of the compound [W(≡CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>(dmpe)(NCS)] (1c)

chlorobis(pyridine) complex, they could also be prepared by treating the bromo analogues with an excess of AsPh<sub>4</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub>. This halogen exchange is analogous to that observed

in the case of the parent tetracarbonyls [W(≡CR)(CO)<sub>4</sub>X],<sup>8</sup> and is also reversible with the equilibrium shifted to the species having the Cl bonded to the tungsten.

The thiocyanate derivative (1c) could be easily prepared in good yield by stirring a mixture of (1a) [or (1b)] and TlSCN in CH<sub>2</sub>Cl<sub>2</sub>. In order to remove any ambiguity about the co-ordination mode of the NCS ligand, the structure of this compound was determined by X-ray diffraction. The results are summarized in Tables 3 and 4 and the structure is shown in Figure 1.

In complex (1c) the tungsten is in a slightly distorted octahedral co-ordination with the two *cis*-carbonyl ligands and the chelating 1,2-bis(dimethylphosphino)ethane (dmpe), in the equatorial positions, while the NCS and the carbyne ligands are in the apical positions. The angles S–C–N [177.7(6)°] and W–N–C [174.1(5)°] showed that the thiocyanate group is

**Table 3.** Atomic co-ordinates for the compound  $[W(\equiv CC_6H_4Me-4)-(CO)_2(dmpe)(NCS)]$  (**1c**)

Atom	X/a	Y/b	Z/c
W	-0.024 20(3)	0.255 52(3)	0.256 41(2)
S	-0.375 3(3)	0.262 0(2)	0.557 1(1)
P(1)	0.214 3(2)	0.228 1(2)	0.364 6(1)
P(2)	0.006 9(3)	0.503 0(2)	0.256 0(2)
O(2)	-0.323 6(8)	0.338 2(8)	0.120 7(5)
O(3)	-0.042(1)	-0.065 1(6)	0.276 9(4)
N	-0.191 6(7)	0.258 1(6)	0.387 8(4)
C(1)	-0.262 5(8)	0.260 5(6)	0.456 2(4)
C(2)	-0.218(1)	0.307 2(9)	0.173 2(5)
C(3)	-0.041(1)	0.051 1(8)	0.273 5(4)
C(4)	0.111 7(8)	0.240 9(6)	0.149 3(4)
C(11)	0.274(1)	0.399 1(8)	0.369 4(7)
C(12)	0.411 7(9)	0.141 5(9)	0.327 8(6)
C(13)	0.182(1)	0.145 4(9)	0.489 4(5)
C(21a)	0.129(2)	0.511(1)	0.359(1)
C(21b)	0.228(1)	0.508(1)	0.286 4(9)
C(22)	-0.160(2)	0.599(1)	0.308 9(8)
C(23)	0.059(1)	0.618 3(9)	0.144 1(7)
C(41)	0.209 0(8)	0.213 5(7)	0.066 2(4)
C(42)	0.333 4(9)	0.298 9(9)	0.019 8(5)
C(43)	0.427(1)	0.269(1)	-0.059 7(6)
C(44)	0.399(1)	0.157(1)	-0.096 1(5)
C(45)	0.278(1)	0.073 6(9)	-0.050 2(6)
C(46)	0.183(1)	0.099 8(8)	0.029 7(5)
C(47)	0.504(1)	0.124(1)	-0.183 0(6)

**Table 4.** Selected bond lengths (Å) and angles (°) for  $[W(\equiv CC_6H_4Me-4)-(CO)_2(dmpe)(NCS)]$  (**1c**)

W-C(4)	1.827(6)	W-N	2.218(5)
W-C(2)	1.994(8)	W-C(3)	2.003(8)
W-P(1)	2.515(2)	W-P(2)	2.491(2)
S-C(1)	1.640(7)	C(1)-N	1.094(7)
C(2)-O(2)	1.150(8)	C(3)-O(3)	1.145(8)
P(2)-C(21a)	1.860(10)	P(1)-C(11)	1.826(7)
P(2)-C(21b)	1.860(9)	P(2)-C(23)	1.796(9)
C(21b)-C(21a)	1.250(2)		
N-W-C(4)	176.1(2)	C(2)-W-C(4)	88.0(3)
C(2)-W-N	92.1(3)	C(3)-W-C(4)	85.5(3)
C(3)-W-N	90.6(3)	C(3)-W-C(2)	93.9(3)
P(1)-W-C(4)	95.2(2)	P(1)-W-N	85.3(1)
P(1)-W-C(2)	171.2(2)	P(1)-W-C(3)	94.5(2)
P(2)-W-C(4)	98.7(2)	P(2)-W-N	85.2(2)
P(2)-W-C(2)	92.0(2)	P(2)-W-C(3)	172.9(2)
P(2)-W-P(1)	79.5(6)	N-C(1)-S	177.7(6)
C(41)-C(4)-W	172.9(5)	C(1)-N-W	174.1(5)
O(2)-C(2)-W	176.0(7)	O(3)-C(3)-W	174.7(7)

essentially linear with N-C [1.094(7) Å] and C-S [1.640(7) Å] distances within the range observed for typical terminal NCS ligands.<sup>9</sup> These bond lengths suggest the presence of an N≡C triple bond and a C-S single bond. The tungsten-carbon separation is consistent with a formal W≡C triple bond.<sup>10</sup>

