

# Crystal Structure of $[W(\eta\text{-C}_6\text{F}_6)_2]$ synthesised together with Other Sandwich Complexes of Tungsten and Molybdenum containing $\eta^6\text{-C}_6\text{F}_6$ or $\eta^6\text{-C}_6\text{H}_3\text{F}_3\text{-1,3,5}$ Ligands, from Atoms of the Metals†

John J. Barker, A. Guy Orpen, Andrew J. Seeley and Peter L. Timms\*  
School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK

Reaction of molybdenum or tungsten atoms with hexafluorobenzene or 1,3,5-trifluorobenzene or with mixtures of these ligands and benzene or 1,3,5-trimethylbenzene gave the new compounds  $[M(\text{C}_6\text{F}_6)_2]$ ,  $[M(\text{C}_6\text{H}_3\text{F}_3\text{-1,3,5})_2]$ ,  $[M(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$ ,  $[M(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3\text{-1,3,5})]$  and  $[M(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]$  ( $M = \text{Mo}$  or  $\text{W}$ ) in yields ranging from <1 to 5% as stable crystalline solids. A single-crystal X-ray study of  $[W(\text{C}_6\text{F}_6)_2]$  showed it to have the same symmetry as  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$  and the same W–C bond lengths as in  $[W(\text{C}_6\text{H}_5\text{Me})_2]$ . The  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra of the mixed-ligand products show interesting coupling with large coupling constants which make some of the spectra exceptionally easy to interpret.

As part of a study of reactions of metal atoms with potentially oxidising ligands, we have investigated reactions of molybdenum and tungsten atoms with hexafluorobenzene and 1,3,5-trifluorobenzene. Much earlier work<sup>1,2</sup> had shown that  $[\text{Cr}(\eta^6\text{-C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$  and  $[\text{Cr}(\eta^6\text{-C}_6\text{F}_6)(\text{PF}_3)_3]$  can be prepared from chromium atoms, but that  $[\text{Cr}(\text{C}_6\text{F}_6)_2]$  could not be isolated. In another study on chromium atoms, it was found that  $[\text{Cr}(\text{C}_6\text{F}_2\text{H}_4)_2]$  but not  $[\text{Cr}(\text{C}_3\text{H}_3\text{F}_3\text{-1,3,5})_2]$  could be prepared.<sup>3</sup> A poorly defined but highly reactive  $[\text{Ni}(\text{C}_6\text{F}_6)]$  was also reported to be formed from nickel atoms and  $\text{C}_6\text{F}_6$ .<sup>4</sup> In a matrix-isolation ESR study with vanadium atoms, the electron distribution in the half-sandwich species  $[\text{V}(\text{C}_6\text{F}_6)]$  and  $[\text{V}(\text{C}_6\text{H}_6)]$  was compared but  $[\text{V}(\text{C}_6\text{F}_6)_2]$  was not detected.<sup>5</sup> From reactions of organometallic compounds, several  $\eta^2$ - and  $\eta^4$ -complexes and one  $\eta^6\text{-C}_6\text{F}_6$  complex of second- and third-row transition metals have been described recently,<sup>6,7</sup> but the chemistry is complicated by the competing tendency of  $\text{C}_6\text{F}_6$  to oxidatively add to the metal centres. We now report the synthesis of the first bis( $\eta^6$ -hexafluorobenzene) complexes and a series of related  $\eta^6$ -arene complexes readily isolated, albeit in low yield, from reactions of molybdenum or tungsten atoms with the arenes at liquid-nitrogen temperature.

## Results

On evaporating tungsten under high vacuum by electron bombardment and condensing the W atoms with an excess of  $\text{C}_6\text{F}_6$  at  $-196^\circ\text{C}$ , warming the condensate to room temperature and pumping away unreacted  $\text{C}_6\text{F}_6$ , a solid remained from which, either by extraction with pentane or by prolonged vacuum pumping, a volatile yellow solid could be isolated. Sublimation at  $30^\circ\text{C}$  under high vacuum followed by recrystallization from pentane gave an air-stable product, **1**, in a yield of about 2% based on the tungsten condensed, whose structure was confirmed as  $[W(\eta^6\text{-C}_6\text{F}_6)_2]$  by a single-crystal X-ray study.

The unit cell contains two distinct molecules each of which has exact (crystallographic)  $C_i$  and approximate  $D_{6h}$  symmetry (see Fig. 1) with eclipsed  $\text{C}_6\text{F}_6$  rings. Average W–C, C–C and C–F distances are 2.268(4), 1.407(5) and 1.342(4) Å respectively,

individual bond lengths and angles are listed in Table 1. These may be compared to mean W–C and C–C distances in  $[W(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]$  of 2.273(6) and 1.406(6) Å respectively, and to the mean W–C distance in other tungsten- $\eta$ -arenes (mean 2.291 Å, sample standard deviation 0.021 Å). Atomic displacement parameters show no compelling evidence for disorder in the structure. The fluorine atoms lie out of their  $\text{C}_6$  plane, away from the tungsten atom, by an average of 0.043(4) Å. The molecular packing is pseudo-body-centred with the molecule at the centre of the unit cell rotated by ca.  $90^\circ$  about the unit cell  $a$  axis relative to those at the cell corners (see Fig. 2). The shortest intermolecular contacts are F...F distances of  $\geq 2.88$  Å and F...C contacts of  $\geq 2.93$  Å.

