

# Preparation of Dimolybdenum Carbonyl and Ditungsten Carbonyl Complexes containing Triple Fluoro Bridges†

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The reaction of  $[\text{WH}_6(\text{PMe}_2\text{Ph})_3]$  with  $\text{HBF}_4 \cdot \text{OEt}_2$ , under an atmosphere of carbon monoxide, in tetrahydrofuran gives  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]\text{BF}_4$ . The X-ray crystal structure of this compound reveals that the geometry about each tungsten atom is best considered as having a basal plane containing three fluorine atoms,  $(\text{W-F})_{\text{av}}$  2.12(1) Å, with the remaining four ligands (two carbon monoxide and two phosphines) forming a second, parallel plane, in which the two carbon monoxide ligands are mutually *trans*,  $(\text{W-C})_{\text{av}}$  1.949(6) Å, as are the two phosphines,  $(\text{W-P})_{\text{av}}$  2.457(1) Å. The spectroscopic characteristics of  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]^+$  are discussed and from this the nature of species formed in the reactions of  $[\text{MoH}_4(\text{PR}_3)_4]$  ( $\text{R}_3 = \text{Et}_3$  or  $\text{MePh}_2$ ) with  $\text{HBF}_4 \cdot \text{OEt}_2$  under an atmosphere of carbon monoxide can be inferred.

Early studies<sup>1</sup> on the protonation of polyhydrido complexes indicated that the reaction of  $[\text{MoH}_4(\text{PMePh}_2)_4]$  with  $\text{HBF}_4$  or  $\text{HPF}_6$  in tetrahydrofuran (thf) gave  $[\text{MoH}_3(\text{PMePh}_2)_3]^+$ . A subsequent reinvestigation of this reaction resulted in crystals of the product suitable for X-ray crystallographic analysis.<sup>2</sup> This study showed that the product was in fact  $[\{\text{MoH}_2(\text{PMePh}_2)_3\}_2(\mu\text{-F})_3]^+$ . To date this was the only example of a crystallographically confirmed trifluoro bridge. In this paper we describe the preparation and characterisation of other trifluoro-bridged species,  $[\{\text{M}(\text{CO})_2(\text{PR}_3)_2\}_2(\mu\text{-F})_3]\text{BF}_4$  ( $\text{M} = \text{Mo}$ ,  $\text{R}_3 = \text{Et}_3$  or  $\text{MePh}_2$ ;  $\text{M} = \text{W}$ ,  $\text{R}_3 = \text{Me}_2\text{Ph}$ ), including the X-ray crystal structure of the tungsten complex.

## Results and Discussion

Treatment of  $[\text{WH}_6(\text{PMe}_2\text{Ph})_3]$ , in thf saturated with carbon monoxide, with  $\text{HBF}_4 \cdot \text{OEt}_2$  gives an immediate clear yellow solution from which bright yellow crystals can be isolated. X-Ray crystallographic analysis and spectroscopic characterisation show this material to be  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]\text{BF}_4$ .

**Crystal Structure of  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]\text{BF}_4$ .**—Single crystals of this compound were formed by slow crystallisation from a  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$  mixture. The structure is shown in Fig. 1 with the atomic coordinates shown in Table 1 and selected molecular dimensions in Table 2.

The coordination patterns and dimensions around the two tungsten atoms are very similar. The best description of the geometry is that the molecule adopts a '4:3:4' configuration of ligands around the two tungsten centres. The three bridging fluorine atoms form a trigonal '3' plane for each W atom; virtually parallel to this plane, beyond each W atom, there is a rhombic '4' arrangement of two carbonyl C atoms and two phosphine P atoms. Within each  $\text{C}_2\text{P}_2$  plane, the carbonyl groups occupy opposite corners of the rhombus, with  $(\text{W-C})_{\text{av}}$  1.949(6) Å; similarly the phosphine ligands are diagonally arranged with  $(\text{W-P})_{\text{av}}$  2.457(1) Å. The two rhombic planes are twisted *ca.* 26° from the eclipsing position. The dimensions of the bridging unit, 'W<sub>2</sub>(μ-F)<sub>3</sub>' are very similar to those found<sup>2</sup> for  $[\{\text{MoH}_2(\text{PMePh}_2)_3\}_2(\mu\text{-F})_3]^+$  in spite of the different