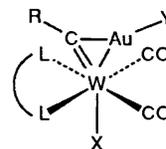
The dmpe-containing carbynes (**1a**)–(**1c**) reacted with

$[Au(C_6F_5)(tht)]$  to give the bimetallic species  $[AuW(\mu-CR)-(CO)_2(dmpe)(C_6F_5)X]$ , having  $Au(C_6F_5)$  fragments co-ordinated to the W=C bond, which are analogous to the previously reported compound  $[AuW(\mu-CR)(CO)_2(bipy)(C_6F_5)Br]$ , the structure of which was determined in the solid state by X-ray diffraction.<sup>5</sup> The spectroscopic data for those products (Table 2) indicated that, in solution, they exist as mixtures of the two isomeric forms (**2**) and (**3**).\* For X = Cl and Br, (**2**) is by far the most abundant, but for X = NCS the proportion of (**3**) is higher and depends on the solvent (*ca.* 20% in benzene, 27% in chloroform, and 50% in dichloromethane).

Monitoring the reaction between (**1c**) and  $[Au(C_6F_5)(tht)]$  by i.r. spectroscopy indicated that the isomer (**2c**) was formed first and that it subsequently isomerized giving the other form (**3c**). By slow crystallization, the single product (**3c**) could be obtained as red microcrystals which regenerated the isomeric mixture when redissolved.

The structure of compound (**2**) was proposed by analogy with that of the previously reported bipy derivative,<sup>5</sup> and is in accord with the spectroscopic data in Tables 1 and 2. The structure for the isomeric form (**3**) was proposed on the basis of the two signals in the <sup>31</sup>P n.m.r. spectra showing that the two phosphorus atoms are not equivalent. In the case of X = Cl or Br, the signals of compound (**3**) were very weak compared with that of (**2**), but for X = NCS, they were of sufficient intensity to show the <sup>183</sup>W satellites. One of the *J*(WP) coupling constants was *ca.* 207 Hz, while the other was about 130 Hz, indicating that only one of the phosphorus atoms is 'trans' (see footnote \*) to a CO.<sup>11,†</sup> Unfortunately, however, the <sup>13</sup>C n.m.r. spectra showed very weak signals for the CO and  $\mu$ -CR groups corresponding to (**3**), even in the case of the NCS derivative in dichloromethane, where this form is more abundant. On the other hand, the two  $\nu$ (CO) stretching frequencies corresponding to form (**3**), which were clearly observed in the i.r. spectrum of the NCS derivative (but not in the other cases because of the low relative concentration of this form), were very close to those of the unco-ordinated carbyne thiocyanate complex (**1c**). In spite of this fact, the possibility of a structure having the  $Au(C_6F_5)$  bonded to the S atom of the NCS ligand seems less likely taking into account that the  $\nu$ (CN) stretching frequency (2 067 cm<sup>-1</sup>) is very close to that of (**1c**), and is low for a complex having an M-SCN-M' group.<sup>12</sup>

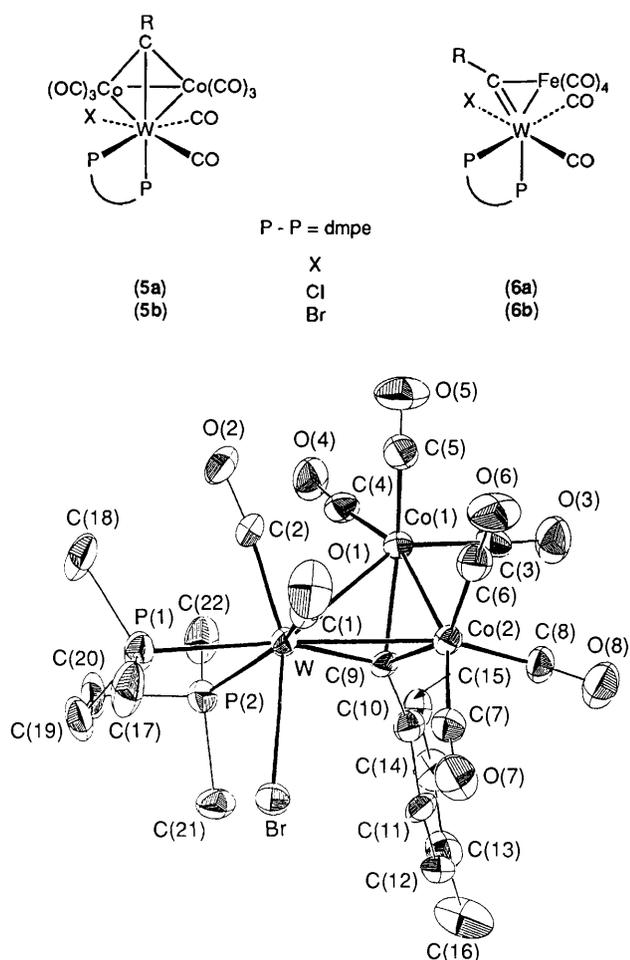
Similarly to the  $[W(\equiv CR)(CO)_2(bipy)Br]$  complex,<sup>5</sup> all the carbynes (**1**) reacted with  $[AuCl(tht)]$  to give bimetallic compounds (**4**) with a W-Au bond and a  $\mu$ -CR ligand. However, while the bipyridine-containing chloro-complex (**1e**) gave only the bimetallic species (**4e**), the reaction between the bromo analogue (**1f**) with  $[AuCl(tht)]$  gave a mixture of products that contained (**4e**)–(**4h**) (the data were insufficient to determine the proportions, which seemed to depend on the reaction time). This mixture, originally believed<sup>5</sup> to be the single product (**4f**), displayed a complex 300-MHz <sup>1</sup>H n.m.r. spectrum and reacted