The reaction between molybdenum atoms and hexafluorobenzene gave a lower yield of a stable yellow solid, identified by its single-line  $^{19}\text{F}$  NMR spectrum (see Table 2 for comparative data) and high-resolution mass spectrum (Table 3) as  $[\text{Mo}(\text{C}_6\text{F}_6)_2]$  **2**, which is very likely structurally analogous to **1**. Compound **2** decomposed in air at  $135^\circ\text{C}$  compared to  $180^\circ\text{C}$  for **1**.

With an equimolar mixture of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{F}_6$ , Mo and W atoms each gave low yields of easily sublimed, greenish-yellow solids. The low- and high-resolution mass spectrum of each showed the presence of  $[\text{M}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$  species with no  $[\text{Mo}(\text{C}_6\text{H}_6)_2]$ ,  $[\text{W}(\text{C}_6\text{H}_6)_2]$  or **2** present and only a trace of **1**. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra both showed septets analogous to those seen in  $[\text{Cr}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$ <sup>1,2</sup> strongly indicating that these were the structurally equivalent compounds  $[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$  **3** and  $[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$  **4**. An attempt to obtain a detailed structure of **3** by X-ray crystallography was thwarted by disorder problems although it was clear that the compound had the same type of sandwich structure as **1**. Condensing 1,3,5-trimethylbenzene and hexafluorobenzene with Mo and W atoms gave  $[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]$  **5** and  $[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]$  **6**, each identifiable from the evidence of its  $^{19}\text{F}$  NMR spectrum which showed a quartet and its  $^1\text{H}$  NMR spectra which showed a septet for the ring protons and a singlet for the methyl protons. These compounds were rather less stable than compounds **1–4** and decomposed on prolonged exposure to air and seemed also to be light sensitive.

Confirming a negative result reported earlier,<sup>3</sup> we could not isolate any molecular organometallic product from reacting Cr atoms and 1,3,5-trifluorobenzene, but from Mo or W atoms  $[\text{Mo}(\text{C}_6\text{H}_3\text{F}_3\text{-1,3,5})_2]$  **7** and  $[\text{W}(\text{C}_6\text{H}_3\text{F}_3\text{-1,3,5})_2]$  **8** were

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

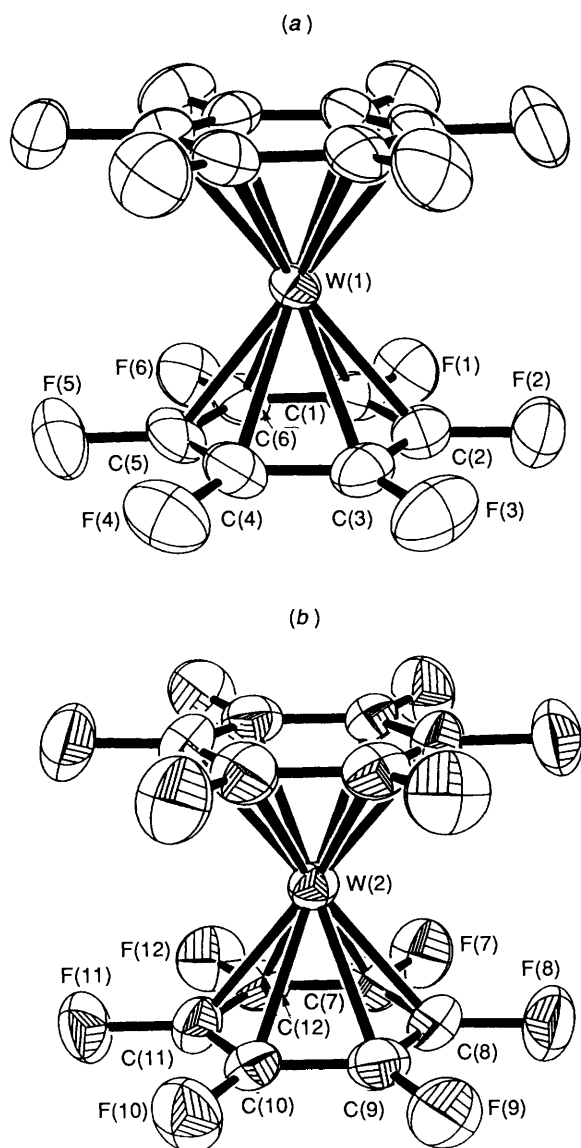


Fig. 1 Molecular structure of the two independent molecules of  $[\text{W}(\text{C}_6\text{F}_6)_2]$  **1**, (a) and (b), showing labelling scheme. Displacement ellipsoids are drawn to enclose 50% probability density