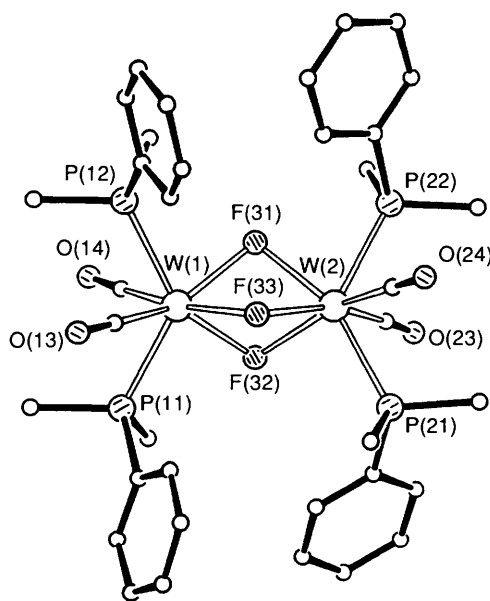


Fig. 1 View of  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]^+$

co-ordination geometries of the metal atoms. Thus in the molybdenum complex  $(\text{Mo-F})_{\text{av}}$  2.16(1) Å with the Mo-Mo separation 3.256(2) Å and the angle  $(\text{MoFMo})_{\text{av}}$  97.7(2)°, compared with  $(\text{W-F})_{\text{av}}$  2.12(1), W-W separation 3.216(3) Å and  $(\text{WFW})_{\text{av}}$  98.3(6)° for our complex. In both species the M-M separation is sufficiently large to preclude the occurrence of a metal-metal bond.

**Spectroscopic Characterisation of  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]\text{BF}_4$ .**—The analytical and spectroscopic characterisation of this complex is shown in Table 3. The most diagnostic features associated with the cation are the quartet pattern in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectrum and the quintet in the  $^{19}\text{F}$  NMR spectrum, demonstrating the presence of three equivalent fluorine atoms and four equivalent phosphine ligands. We have used these characteristic NMR spectral patterns to identify the reaction products formed between  $[\text{MoH}_4(\text{PR}_3)_4]$  ( $\text{R}_3 = \text{Et}_3$  or  $\text{MePh}_2$ ) and  $\text{HBF}_4 \cdot \text{OEt}_2$  in thf, under an atmosphere of

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

**Table 1** Final atomic coordinates (fractional  $\times 10^4$ ) for  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_3]BF_4$  with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
W(1)	-2003.9(1)	5671.6(1)	3746.1(1)
P(11)	-2215(1)	6177.6(6)	4834.3(6)
C(111)	-2315(4)	7104(2)	4867(2)
C(112)	-2231(5)	7426(3)	5494(3)
C(113)	-2280(6)	8130(3)	5522(3)
C(114)	-2459(6)	8509(3)	4944(3)
C(115)	-2611(6)	8198(3)	4319(3)
C(116)	-2514(5)	7496(2)	4286(2)
C(117)	-852(5)	5994(3)	5487(3)
C(118)	-3527(5)	5900(3)	5194(3)
P(12)	-3400(1)	4828.8(6)	3079.8(6)
C(121)	-4130(4)	5064(3)	2208(2)
C(122)	-4133(5)	5723(3)	1983(3)
C(123)	-4700(5)	5907(4)	1332(3)
C(124)	-5250(6)	5412(5)	891(3)
C(125)	-5266(5)	4749(4)	1098(3)
C(126)	-4711(5)	4573(3)	1748(3)
C(127)	-4699(5)	4545(3)	3439(3)
C(128)	-2588(6)	4041(3)	2968(3)
C(13)	-3661(4)	6065(2)	3612(2)
O(13)	-4641(3)	6309(2)	3514(2)
C(14)	-2084(4)	4913(2)	4369(2)
O(14)	-2106(4)	4452(2)	4722(2)
W(2)	394.1(2)	6105.2(1)	3153.5(1)
P(21)	1355(1)	7222.3(6)	3646.2(6)
C(211)	1934(5)	7346(2)	4367(3)
C(212)	1108(6)	7477(3)	4787(3)
C(213)	1535(8)	7574(4)	5472(3)
C(214)	2743(9)	7523(4)	5754(3)
C(215)	3603(8)	7372(4)	5365(4)
C(216)	3184(6)	7283(3)	4656(3)
C(217)	293(6)	7924(3)	3215(3)
C(218)	2683(6)	7427(3)	3085(3)
P(22)	1204(1)	5288.8(6)	2426.1(6)
C(221)	147(4)	5022(2)	1645(2)
C(222)	584(5)	4649(3)	1161(3)
C(223)	-226(6)	4397(3)	590(3)
C(224)	-1476(6)	4504(3)	510(3)
C(225)	-1930(5)	4884(3)	979(3)
C(226)	-1112(5)	5147(3)	1548(3)
C(227)	1600(6)	4466(3)	2834(3)
C(228)	2585(5)	5543(3)	2145(3)
C(23)	2114(5)	5892(2)	3601(2)
O(23)	3098(3)	5761(2)	3904(2)
C(24)	462(5)	6562(2)	2307(2)
O(24)	422(4)	6853(2)	1801(2)
F(31)	-722(3)	5219(1)	3215(2)
F(32)	-159(3)	6030(2)	4104(2)
F(33)	-1473(3)	6364(2)	3043(2)