	X	Y	L-L
(4a)	Cl	Cl	dmpe
(4b)	Br	Cl	dmpe
(4c)	Cl	Br	dmpe
(4d)	Br	Br	dmpe
(4e)	Cl	Cl	bipy
(4f)	Br	Cl	bipy
(4g)	Cl	Br	bipy
(4h)	Br	Br	bipy
(4i)	NCS	Cl	dmpe

\* It should be noted that the compounds cannot strictly be considered as octahedral. Therefore the structures shown should be taken only as approximate simplified descriptions (see ref. 5).

† There is another possibility with one P atom *trans* to a CO, the other P *trans* to X, and one CO *trans* to the  $\mu$ -CRAu(C<sub>6</sub>F<sub>5</sub>) group. However, although this structure cannot be ruled out, the X-ray structure determination on compound (**5b**) (see Figure 2) suggested the stereochemistry shown to be the more probable.



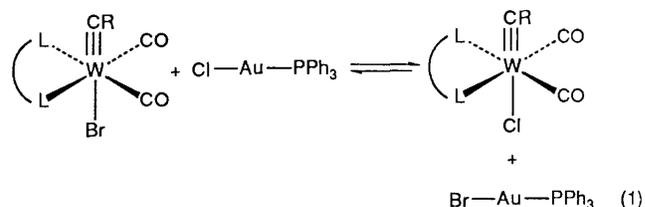
**Figure 2.** A view of the molecular structure of the compound  $[\text{Co}_2\text{W}(\mu_3\text{-C}_6\text{H}_4\text{Me-4})(\text{CO})_8(\text{dmpe})\text{Br}]$  (**5b**)

with  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$  [and in tetrahydrofuran (thf)] to give the two carbynes (**1e**) + (**1f**) together with  $[\text{AuCl}(\text{PPh}_3)]$  and  $[\text{AuBr}(\text{PPh}_3)]$ . It should be noted however that, as discussed later [equation (1)], the carbynebromo complexes can react with  $[\text{AuCl}(\text{PPh}_3)]$  to give the chloro derivatives and  $[\text{AuBr}(\text{PPh}_3)]$ . Therefore the single compound (**4f**) would have reacted with  $\text{PPh}_3$  to give (**1b**) and  $[\text{AuCl}(\text{PPh}_3)]$  in a first step, but subsequently (**1a**) and  $[\text{AuBr}(\text{PPh}_3)]$  would also have been formed.

The reaction of the bromo derivative having dmpe (**1b**) with  $[\text{AuCl}(\text{tht})]$  also gave a mixture of products (**4a**)—(**4d**), as revealed by  $^{31}\text{P}$  n.m.r. spectroscopy {in  $\text{C}_6\text{D}_6$ : (**4b**),  $\delta$  4.4 [ $J(\text{PW})$  194]; (**4c**), 9.3 [ $J(\text{PW})$  196]; and (**4d**), 4.5 [ $J(\text{PW})$  196 Hz]}. However, after some time in solution only (**4c**) and (**4b**) could be detected, and the formation of (**1a**) + (**1b**) revealed decomposition. The single compound (**4a**) was prepared in good yield from (**1a**) and  $[\text{AuCl}(\text{tht})]$ .

It is, therefore, evident that in the reaction of the carbynes  $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{L}-\text{L})\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with  $[\text{AuCl}(\text{tht})]$  there is an interchange of the halogens between the tungsten and gold centres. Although this interchange may occur intramolecularly after the formation of the bimetallic carbyne-bridged species

with the  $\text{AuCl}$  fragment, it seems more likely that it takes place before these have been formed. Thus, we observed that the bromocarbynes (**1b**) and (**1f**) reacted with  $[\text{AuCl}(\text{PPh}_3)]$  to generate the equilibrium shown in equation (1) ( $\text{L} = \text{PPh}_3$ )



[which probably proceeds *via* an associative exchange involving  $\text{Au}(\mu\text{-X},\mu\text{-Y})\text{W}$  intermediates], and that this equilibrium is shifted to the species having the Cl bonded to the tungsten atom. Therefore, a similar Br/Cl exchange can occur quickly between the carbynebromo complexes and  $[\text{AuCl}(\text{tht})]$  before the bimetallic species (**4**) are formed. This could account for the mixtures (**4**) having higher proportions of the ClW derivatives.