Table 1 Selected bond lengths (Å) and angles (°) for  $[\text{W}(\text{C}_6\text{F}_6)_2]$  **1**

W(1)–C(1)	2.247(10)	W(2)–C(8)	2.279(10)
W(1)–C(4)	2.244(8)	W(2)–C(11)	2.281(10)
C(1)–F(1)	1.352(11)	C(7)–C(8)	1.402(15)
C(2)–F(2)	1.350(12)	C(8)–C(9)	1.403(15)
C(3)–C(4)	1.381(13)	C(10)–F(10)	1.325(11)
C(5)–F(5)	1.327(11)	C(11)–C(12)	1.420(15)
W(2)–C(7)	2.268(10)	W(1)–C(3)	2.260(8)
W(2)–C(10)	2.272(8)	W(1)–C(6)	2.267(10)
C(7)–F(7)	1.329(12)	C(1)–C(6)	1.378(13)
C(8)–F(8)	1.350(11)	C(3)–F(3)	1.348(12)
C(9)–C(10)	1.422(12)	C(4)–C(5)	1.404(15)
C(11)–F(11)	1.346(11)	C(6)–F(6)	1.341(12)
W(1)–C(2)	2.273(9)	W(2)–C(9)	2.253(9)
W(1)–C(5)	2.271(9)	W(2)–C(12)	2.273(10)
C(1)–C(2)	1.418(15)	C(7)–C(12)	1.408(12)
C(2)–C(3)	1.411(14)	C(9)–F(9)	1.349(11)
C(4)–F(4)	1.350(11)	C(10)–C(11)	1.421(14)
C(5)–C(6)	1.419(15)	C(12)–F(12)	1.337(12)
C(1)–W(1)–C(2)	36.6(4)	C(1)–W(1)–C(3)	65.6(3)
C(2)–W(1)–C(3)	36.3(3)	C(1)–W(1)–C(4)	77.1(3)
C(2)–W(1)–C(4)	64.8(3)	C(3)–W(1)–C(4)	35.7(3)
C(1)–W(1)–C(5)	64.9(4)	C(2)–W(1)–C(5)	76.3(4)
C(3)–W(1)–C(5)	64.6(4)	C(4)–W(1)–C(5)	36.2(4)
C(1)–W(1)–C(6)	35.5(3)	C(2)–W(1)–C(6)	64.6(4)
C(3)–W(1)–C(6)	76.6(3)	C(4)–W(1)–C(6)	65.4(3)
C(5)–W(1)–C(6)	36.4(4)	C(2)–W(1)–C(1A)	143.4(4)
C(3)–W(1)–C(1A)	114.5(3)	C(4)–W(1)–C(1A)	102.9(3)
C(5)–W(1)–C(1A)	115.1(4)	C(6)–W(1)–C(1A)	144.5(3)
C(3)–W(1)–C(2A)	143.7(3)	C(4)–W(1)–C(2A)	115.2(3)
C(5)–W(1)–C(2A)	103.7(4)	C(6)–W(1)–C(2A)	115.4(4)
C(4)–W(1)–C(3A)	144.3(3)	C(5)–W(1)–C(3A)	115.4(4)
C(6)–W(1)–C(3A)	103.4(3)	C(5)–W(1)–C(4A)	143.8(4)
C(6)–W(1)–C(4A)	114.6(3)	C(6)–W(1)–C(5A)	143.6(4)
C(5)–W(1)–C(6A)	143.6(4)	C(7)–W(2)–C(8)	35.9(4)
C(7)–W(2)–C(9)	65.2(4)	C(8)–W(2)–C(9)	36.1(4)
C(7)–W(2)–C(10)	77.6(3)	C(8)–W(2)–C(10)	65.4(3)
C(9)–W(2)–C(10)	36.6(3)	C(7)–W(2)–C(11)	65.3(3)
C(8)–W(2)–C(11)	76.4(4)	C(9)–W(2)–C(11)	65.2(3)
C(10)–W(2)–C(11)	36.4(3)	C(7)–W(2)–C(12)	36.1(3)
C(8)–W(2)–C(12)	64.5(4)	C(9)–W(2)–C(12)	76.8(4)
C(10)–W(2)–C(12)	65.6(4)	C(11)–W(2)–C(12)	36.3(4)
C(8)–W(2)–C(7A)	144.1(4)	C(9)–W(2)–C(7A)	114.8(4)
C(10)–W(2)–C(7A)	102.4(3)	C(11)–W(2)–C(7A)	114.7(3)
C(12)–W(2)–C(7A)	143.9(3)	C(9)–W(2)–C(8A)	143.9(4)
C(10)–W(2)–C(8A)	114.6(3)	C(11)–W(2)–C(8A)	103.6(4)
C(12)–W(2)–C(8A)	115.5(4)	C(10)–W(2)–C(9A)	143.4(3)
C(11)–W(2)–C(9A)	114.8(3)	C(12)–W(2)–C(9A)	103.2(4)
C(11)–W(2)–C(10A)	143.6(3)	C(12)–W(2)–C(10A)	114.4(4)
C(12)–W(2)–C(11A)	143.7(4)		