In the  $BF_4^-$  anion

B(5)	3723(8)	2829(3)	2772(4)
F(51)	3713(6)	3116(2)	3360(2)
F(52)	3526(7)	3323(3)	2298(2)
F(53)	2916(7)	2351(3)	2591(3)
F(54)	4790(8)	2588(6)	2772(5)

**Table 2** Selected dimensions (lengths in Å, angles in  $^\circ$ ) in  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_3]BF_4$  with e.s.d.s in parentheses

## (a) In the co-ordination spheres of the tungsten atoms

W(1)-P(11)	2.457(1)	W(2)-P(21)	2.458(1)
W(1)-P(12)	2.457(1)	W(2)-P(22)	2.456(1)
W(1)-C(13)	1.942(4)	W(2)-C(23)	1.962(5)
W(1)-C(14)	1.959(5)	W(2)-C(24)	1.938(5)
W(1)-F(31)	2.126(4)	W(2)-F(31)	2.146(3)
W(1)-F(32)	2.124(3)	W(2)-F(32)	2.126(3)
W(1)-F(33)	2.127(4)	W(2)-F(33)	2.077(3)
P(11)-W(1)-P(12)	126.6(1)	P(21)-W(2)-P(22)	123.1(1)
P(11)-W(1)-C(13)	73.0(1)	P(21)-W(2)-C(23)	75.6(1)
P(12)-W(1)-C(13)	74.4(1)	P(22)-W(2)-C(23)	72.7(1)
P(11)-W(1)-C(14)	73.3(1)	P(21)-W(2)-C(24)	73.7(1)
P(12)-W(1)-C(14)	74.5(1)	P(22)-W(2)-C(24)	72.3(1)
C(13)-W(1)-C(14)	103.2(2)	C(23)-W(2)-C(24)	107.2(2)
P(11)-W(1)-F(31)	144.0(1)	P(21)-W(2)-F(31)	158.3(1)
P(12)-W(1)-F(31)	81.2(1)	P(22)-W(2)-F(31)	77.6(1)
C(13)-W(1)-F(31)	142.4(2)	C(23)-W(2)-F(31)	107.9(2)
C(14)-W(1)-F(31)	97.1(2)	C(24)-W(2)-F(31)	123.4(2)
P(11)-W(1)-F(32)	79.7(1)	P(21)-W(2)-F(32)	91.1(1)
P(12)-W(1)-F(32)	148.4(1)	P(22)-W(2)-F(32)	134.0(1)
C(13)-W(1)-F(32)	135.6(2)	C(23)-W(2)-F(32)	89.8(2)
C(14)-W(1)-F(32)	101.5(2)	C(24)-W(2)-F(32)	153.0(2)
F(31)-W(1)-F(32)	68.1(1)	F(31)-W(2)-F(32)	67.7(2)
P(11)-W(1)-F(33)	115.0(1)	P(21)-W(2)-F(33)	99.8(1)
P(12)-W(1)-F(33)	107.0(1)	P(22)-W(2)-F(33)	124.4(1)
C(13)-W(1)-F(33)	91.6(2)	C(23)-W(2)-F(33)	159.3(2)
C(14)-W(1)-F(33)	164.8(2)	C(24)-W(2)-F(33)	90.4(2)
F(31)-W(1)-F(33)	68.6(1)	F(31)-W(2)-F(33)	69.1(1)
F(32)-W(1)-F(33)	69.1(1)	F(32)-W(2)-F(33)	69.9(1)