By contrast, the thiocyanate derivative (**1c**) reacted with  $[\text{AuCl}(\text{tht})]$  to give only (**4i**). Although, after several hours in solution, it decomposed and some (**4a**) could be detected, we found no evidence for an interchange of Cl for NCS. However, similarly to the  $\text{AuC}_6\text{F}_5$  derivative mentioned above, the i.r. and the n.m.r. spectra showed that (**4i**) is a mixture of the isomeric forms analogous to the  $\text{Au}(\text{C}_6\text{F}_5)$  derivatives, (**2**) and (**3**), although in solution the form (**4**) is much more abundant.

Similarly to other alkylidyne,<sup>13</sup> the complexes (**1a**) and (**1b**) reacted readily with  $[\text{Co}_2(\text{CO})_8]$  in toluene at room temperature to give the deep green to brown trimetallic clusters of formulae  $[\text{Co}_2\text{W}(\mu_3\text{-CR})(\text{CO})_8(\text{dmpe})\text{X}]$  (**5**) ( $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ ). This type of reaction was not observed in the case of the octahedral alkylidyne (**1**) having bidentate ligands other than dmpe, but this was probably due to the low solubility of those complexes in the non-polar solvents needed to prevent the decomposition of  $[\text{Co}_2(\text{CO})_8]$ .

In the case of  $\text{X} = \text{Br}$  the compound decomposes slowly in solution at room temperature with formation of (**1b**). On the other hand, when the solutions of (**5b**) are evaporated *in vacuo* a very unstable new product is formed. Although only limited spectroscopic data were available,\* it seems highly probable that this product is  $[\text{Co}_2\text{W}(\mu_3\text{-CR})(\mu\text{-Br})(\text{CO})_7(\text{dmpe})]$  (**5c**), formed by an intramolecular CO substitution by the terminal bromo ligand in (**5b**). A very similar observation has been made in the case of the compound  $[\text{NET}_4][\text{Co}_2\text{W}(\mu_3\text{-CR})(\text{CO})_8(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ .<sup>13b</sup> By cooling a concentrated solution of (**5b**) in toluene, some crystals of sufficient quality for a crystal-structure determination were obtained. The results are summarized in Tables 5 and 6, and the structure is shown in Figure 2.

The molecule consists of a  $\text{Co}_2\text{W}$  triangle, capped by a triply bridging tolylmethylidyne ligand. Each cobalt carries three terminal carbonyl ligands and the tungsten two, one bromine atom, and the two phosphorus atoms of the chelating dmpe. The stereochemistry of the  $\text{W}(\text{CO})_2(\text{dmpe})$  fragment in (**5b**) clearly indicated that, upon co-ordination to the  $\text{Co}_2(\text{CO})_6$  group, there has been a change in the structure of the carbyne complex (the Br, originally *trans* to CR, is now *cis*). This change is reminiscent of that observed when the manganese alkynyl complex *cis*- $[\text{Mn}(\text{CCPh})(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_4\text{Me}_2)_3\}]$  was treated with  $[\text{Co}_2(\text{CO})_8]$  to produce the corresponding tetrahedrane.<sup>14</sup>

However, the  $^{31}\text{P}$  n.m.r. spectrum of compound (**5b**) [and also of (**5a**)] in toluene solution was temperature dependent. At room temperature it consisted of a very broad signal which on cooling gave two well resolved doublets (AX system), one with  $J(\text{WP}) = 217$  Hz and the other with  $J(\text{WP}) = 88$  Hz, as

\* I.r. (toluene):  $\nu(\text{CO})$  2 065, 2 045, 2 013, 2 002, 1 905, and 1 847  $\text{cm}^{-1}$  [some hidden by the bands of (**5b**)]. N.m.r. ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ ,  $\delta$  7.9, 7.0 [(AB)<sub>2</sub>, 4 H,  $\text{C}_6\text{H}_4$ ,  $J(\text{HH})$  8], 1.94 (s, 3 H, Me-4), and 1.4–0.8 (m, dmpe);  $^{31}\text{P}$ ,  $\delta$  14.5 [d,  $J(\text{PP})$  8,  $J(\text{PW})$  199], and 7.5 [d,  $J(\text{PP})$  8,  $J(\text{PW})$  234 Hz].

**Table 5.** Atomic co-ordinates for the compound  $[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{-Me-4})(\text{CO})_8(\text{dmpe})\text{Br}]$  (**5b**)