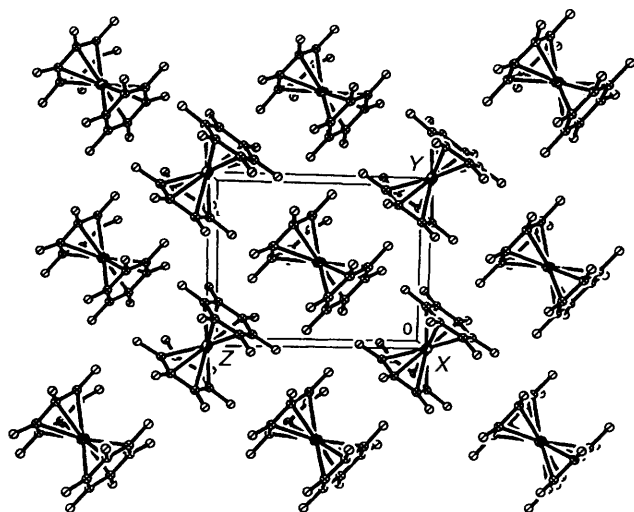


Fig. 2 Crystal structure of  $[\text{W}(\text{C}_6\text{F}_6)_2]$  **1**

obtained as red solids in *ca.* 1% yield. These products were also stable in air at room temperature but both decomposed explosively on heating above 130 °C. Using a 1:1 mixture of  $\text{C}_6\text{F}_6$  and  $\text{C}_6\text{H}_3\text{F}_3$ -1,3,5, Mo yielded **7** and  $[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3$ -1,3,5)] **9** (mole ratio *ca.* 9:1) while W gave **8**, plus  $[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3$ -1,3,5)] **10** and a detectable amount of **1**. Pure samples of **9** and **10** were not isolated from these mixtures but molecular formulae of the products were established by high-resolution mass spectroscopy and NMR spectroscopy (see Tables 3 and 4). The  $^{19}\text{F}$  NMR spectra of **9** and **10** were fully resolvable because of the large inter-ring F–F and F–H coupling constants and are nice text-book examples of spectra (see Fig. 3). Thus, the  $^{19}\text{F}$  resonances of the co-ordinated 1,3,5-trifluorobenzene molecules in **9** and **10** and the  $^1\text{H}$  resonance of **10** appear as septets of quartets. The  $^{19}\text{F}$  resonance of the hexafluorobenzene in **10** has the form of a quartet of quartets. In **9**, a 10-line 1:3:6:10:12:12:10:6:3:1 multiplet is observed. This is as expected for an overlapping quartet of quartets with  $J = 2J'$ . Similarly, the  $^1\text{H}$  resonance of **9** appears as a 16-line 1:3:9:19:33:51:65:75:75:65:51:33:19:9:3:1 multiplet (the 1 and 3 lines were barely visible) due to an overlapping septet of