## (b) In the carbonyl ligands

C(13)-O(13)	1.156(5)	C(23)-O(23)	1.155(5)
C(14)-O(14)	1.154(6)	C(24)-O(24)	1.160(6)
W(1)-C(13)-O(13)	177.9(4)	W(2)-C(23)-O(23)	175.4(4)
W(1)-C(14)-O(14)	177.5(4)	W(2)-C(24)-O(24)	175.3(5)

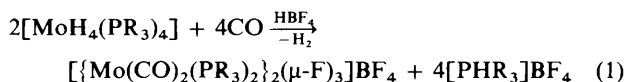
## (c) Angles around the bridging fluorine atoms

W(1)-F(31)-W(2)	97.7(1)	W(1)-F(32)-W(2)	98.3(1)
W(1)-F(33)-W(2)	99.8(2)		

## (d) In the tetrafluoroborate anion

B(5)-F(51)	1.312(9)	B(5)-F(53)	1.291(10)
B(5)-F(52)	1.345(8)	B(5)-F(54)	1.263(12)
F(51)-B(5)-F(52)	107.5(6)	F(52)-B(5)-F(53)	108.9(6)
F(51)-B(5)-F(53)	115.7(8)	F(52)-B(5)-F(54)	106.6(9)
F(51)-B(5)-F(54)	109.8(7)	F(53)-B(5)-F(54)	108.0(8)

consistent with this signal being attributable to  $[PHMePh_2]^+$  formed according to reaction (1). The relatively low isolated



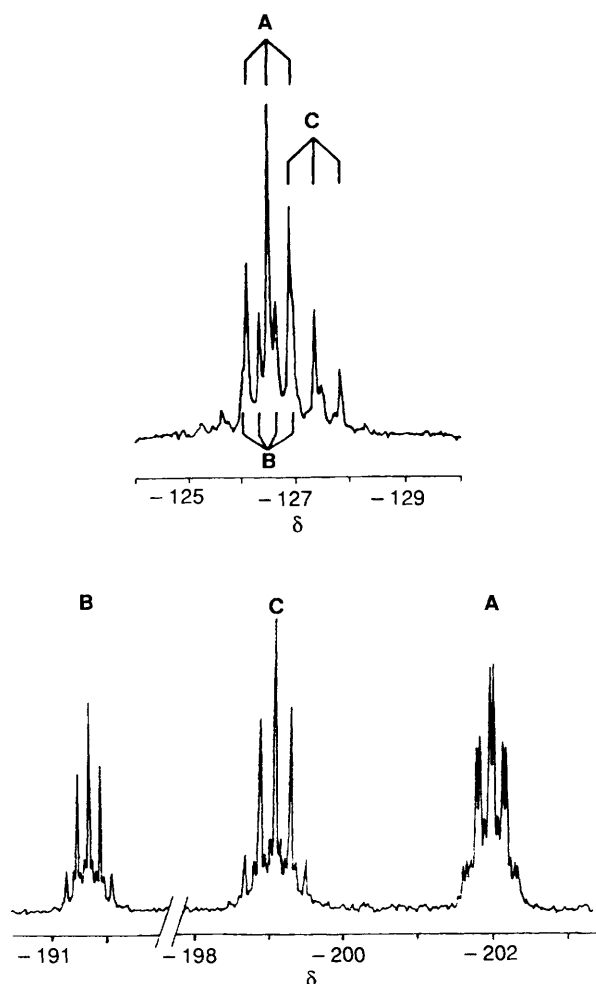
carbon monoxide. The use of  $^{31}P\{-^1H\}$  and  $^{19}F$  NMR spectroscopy for these molybdenum systems is particularly useful because, as we have noted before,<sup>3</sup> it is difficult to isolate analytically clean products from these reaction mixtures since they are contaminated with the side products, phosphonium salts. The spectroscopic characteristics of the molybdenum products are shown in Table 3, and are fully consistent with a triply bridged structure,  $[\{Mo(CO)_2(PR_3)_2\}_2(\mu-F)_3]^+$ . The  $^{31}P\{-^1H\}$  NMR spectra of the reaction products show, besides the quartet pattern attributable to the dinuclear species, a singlet ( $\delta -138.0$  when  $R_3 = MePh_2$ ). When proton uncoupled this singlet becomes a doublet  $J(PH) = 534$  Hz