Atom	X/a	Y/b	Z/c
W	0.052 43(3)	0.169 21(2)	0.074 48(2)
Br	0.237 68(9)	0.181 86(7)	0.047 88(6)
Co(1)	-0.058 7(1)	0.171 09(8)	0.178 47(6)
Co(2)	0.097 2(1)	0.116 03(7)	0.185 21(7)
P(1)	0.054 3(3)	0.161 9(2)	-0.043 8(1)
P(2)	0.044 9(2)	0.284 6(1)	0.040 7(1)
O(1)	0.074(1)	0.022 7(4)	0.053 3(5)
O(2)	-0.162 5(7)	0.150 0(6)	0.043 1(4)
O(3)	-0.063 6(7)	0.196 1(6)	0.310 1(4)
O(4)	-0.203 9(7)	0.265 5(5)	0.150 4(4)
O(5)	-0.179 7(8)	0.056 1(5)	0.164 2(7)
O(6)	0.016 5(8)	-0.011 5(5)	0.197 9(6)
O(7)	0.292 8(8)	0.073 7(6)	0.159 0(5)
O(8)	0.149 0(7)	0.150 0(6)	0.311 3(5)
C(1)	0.066(1)	0.076 7(7)	0.065 6(6)
C(2)	-0.083 6(8)	0.157 3(6)	0.059 4(5)
C(3)	-0.060 5(8)	0.184 3(6)	0.259 2(6)
C(4)	-0.145 3(8)	0.230 8(6)	0.159 6(6)
C(5)	-0.132 7(9)	0.100 7(8)	0.169 8(7)
C(6)	0.049(1)	0.036 9(7)	0.191 3(7)
C(7)	0.216 4(9)	0.092 5(6)	0.166 0(6)
C(8)	0.125 5(9)	0.137 1(7)	0.262 4(5)
C(9)	0.069 4(6)	0.203 4(5)	0.161 7(5)
C(10)	0.116 7(8)	0.258 9(5)	0.190 8(5)
C(11)	0.215 5(8)	0.264 4(5)	0.190 9(5)
C(12)	0.263 6(8)	0.316 4(6)	0.212 4(5)
C(13)	0.212(1)	0.366 0(6)	0.236 4(6)
C(14)	0.113(1)	0.362 1(6)	0.238 1(6)
C(15)	0.067 5(9)	0.309 1(5)	0.216 5(5)
C(16)	0.264(1)	0.424 3(8)	0.261 8(8)
C(17)	0.133(1)	0.104(1)	-0.077 4(6)
C(18)	-0.060(1)	0.145 0(9)	-0.081 5(6)
C(19)	0.087(1)	0.237 6(8)	-0.075 1(6)
C(20)	0.029(1)	0.289 2(8)	-0.043 2(6)
C(21)	0.148 6(9)	0.335 3(6)	0.053 5(7)
C(22)	-0.054(1)	0.334 3(7)	0.064 5(6)

**Table 6.** Selected bond lengths (Å) and angles (°) for  $[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_8(\text{dmpe})\text{Br}]$  (**5b**)

W-Co(2)	2.738(2)	W-Co(1)	2.749(1)
W-Br	2.666(1)	W-C(9)	2.05(1)
W-P(1)	2.585(3)	W-P(2)	2.558(3)
W-C(1)	1.98(1)	W-C(2)	1.94(1)
Co(1)-Co(2)	2.475(2)	Co(2)-C(6)	1.810(1)
Co(2)-C(9)	1.96(1)	Co(1)-C(9)	1.952(9)
O(1)-C(1)	1.18(2)	C(9)-C(10)	1.49(1)
Co(1)-W-Co(2)	53.63(4)	P(2)-W-P(1)	76.7(1)
P(1)-W-Br	77.22(9)	P(2)-W-Br	83.17(8)
P(1)-W-Co(2)	148.62(9)	P(2)-W-Co(2)	131.14(8)
P(1)-W-Co(1)	146.12(9)	P(2)-W-Co(1)	101.58(8)
C(1)-W-Br	89.0(4)	C(1)-W-Co(2)	69.9(4)
C(1)-W-P(1)	80.9(4)	C(2)-W-P(1)	80.4(4)
C(1)-W-P(2)	157.4(4)	C(2)-W-C(1)	87.2(6)
C(9)-W-Br	93.1(3)	C(9)-W-Co(2)	45.6(3)
C(9)-W-P(1)	161.1(3)	C(9)-W-P(2)	86.2(3)
O(1)-C(1)-W	172.5(12)	O(2)-C(2)-W	172.1(11)
O(3)-C(3)-Co(1)	176.2(13)		

expected for the structure observed in the solid state (Figure 2). [A very small amount of another isomer is also clearly evident in the low-temperature spectra of (**5**) (Table 2).] These data, and the number of  $\nu(\text{CO})$  stretching frequencies (Table 1), suggested that in solution there may be a mixture of interconverting isomers. On the other hand, it is also possible that the  $\text{W}(\text{CO})_2(\text{dmpe})\text{X}$  fragment is rotating relative to the  $\text{Co}_2\text{CR}$

triangle, because the coexistence of rotamers in solution has already been noted in the case of  $\text{WCo}_2(\mu_3\text{-CR})$  clusters.<sup>15</sup>

As observed with other tungsten alkylidyne complexes,<sup>16</sup> the octahedral carbynes (**1a**) and (**1b**) [but not the other derivatives (**1**)] reacted also with  $[\text{Fe}_2(\text{CO})_9]$  to give the bimetallic species  $[\text{FeW}(\mu\text{-CR})(\text{CO})_6(\text{dmpe})\text{X}]$  (**6**) ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). The structure proposed is consistent with the analytical and spectroscopic data (Tables 1 and 2). Significantly, the  $^{13}\text{C}$  n.m.r. signal for the  $\mu\text{-CR}$  group appeared *ca.* 30 p.p.m. to higher frequency than that of (**1b**), and the  $^{31}\text{P}$  n.m.r. spectra were similar to those of (**3**), and the low-temperature spectra of (**5**) (as noted above, however, with these data it is not possible to rule out other geometries).