**Table 2** NMR data ( $^1\text{H}$  and  $^{19}\text{F}$ ) for the complexes\*

Compound	$\delta(^1\text{H}), \text{J/Hz}$	$\delta(^{19}\text{F}), \text{J/Hz}$
$[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{Me}_3-1,3,5)]$ <b>5</b>	4.64 (spt, $\text{C}_6\text{H}_3\text{Me}_3$ , $J_{\text{HF}} = 1.7$ ), 1.77 (s, $\text{C}_6\text{H}_3\text{Me}_3$ )	-179.2 (q, $\text{C}_6\text{F}_6$ , $J_{\text{HF}} = 1.7$ )
$[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$ <b>3</b>	4.47 (spt, $\text{C}_6\text{H}_6$ , $J_{\text{HF}} = 1.9$ )	-176.8 (spt, $\text{C}_6\text{F}_6$ , $J_{\text{HF}} = 1.9$ )
$[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3-1,3,5)]$ <b>9</b>	4.85 (m, $\text{C}_6\text{H}_3\text{F}_3$ )	-177.3 (qq, $\text{C}_6\text{F}_6$ , $J_{\text{HF}'} = 2.8$ , $J_{\text{F}''} = 5.6$ ) -150.6 (spq, $\text{C}_6\text{H}_3\text{F}_3$ , $J_{\text{HF}'} = 1.4$ , $J_{\text{F}''} = 5.6$ ) -177.7 (s, $\text{C}_6\text{F}_6$ ) -157.3 (m, $\text{C}_6\text{H}_3\text{F}_3$ )
$[\text{Mo}(\text{C}_6\text{F}_6)_2]$ <b>2</b>		-173.7 (q, $\text{C}_6\text{F}_6$ , $J_{\text{HF}} = 2.6$ ) -170.1 (spt, $\text{C}_6\text{F}_6$ , $J_{\text{HF}} = 2.5$ )
$[\text{Mo}(\text{C}_6\text{H}_3\text{F}_3-1,3,5)_2]$ <b>7</b>	5.20 (m, $\text{C}_6\text{H}_3\text{F}_3$ )	-173.8 (qq, $\text{C}_6\text{F}_6$ , $J_{\text{HF}'} = 3.5$ , $J_{\text{F}''} = 8.3$ ) -153.5 (spq, $\text{C}_6\text{H}_3\text{F}_3$ , $J_{\text{HF}'} = 1.2$ , $J_{\text{F}''} = 8.3$ )
$[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{Me}_3-1,3,5)]$ <b>6</b>	4.56 (spt, $\text{C}_6\text{H}_3\text{Me}_3$ , $J_{\text{HF}} = 2.6$ ), 1.86 (s, $\text{C}_6\text{H}_3\text{Me}_3$ )	-176.9 (s, $\text{C}_6\text{F}_6$ ) [ $^{183}\text{W}$ (14%) d, $J_{\text{WF}} = 14.6$ ] -157.9 (m, $\text{C}_6\text{H}_3\text{F}_3$ )
$[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$ <b>4</b>	4.38 (spt, $\text{C}_6\text{H}_6$ , $J_{\text{HF}} = 2.5$ )	
$[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3-1,3,5)]$ <b>10</b>	5.00 (m, $\text{C}_6\text{H}_3\text{F}_3$ )	
$[\text{W}(\text{C}_6\text{F}_6)_2]$ <b>1</b>		
$[\text{W}(\text{C}_6\text{H}_3\text{F}_3-1,3,5)_2]$ <b>8</b>	5.51 (m, $\text{C}_6\text{H}_3\text{F}_3$ )	

\* Proton NMR spectra run in  $\text{C}_6\text{D}_6$  on a JEOL GX270 instrument, chemical shifts quoted in ppm from  $\text{SiMe}_4$  referenced against  $\text{C}_6\text{H}_6$  at  $\delta$  7.2;  $^{19}\text{F}$  NMR run in  $\text{C}_6\text{D}_6$  on JEOL FX90Q and JNM-A500 instruments, chemical shifts quoted in ppm from  $\text{CFCl}_3$  (external reference). Abbreviations: s = singlet, q = quartet, spt = septet, m = multiplet, spq = septet of quartets, qq = quartet of quartets.

**Table 3** High-resolution mass spectral data<sup>a</sup>

Compound	$m/z^b$
<b>1</b> $\text{C}_{12}\text{F}_{12}\text{W}$	553.9310 (553.9291)
<b>2</b> $\text{C}_{12}\text{F}_{12}\text{Mo}$	463.8905 (463.8871)
<b>3</b> $\text{C}_{12}\text{H}_6\text{F}_6\text{Mo}$	355.9445 (355.9436)
<b>4</b> $\text{C}_{12}\text{H}_6\text{F}_6\text{W}$	445.9832 (445.9857)
<b>5</b> $\text{C}_{15}\text{H}_{12}\text{F}_6\text{Mo}$	397.9940 (397.9906)
<b>6</b> $\text{C}_{15}\text{H}_{12}\text{F}_6\text{W}$	488.0310 (488.0326)
<b>7</b> $\text{C}_{12}\text{H}_6\text{F}_6\text{Mo}$	355.9432 (355.9436)
<b>8</b> $\text{C}_{12}\text{H}_6\text{F}_6\text{W}$	445.9892 (445.9857)
<b>9</b> $\text{C}_{12}\text{H}_3\text{F}_9\text{Mo}$	409.9178 (409.9154)
<b>10</b> $\text{C}_{12}\text{H}_3\text{F}_9\text{W}$	499.9606 (499.9571)

<sup>a</sup> Measurements on  $^{92}\text{Mo}$  and  $^{182}\text{W}$  peaks. <sup>b</sup> Required values given in parentheses.

quartets with  $J = 2J'$ . This marked inter-ring coupling was noted earlier as a feature of the NMR spectra of  $[\text{Cr}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)]$ .<sup>1,2</sup> However, with **7** and **8**, the  $^{19}\text{F}$  or  $^1\text{H}$  spectra had the form of a centre peak with shoulders which could not be resolved at 500 MHz implying a much less favourable balance of intra- and inter-ring coupling constants.