yield of  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_3]BF_4$  (32%) led us to investigate by NMR spectroscopy the reaction mixture from which this material was isolated. The  $^{31}P\{-^1H\}$  and  $^{19}F$  NMR spectra shown in Fig. 2 demonstrate that three species are present in solution. These spectra further show that all the species contain the  $\{W(PMe_2Ph)_2\}_2(\mu-F)_2$  core. Besides the signals attributable to the isolated  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_3]^+$ , species B, two other species are present. We propose that species C is  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_2]^{2+}$ , formed by the loss of one fluoride from species B; however it may be that a molecule of solvent (thf) is present in a bridging position in

**Table 3** Analytical and spectroscopic characterisation of the complexes

Complex	Elemental analysis <sup>a</sup> (%)		IR bands/cm <sup>-1</sup>	$\delta^b$		
	C	H		<sup>1</sup> H	<sup>31</sup> P- <sup>1</sup> H	<sup>19</sup> F <sup>c</sup>
[{W(CO) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> } <sub>2</sub> ( $\mu$ -F) <sub>3</sub> ]BF <sub>4</sub>	36.8 (36.6)	3.7 (3.7)	1910s, 1800s, v(CO) 1060, v(BF)	7.5(5) (br, PMe <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ), 1.8(6) [br, P(CH <sub>3</sub> ) <sub>2</sub> Ph]	-126.5 [q, J(PF) 34.0, PMe <sub>2</sub> Ph], J(PW) 97.0	-191.7 [qnt, J(PF) 32.4, $\mu$ -F] J(WF) 17.0
[{Mo(CO) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub> } <sub>2</sub> ( $\mu$ -F) <sub>3</sub> ]BF <sub>4</sub> <sup>d</sup>			1944m, 1851s, v(CO) <sup>e</sup>	7.2(10) [m, PMe(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>f</sup> , 2.1(3) [br, P(CH <sub>3</sub> )Ph <sub>2</sub> ]	-87.3 [q, J(PF) 32.7, PMePh <sub>2</sub> ] <sup>g</sup>	-194.8 [qnt, J(PF) 32.6, $\mu$ -F]
[{Mo(CO) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> ( $\mu$ -F) <sub>3</sub> ]BF <sub>4</sub> <sup>d</sup>			1920s, 1830s, v(CO)		-82.7 [q, J(PF) 27.7, PEt <sub>3</sub> ]	-198.1 [qnt, J(PF) 27.8, $\mu$ -F]