Previously it has been shown<sup>16</sup> that the results of the reactions of the carbynes  $[\text{W}(\equiv\text{CR})(\text{CO})_2\text{L}]$  ( $\text{L} =$  various polyhaptoligands) with  $[\text{Fe}_2(\text{CO})_9]$  are very dependent on the natures of  $\text{L}$  and  $\text{R}$ , and may lead, among others, to binuclear species  $[\text{FeW}(\mu_2\text{-CR})(\text{CO})_6\text{L}]$ , analogous to (**6**), or to the 32-electron unsaturated species  $[\text{FeW}(\mu\text{-CR})(\text{CO})_5\text{L}]$ , having the fragment  $\text{Fe}(\text{CO})_3$  co-ordinated to the  $\text{W}\equiv\text{CR}$  bond. The compounds (**6**) are very unstable, decomposing above  $-10^\circ\text{C}$  even in the solid state. In solution the decomposition is accompanied by the formation of (**1a**) or (**1b**), instead of the isomeric form that is co-ordinated to the  $\text{Fe}(\text{CO})_4$  fragment in the bimetallic species. It is therefore apparent that this stereochemistry for the octahedral tungsten carbynes is thermodynamically and kinetically unstable with respect to structure (**1**). Therefore, the fact that in compounds (**3**), (**5**), and (**6**) the fragment  $\text{W}(\text{CO})_2(\text{dmpe})\text{X}$  adopts a different stereochemistry to that in the free carbynes (**1a**) and (**1b**) is due to a co-ordinatively induced isomerization, which probably occurs for steric reasons.

## Experimental

All reactions were carried out under dry nitrogen. Solvents were purified and distilled prior to use. I.r. spectra were recorded using a Perkin-Elmer 1720X-FT spectrometer, n.m.r. spectra on a Bruker AC-300 instrument. The compounds  $[\text{AuCl}(\text{tht})]$ ,<sup>17</sup>  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ ,<sup>17</sup>  $\text{dmpe}$ ,<sup>18</sup> and the carbynes  $[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{py})_2\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ )<sup>6</sup> were synthesized by the methods reported in the literature.

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dmpe})\text{Br}]$  (**1b**).—The ligand  $\text{dmpe}$  ( $0.27\text{ cm}^3$ ,  $1.62\text{ mmol}$ ) was added to a well stirred solution of  $[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{py})_2\text{Br}]$  ( $0.9\text{ g}$ ,  $1.56\text{ mmol}$ ) in  $\text{CH}_2\text{Cl}_2$  ( $30\text{ cm}^3$ ). Stirring was continued at room temperature for 3 h and the solvent was removed *in vacuo*. The resultant yellow oil was washed with light petroleum (b.p.  $40\text{--}60^\circ\text{C}$ ) ( $2 \times 50\text{ cm}^3$ ) and the residue extracted with diethyl ether ( $4 \times 30\text{ cm}^3$ ). The extracts were filtered through Celite and concentrated to give bright yellow microcrystals of compound (**1b**) ( $0.6\text{ g}$ ,  $68\%$ ). An excess of  $\text{dmpe}$  and more prolonged reaction times led to the formation of a new unidentified cationic dicarbonyl still uncharacterized, which can easily be separated from (**1b**).

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dmpe})\text{Cl}]$  (**1a**).—Solid  $\text{AsPh}_4\text{Cl}$  ( $0.24\text{ g}$ ,  $0.53\text{ mmol}$ ) was added to a solution of compound (**1b**) ( $0.15\text{ g}$ ,  $0.26\text{ mmol}$ ) in  $\text{CH}_2\text{Cl}_2$  ( $15\text{ cm}^3$ ) and the mixture stirred for 10 h. The solvent was removed *in vacuo* and the solid extracted with diethyl ether ( $4 \times 10\text{ cm}^3$ ). The extracts were filtered and concentrated to give bright yellow microcrystals of compound (**1a**) ( $0.12\text{ g}$ ,  $88\%$ ). The product should be checked, by  $^{31}\text{P}$  n.m.r. spectroscopy, because occasionally it may contain (**1b**). In this case the conversion can be completed by treating the product with more  $\text{AsPh}_4\text{Cl}$ .

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dmpe})(\text{NCS})]$  (**1c**).—Solid TISCN

(0.2 g, 0.78 mmol) was added to a solution of compound (**1b**) (0.3 g, 0.52 mmol) in  $\text{CH}_2\text{Cl}_2$  (15  $\text{cm}^3$ ), and the mixture was stirred for 48 h at room temperature. The solvent was removed *in vacuo* and the residue extracted with diethyl ether (3  $\times$  10  $\text{cm}^3$ ). After filtration through Celite the solution was concentrated *in vacuo* to give orange microcrystals of (**1c**) (0.28 g, 98%).