## Discussion

Compounds **1** and **2**, the first bis(hexafluorobenzene) complexes of metals to be reported, are remarkably stable and resistant to air oxidation compared with many other bis(arene) complexes of Mo and W with less electron withdrawing substituents. In **1**, the average W-C and C-C bond lengths are effectively the same as those reported for bis(toluene)tungsten.<sup>8</sup> The similarity of these values indicates the metal-arene bonding in **1** is not apparently unusual. This is surprising and may be a result of a balancing of relative  $\sigma$ -donor and  $\pi$ -acceptor properties of hexafluorobenzene and toluene. The former should be a weaker  $\sigma$  donor and stronger  $\pi$  acceptor than the latter.<sup>6</sup>

The low yields in the W and Mo atom reactions with hexafluorobenzene are probably due to a combination of factors. Hexafluorobenzene is clearly not a weakly bonded ligand once it is  $\eta^6$ -co-ordinated. Nevertheless, addition of  $\text{C}_6\text{F}_6$  has a powerful electron withdrawing effect on the metal. Ozin and co-workers<sup>5</sup> have shown that in the co-ordinatively unsaturated half-sandwich  $[\text{V}(\text{C}_6\text{F}_6)]$  the vanadium has an effective oxidation state of  $> 1$ . The effective oxidation states of Mo and W after co-ordination of one hexafluorobenzene molecule will be similarly raised making them less attractive sites for further co-ordination from  $\pi$  bonds. With vanadium or chromium, no  $[\text{M}(\text{C}_6\text{F}_6)_2]$  appears to be formed and this may be because the high effective oxidation of the metal in the

**Table 4** Atomic coordinates ( $\times 10^4$ ) for  $[\text{W}(\text{C}_6\text{F}_6)_2]$  **1**

Atom	x	y	z
W(1)	5000	5000	5000
C(1)	4705(12)	4142(11)	3064(9)
F(1)	3389(9)	4600(8)	2260(5)
C(2)	6351(14)	4825(12)	2951(9)
F(2)	6529(10)	5973(8)	2096(6)
C(3)	7768(13)	4300(11)	3749(8)
F(3)	9333(9)	4950(9)	3615(6)
C(4)	7565(12)	3113(10)	4610(9)
F(4)	8977(8)	2568(7)	5319(6)
C(5)	5976(16)	2389(10)	4682(10)
F(5)	5819(10)	1220(7)	5488(6)
C(6)	4532(13)	2927(10)	3896(9)
F(6)	3035(8)	2209(7)	3948(6)
W(2)	0	0	0
C(7)	2103(13)	1630(12)	-445(10)
F(7)	3701(8)	1688(8)	40(6)
C(8)	2141(13)	735(13)	-1535(9)
F(8)	3786(9)	-110(9)	-2076(7)
C(9)	462(15)	672(12)	-2059(9)
F(9)	498(10)	-156(8)	-3125(5)
C(10)	-1296(12)	1564(10)	-1530(8)
F(10)	-2873(8)	1586(8)	-2057(5)
C(11)	-1319(14)	2511(12)	-450(9)
F(11)	-2935(8)	3404(8)	75(6)
C(12)	381(14)	2530(11)	92(9)
F(12)	334(10)	3477(8)	1076(5)

$\text{M}(\text{C}_6\text{F}_6)$  half sandwich precludes addition of a second  $\text{C}_6\text{F}_6$  molecule, an effect less important for second- and third-row transition metals.<sup>1,2,5</sup>

With a mixture of benzene and hexafluorobenzene, no bis(benzene)-molybdenum or -tungsten was isolated. As these compounds are quite stable and are not reactive towards hexafluorobenzene at room temperature or below, it seems very likely that they were never formed. Instead, we hypothesise that any  $\text{M}(\text{C}_6\text{H}_6)$  half-sandwich species formed were destroyed by oxidative addition of  $\text{C}_6\text{F}_6$ . So the only successful route to the mixed sandwich products  $\text{M}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)$  was through formation of a  $\text{M}(\text{C}_6\text{F}_6)$  half-sandwich which then added  $\text{C}_6\text{H}_6$ . Very little  $\text{M}(\text{C}_6\text{F}_6)_2$  was formed suggesting that  $\text{C}_6\text{H}_6$  competes successfully with  $\text{C}_6\text{F}_6$  for addition to the  $\text{M}(\text{C}_6\text{F}_6)$  half-sandwich species.