<sup>a</sup> Calculated values shown in parentheses. <sup>b</sup> Chemical shifts are relative to SiMe<sub>4</sub> (<sup>1</sup>H), P(OMe)<sub>3</sub> (<sup>31</sup>P) and CFCl<sub>3</sub> (<sup>19</sup>F); coupling constants (*J*) are in Hz. <sup>c</sup> All spectra show a peak at  $\delta$  -153.1 which is attributable to BF<sub>4</sub><sup>-</sup>. <sup>d</sup> Not isolated as analytically clean products. <sup>e</sup> Spectrum also contains absorption at 2450s cm<sup>-1</sup>, v(PH), due to presence of [PHMePh<sub>2</sub>]BF<sub>4</sub>. <sup>f</sup> Peaks attributable to [PHMePh<sub>2</sub>]BF<sub>4</sub>:  $\delta$  6.3 [1, d of q, J(PH) 530, J(PMe) 5.6, P-H], 7.8 (10, m, Ph), 2.6 [3, d of d, J(PH) 5.7, J(PMe) 15.2 Hz, Me]. <sup>g</sup> Peak attributable to [PHMePh<sub>2</sub>]BF<sub>4</sub>,  $\delta$  -138.0, in <sup>1</sup>H uncoupled spectrum, J(PH) 534 Hz.



**Fig. 2** <sup>31</sup>P-<sup>1</sup>H (top) and <sup>19</sup>F (bottom) NMR spectra of the reaction mixture formed in the reaction of [WH<sub>6</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] with HBF<sub>4</sub>·OEt<sub>2</sub> in thf under an atmosphere of CO. Signals are attributable to the species, A, [{W(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>( $\mu$ -F)<sub>2</sub>( $\mu$ -H)]<sup>+</sup>, <sup>31</sup>P:  $\delta$  -126.5 [t, J(PF) 43.6, J(PW) 93.5], <sup>19</sup>F:  $\delta$  -201.9 [d of qnt, J(PF) 43.7]; B, [{W(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>( $\mu$ -F)<sub>3</sub>]<sup>+</sup> (see Table 3); and C, [{W(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>( $\mu$ -F)<sub>2</sub>]<sup>2+</sup>, <sup>31</sup>P:  $\delta$  -124.5 [t, J(PF) 51.8, J(PW) 100.8], <sup>19</sup>F:  $\delta$  -199.1 [qnt, J(PF) 52.5 Hz]. All three species show J(WF) 17 ± 1.2 Hz

place of the lost fluoride. Finally species A appears to contain a bridging hydride as well as the two fluoride bridges, [{W(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>( $\mu$ -F)<sub>2</sub>( $\mu$ -H)]<sup>+</sup>, only in this way can we

account for the doublet of quintet pattern observed in the <sup>19</sup>F NMR spectrum. Proton uncoupling the <sup>31</sup>P NMR spectrum did not reveal any resolvable phosphorus hydrogen coupling. However, broad band <sup>1</sup>H decoupling is not very satisfactory in these systems,<sup>2</sup> particularly with a mixture of complexes present.

In conclusion, we have shown that the reaction of polyhydrido-phosphine complexes with HBF<sub>4</sub>·OEt<sub>2</sub> in the presence of carbon monoxide gives [{M(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -F)<sub>3</sub>]<sup>+</sup>, authenticated by X-ray crystallography and exhibiting diagnostic <sup>31</sup>P and <sup>19</sup>F NMR spectra.

### Experimental

All manipulations were routinely performed under an atmosphere of argon using standard Schlenk techniques. Pre-dried solvents were further dried by distillation from the appropriate drying agents immediately prior to use. Microanalyses were performed at the Nitrogen Fixation Laboratory by Mr. C. Macdonald. The following spectroscopic instruments were used: IR, Perkin-Elmer 883 spectrophotometer; NMR, JEOL GSX 270 spectrometer.

The complexes [MoH<sub>4</sub>(PEt<sub>3</sub>)<sub>4</sub>]<sup>3</sup>, [MoH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub>]<sup>4</sup> and [WCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>5</sup> were prepared by the literature methods. The reagents Na[AlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OMe)<sub>2</sub>] (red-Al) (Aldrich) and HBF<sub>4</sub>·OEt<sub>2</sub> (BDH) were used as supplied.

*Tris(dimethylphenylphosphine)hexahydridotungsten.*—The complex was prepared by the literature method<sup>6</sup> with a few modifications. The excess of red-Al employed was reduced from 11.6 to 8.0 equivalents with respect to [WCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]. The work-up procedure was facilitated by using acetone instead of diethyl ether. This assisted the isolation of clean product as well as reducing the loss of highly soluble product caused by repeated recrystallisation. Yield {from 3.0 g of [WCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]} 1.35 g, 55%.