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dppb})\text{Br}]$  (**1d**).—The ligand 1,2-bis-(diphenylphosphino)benzene (dppb) (0.08 g, 0.18 mmol) was added to a solution of  $[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{py})_2\text{Br}]$  (0.1 g, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). After 3.5 h the solution was filtered and concentrated *in vacuo* to ca. 4  $\text{cm}^3$ . Addition of light petroleum gave yellow microcrystals of compound (**1d**) (0.11 g, 84%).

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{bipy})\text{Br}]$  (**1f**).—To a stirred solution of  $[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{py})_2\text{Br}]$  (0.75 g, 1.28 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ), solid 2,2'-bipyridine (0.23 g, 1.47 mmol) was added. After stirring for 7 h the solvent was removed *in vacuo*, the residue was washed with light petroleum (3  $\times$  25  $\text{cm}^3$ ), and extracted with thf (3  $\times$  25  $\text{cm}^3$ ). The solution was filtered and concentrated *in vacuo* to give a red solid that was recrystallized from  $\text{CH}_2\text{Cl}_2$ -light petroleum to give red microcrystals of compound (**1f**) (0.54 g, 73%).

$[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{bipy})\text{Cl}]$  (**1e**).—Solid  $\text{AsPh}_4\text{Cl}$  (0.21 g, 0.5 mmol) was added to a solution of compound (**1f**) (0.13 g, 0.22 mmol) in  $\text{CH}_2\text{Cl}_2$  (15  $\text{cm}^3$ ), and the mixture stirred at room temperature for 7 h. The solvent was removed *in vacuo* and the residue dissolved in thf (30  $\text{cm}^3$ ). Filtration followed by concentration and addition of light petroleum gave solid compound (**1e**) (0.11 g, 93%).

$[\text{AuW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dmpe})(\text{C}_6\text{F}_5)\text{X}]$  [ $\text{X} = \text{Cl}$ , (**2a**);  $\text{Br}$ , (**2b**); *or*  $\text{NCS}$ , (**2c**)].—To a stirred solution of compound (**1a**) (0.06 g, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was added solid  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  (0.05 g, 0.11 mmol). After stirring for 5 min the resultant solution was evaporated *in vacuo* and the solid washed with light petroleum (20  $\text{cm}^3$ ) and extracted with diethyl ether (3  $\times$  10  $\text{cm}^3$ ). The solution was filtered and concentrated *in vacuo* to ca. 5  $\text{cm}^3$ . Addition of light petroleum in excess gave an orange precipitate of compound (**2a**) (0.039 g, 40%).

Compound (**2b**) was similarly prepared in 28% yield from (**1b**). The mixture of isomers (**2c**) + (**3c**) was similarly prepared in 60% yield from (**1c**), although toluene instead of diethyl ether was used to extract the product.

$[\text{AuW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{dmpe})\text{Cl}(\text{X})]$  [ $\text{X} = \text{Cl}$ , (**4a**); *or*  $\text{NCS}$ , (**4i**)].—Solid  $[\text{AuCl}(\text{tht})]$  (0.024 g, 0.075 mmol) was added to a stirred solution of compound (**1a**) (0.04 g, 0.075 mmol) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). Stirring was continued for 10 min at room temperature and the solvent was removed *in vacuo*. The residue was washed with light petroleum (10  $\text{cm}^3$ ) and extracted with toluene (2  $\times$  10  $\text{cm}^3$ ). The extracts were filtered and concentrated *in vacuo*. Addition of light petroleum gave orange microcrystals of compound (**4a**) (0.04 g, 72%). Compound (**4i**) was similarly prepared from (**1c**) (0.035 g, 0.063 mmol) in 60% yield.

$[\text{AuW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{bipy})\text{Cl}_2]$  (**4e**).—Solid  $[\text{AuCl}(\text{tht})]$  (0.036 g, 0.11 mmol) was added to a stirred solution of compound (**1e**) (0.06 g, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  (7  $\text{cm}^3$ ). After stirring for 10 min at room temperature, the solvent was removed *in vacuo* and the residue washed with light petroleum (10  $\text{cm}^3$ ) and redissolved in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). The solution was filtered, concentrated *in vacuo* to ca. 1  $\text{cm}^3$ , and mixed with

excess of hexane to give orange microcrystals of compound (**4e**) (0.08 g, 95%).

$[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_8(\text{dmpe})\text{Cl}]$  (**5a**).—To a solution of compound (**1a**) (0.1 g, 0.19 mmol) in toluene (15  $\text{cm}^3$ ) was added solid  $[\text{Co}_2(\text{CO})_8]$  (0.075 g, 0.22 mmol). After stirring for 3.5 h at room temperature the mixture was filtered and the solvent evaporated *in vacuo*. The dark green solid was washed with light petroleum (2  $\times$  30  $\text{cm}^3$ ) and dried *in vacuo* (0.11 g, 71%).

$[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_8(\text{dmpe})\text{Br}]$  (**5b**).—The procedure was similar to that used for compound (**5a**). However, because of the concentration under vacuum, the product (60% yield) was contaminated with a compound presumed to be  $[\text{Co}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_7(\text{dmpe})\text{Br}]$ . Satisfactory analytical data for (**5b**) were not always obtained. The data in Table 1 came from samples prepared by extracting the product with hexane (4  $\times$  50  $\text{cm}^3$ ), filtering, concentrating *in vacuo* to ca. 10  $\text{cm}^3$ , cooling at  $-20^\circ\text{C}$ , and drying the resulting brown powder *in vacuo*. Crystallization from toluene-hexane gave crystalline samples that consistently had an average of 33.8% C and 3.05% H, and which, according to the  $^1\text{H}$  n.m.r. spectra, did not contain toluene. Crystals suitable for the X-ray diffraction studies were chosen from a sample obtained by cooling a toluene solution.