We note, without offering a convincing explanation, a variety of trends in the  $^{19}\text{F}$  NMR chemical shift data in Table 1. Considering the co-ordinated  $\text{C}_6\text{F}_6$  ligand in the range of compounds  $[\text{M}(\text{C}_6\text{F}_6)(\text{arene})]$ , the  $^{19}\text{F}$  chemical shift moves to lower field as the other arene changes from  $\text{C}_6\text{F}_6$  to  $\text{C}_6\text{H}_3\text{F}_3-1,3,5$  to  $\text{C}_6\text{H}_6$ . However, considering the  $\text{C}_6\text{H}_3\text{F}_3-1,3,5$  ligand in

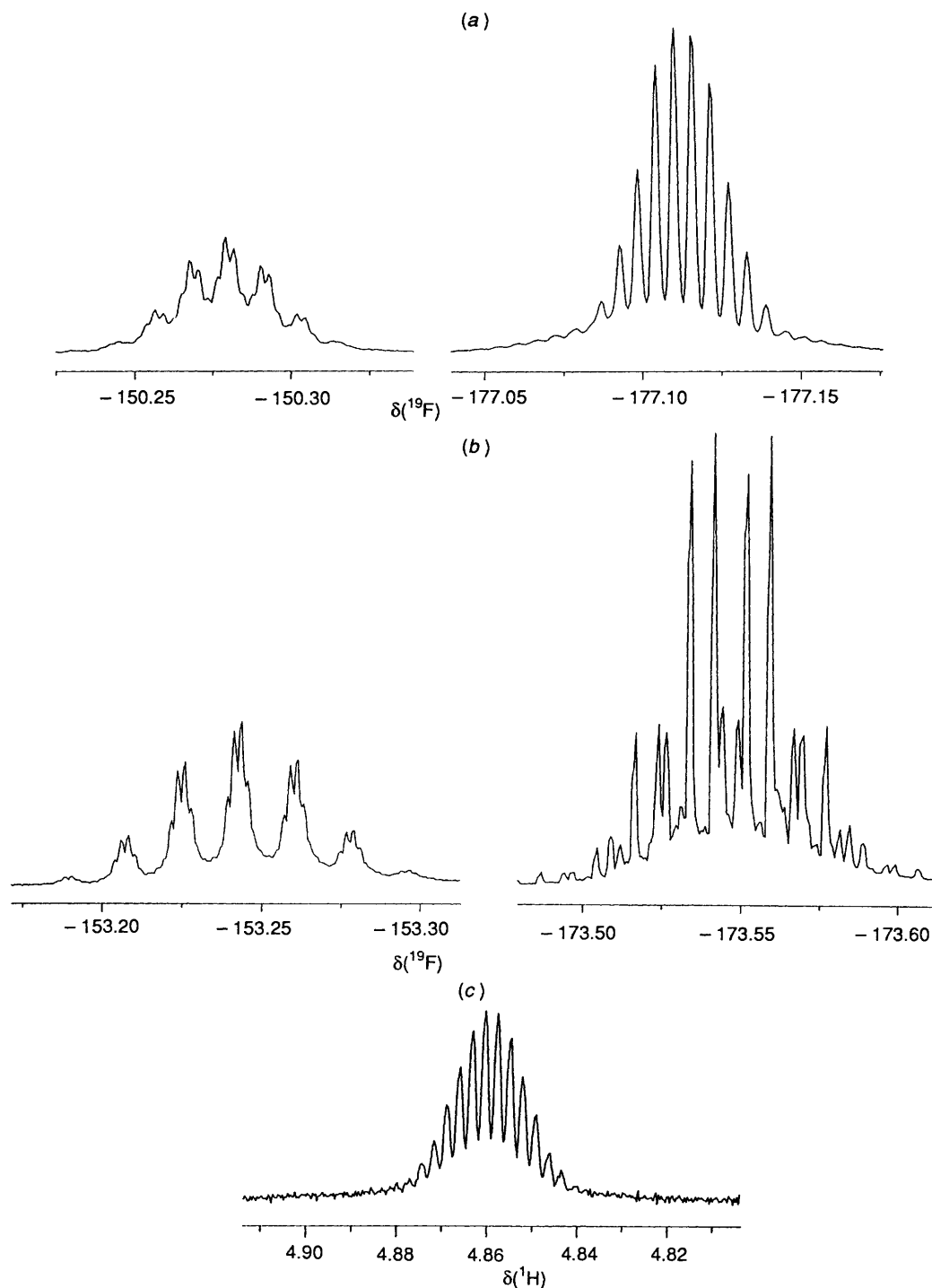


Fig. 3 Fluorine-19 NMR spectrum of  $[\text{Mo}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3-1,3,5)]$  **9** (a) and  $[\text{W}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_3\text{F}_3-1,3,5)]$  **10** (b) and  $^1\text{H}$  NMR spectrum of **9** (c)

the complexes  $[\text{M}(\text{C}_6\text{H}_3\text{F}_3-1,3,5)(\text{arene})]$ , the  $^{19}\text{F}$  chemical shift moves to higher field as the other arene changes from  $\text{C}_6\text{F}_6$  to  $\text{C}_6\text{H}_3\text{F}_3-1,3,5$ . As an additional complication, changing the other ligand from  $\text{C}_6\text{H}_6$  to  $\text{C}_6\text{H}_3\text{Me}_3-1,3,5$  causes the  $\text{C}_6\text{F}_6$   $^{19}\text{F}$  chemical shift to move upfield in both the molybdenum and tungsten compounds.