*Tri- $\mu$ -fluoro-bis[dicarbonylbis(dimethylphenylphosphine)-tungsten] Tetrafluoroborate.*—A solution of [WH<sub>6</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] (0.10 g, 0.16 mmol) in thf (10 cm<sup>3</sup>) was purged with carbon monoxide for 10 min, and then a solution of HBF<sub>4</sub>·OEt<sub>2</sub> (0.15 cm<sup>3</sup> of 54% HBF<sub>4</sub>, 9.2 mmol) was added, causing a rapid evolution of gas and formation of a yellow solution. The carbon monoxide purge was stopped after a further 5 min and the solvent removed *in vacuo*. The addition of ethanol (15 cm<sup>3</sup>) to the residue resulted in the formation of a bright yellow solid, which was collected by filtration, washed with ethanol (2 × 5 cm<sup>3</sup>) and diethyl ether (2 × 5 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.06 g, 32%. Crystals of this product suitable for X-ray crystallographic analysis were obtained by layering diethyl

ether (100 cm<sup>3</sup>) over a saturated solution of the product in CH<sub>2</sub>Cl<sub>2</sub>. Golden cubic crystals were collected after 1 week.

Analogous procedures were used in the reactions with [MoH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub>] and [MoH<sub>4</sub>(PEt<sub>3</sub>)<sub>4</sub>], but in both cases the product [ $\{\text{Mo}(\text{CO})_2(\text{PR}_3)_2\}_2(\mu\text{-F})_3\text{BF}_4$ ] was contaminated with [PHR<sub>3</sub>]BF<sub>4</sub>, which could not be removed even after extensive fractional crystallisation.

*Crystal Structure Analysis of* [ $\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\mu\text{-F})_3\}_2\text{BF}_4$ ].—*Crystal data.* C<sub>36</sub>H<sub>44</sub>BF<sub>7</sub>O<sub>4</sub>P<sub>4</sub>W<sub>2</sub>, *M* = 1176.1, monoclinic, space group *P*2<sub>1</sub>/*c* (no. 14), *a* = 10.966(3), *b* = 19.637(2), *c* = 20.114(5) Å, β = 101.81(1)°, *U* = 4239 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.842 g cm<sup>-3</sup>, *F*(000) = 2272, μ(Mo-Kα) = 57.5 cm<sup>-1</sup>, λ(Mo-Kα) = 0.710 69 Å. The crystals were opaque and yellow, of irregular shape. One, of wedge shape, ca. 0.55 × 0.35 × 0.25 mm was mounted on a glass fibre and photographed to confirm its quality before being transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation). Accurate cell parameters were refined from the goniometer settings of 25 reflections (θ ca. 10.5°) each centred in four orientations, and intensity data were measured for 7441 unique reflections (θ<sub>max</sub> = 25°).

Corrections were applied for Lorentz and polarisation effects, absorption (by semi-empirical methods from ψ-scan measurements) and to eliminate negative net intensities (by Bayesian statistical methods). No deterioration correction was necessary.

The structure was determined by the heavy-atom method, using the SHELX program system,<sup>7</sup> and refined by large-block-matrix least-squares methods (refining a total of 555 parameters) to convergence at *R* = 0.029, *R'* = 0.034<sup>7</sup> for all data weighted *w* = σ<sub>*F*</sub><sup>-2</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were

included in idealised positions and the CH<sub>3</sub> groups were kept as rigid units, their isotropic thermal parameters were refined freely. In a final difference map, the highest peaks, ca. 0.7 e Å<sup>-3</sup>, were either close to a tungsten atom or in the region of the BF<sub>4</sub><sup>-</sup> anion. Scattering factor curves for neutral atoms were taken from ref. 8. Computer programs used in this analysis have been noted above or in Table 4 of ref. 9 and were run on the MicroVAX II machine in the Nitrogen Fixation Laboratory.

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

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