$[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\text{dmpe})\text{X}]$  [ $\text{X} = \text{Cl}$ , (**6a**); *or*  $\text{Br}$ , (**6b**)].—To a solution of compound (**1b**) (0.05 g, 0.085 mmol) in toluene (10  $\text{cm}^3$ ) was added solid  $[\text{Fe}_2(\text{CO})_9]$  (0.036 g, 0.1 mmol) and the mixture stirred for 2.5 h at room temperature. It was cooled to  $-20^\circ\text{C}$  and filtered. The resulting red solution was concentrated *in vacuo* to ca. 3  $\text{cm}^3$  and kept at  $-20^\circ\text{C}$  overnight to give red crystals of compound (**6b**) (0.046 g, 73%).

Compound (**6a**) was similarly prepared in 61% yield.

*Structure Determination of Compound (1c).*—Crystal data.  $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{P}_2\text{SW}$ ,  $M = 551.23$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.970(3)$ ,  $b = 9.919(2)$ ,  $c = 14.370(2)$  Å,  $\alpha = 77.11(1)$ ,  $\beta = 84.99(2)$ ,  $\gamma = 84.20(2)^\circ$ ,  $U = 1101$  Å<sup>3</sup> (cell dimensions obtained from least-squares refinement of 25 reflections in the range  $\theta$  14–15),  $\lambda = 0.71069$  Å,  $Z = 2$ .  $D_c = 1.66$  g  $\text{cm}^{-3}$ ,  $F(000) = 536$ ,  $\mu(\text{Mo-K}_\alpha) = 56.02$   $\text{cm}^{-1}$ .

4133 Reflections were collected at room temperature with a CAD 4 Enraf-Nonius diffractometer in a  $\omega$ - $2\theta$  scan mode, using  $\text{Mo-K}_\alpha$  radiation (graphite monochromator) and scan width  $1.0 + 0.34 \tan\theta$ , in the range  $1 < \theta < 25^\circ$ . 3364 Reflections with  $F > 3\sigma(F)$  were used for computations. An empirical absorption correction was applied using  $\psi$  scan of one reflection (maximum transmission factor 1.50, minimum 1.0).

The tungsten atom was located on a Patterson map and all the other atoms were found in subsequent Fourier maps. Full-matrix least-squares refinement was carried out with weights. During the refinement a disorder was found affecting one of the chain carbons [C(21)] which had to be refined in two positions (found in a difference map) with a multiplicity of 0.5 [C(21a) and C(21b)]. All the non-hydrogen atoms [except C(21a) and C(21b)] were refined anisotropically; C(21a) and C(21b) were refined isotropically, some restraints being imposed on the distances C(21b)-P(2) and C(21b)-C(11). Hydrogen atoms, except those on C(21a), C(21b), and C(11), were geometrically positioned and were given an isotropic thermal parameter.

A secondary extinction parameter was applied<sup>19</sup> with a correction factor of  $3.2 \times 10^{-6}$ . Final  $R = \Sigma|F_o - F_c|/\Sigma F_o = 0.0257$ ,  $R[\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2} = 0.0287$  ( $w = 1$ ). All calculations were carried out with CRYSTALS.<sup>20</sup> Scattering

factors with corrections for anomalous dispersion were also from CRYSTALS.

**Structure Determination of Compound (5b).**—*Crystal data.*  $C_{22}H_{23}BrCo_2O_8P_2W$ ,  $M = 859.0$ , orthorhombic, space group  $Pbca$ ,  $a = 13.969(2)$ ,  $b = 21.209(2)$ ,  $c = 21.814(3)$  Å,  $U = 6463(3)$  Å<sup>3</sup> (cell dimensions obtained from least-squares refinement of 25 reflections in the range  $\theta$  13–15°),  $Z = 8$ ,  $D_c = 1.76$  g cm<sup>-3</sup>,  $F(000) = 3296$ ,  $\mu = 60$  cm<sup>-1</sup>.

5670 Reflections were measured (see above) at room temperature, and 2672 with  $F > 3\sigma(F)$  were used for the refinements. Two standard reflections were measured every 2 h without decay in intensity. Empirical absorption corrections were applied using the  $\psi$  scan of one of the reflections (minimum and maximum transmission factors: 1.00 and 1.51).

The tungsten atom was located on a Patterson map and all other atoms were found in subsequent Fourier maps. Least-squares refinements were carried out in three blocks (327 parameters). All non-hydrogen atoms were anisotropically refined. Some hydrogen atoms were found on a difference map, others were geometrically positioned. These atoms were not refined and were given an overall isotropic thermal parameter. Final  $R = 0.0417$ ,  $R' = 0.0433$ . All calculations were carried out with CRYSTALS.

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

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