The mass spectra of the tungsten compounds also show fascinating features, notably the formation of  $\text{WC}_5\text{F}_4^+$  from **1** and **4** and the corresponding  $\text{WC}_5\text{FH}_3^+$  from **8**, ions which appear to involve loss of an arene ring and a  $\text{CF}_2$  group, and the formation of  $\text{C}_6\text{F}_2^+$  by fluorine transfer to the tungsten. The observation of both  $\text{WF}_4^+$  and  $\text{WF}_3^+$  attests to the importance of fluorine transfer processes. The corresponding molybdenum

compounds show a high abundance of  $\text{Mo}^+$  and there is no clear evidence of elimination of carbon from metal-bound  $\text{C}_6\text{F}_6$  or  $\text{C}_6\text{H}_3\text{F}_3-1,3,5$ .

The formation of  $[\text{W}(\eta^6\text{-C}_6\text{F}_6)_2]$  and related stable complexes of Mo and W significantly extends the known role of hexafluorobenzene as a ligand. We are finding that reactions involving  $\text{C}_6\text{F}_6$  and atoms of some other second- and third-row transition metal also lead to stable  $\eta^4$ - or  $\eta^6$ - $\text{C}_6\text{F}_6$  complexes so that a much wider range of hexafluorobenzene complexes will become accessible. Metal atom chemistry, while experimentally demanding, has often shown the way to making new types of compounds for which more convenient non-atom syntheses are then devised<sup>9</sup> and we believe our work on hexafluorobenzene

will stimulate conventional organometallic synthesis in this area.

## Experimental

**Reaction Procedures.**—In most experiments, molybdenum or tungsten was evaporated under a vacuum of 0.001 Pa using an electrostatically focussed gun<sup>10</sup> in which the electron beam, generated from a circular tungsten wire filament, was focussed to hit the bottom end of a vertically mounted, uncooled 6.5 mm rod of the metal held at +6 kV with respect to the filament. A pendant drop of evaporating metal formed and, as this was consumed by downward evaporation, the rod was advanced from above into the electron beam using a micrometer screw feed mechanism. The gun was suspended within the 250 mm diameter stainless steel vacuum system used in some of the earliest experiments in metal atom chemistry.<sup>11</sup> Molybdenum and tungsten atoms condensed on the liquid nitrogen cooled reaction vessel walls together with excess of the vapour of the ligand to give a solid matrix containing metal and arene in a 1:10 to 1:15 mol ratio. With optimum electron focussing, the power level required to evaporate molybdenum and tungsten at a rate of 2 g per h was 300 W for molybdenum and 720 W for tungsten. Only about 50% of metal evaporated would have reached the reactor walls as atoms as much was lost in the shield structure of the electron gun. In some experiments, the metal was evaporated from the water-cooled hearth of a magnetically deflected electron gun and at least 50% more electron beam power was required to achieve the same evaporation rate. A slightly higher proportion of evaporated metal reached the reactor walls as atoms from this gun. However, the weight of metal given for each experiment below was simply the amount evaporated and the yield was calculated from this without correction for losses.

At the end of a run lasting from 20 to 120 min, the reactor was warmed to room temperature, unreacted ligand was pumped out as vapour, and the product was either sublimed out with prolonged pumping through a 50 mm pumping line to a liquid-nitrogen cooled trap, or it was washed out with an organic solvent and recovered by sublimation after evaporation of the solvent: <sup>19</sup>F NMR spectroscopy showed some of the sublimed products to be contaminated with a few percent of decafluorobiphenyl which was removed in most cases by recrystallization from pentane. Products were characterised by NMR and high-resolution mass spectrometry.

**Instrumental Procedures.**—Low- and high-resolution mass spectroscopy was carried out on a AEI MS902 instrument *via* a probe inlet: the *m/z* values are given of <sup>92</sup>Mo and <sup>182</sup>W but intensities of these ions have been increased by factors of 6.31 and 3.79 respectively to reflect the total intensity of Mo and W containing ions. Proton and <sup>19</sup>F NMR spectra were run in C<sub>6</sub>D<sub>6</sub> solution on JEOL GX270 and FX90Q or JNM Alpha-500 spectrometers respectively.

**Crystal Structure Analysis of [W(C<sub>6</sub>F<sub>6</sub>)<sub>2</sub>] 1.**—*Crystal data.* C<sub>12</sub>F<sub>12</sub>W, *M* = 556.0, triclinic, space *P*1̄ (no. 2), *a* = 7.235(2), *b* = 8.697(4), *c* = 10.611(3) Å, α = 88.85(3), β = 83.29(2), γ = 79.39(2)°, *U* = 651.8(4) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 2.833 g cm<sup>-3</sup>, λ = 0.710 73 Å, μ = 9.00 mm<sup>-1</sup>, *F*(000) = 508, *T* = 295 K.

Diffraction measurements were made with a Siemens four-circle P3m diffractometer using graphite-monochromated Mo-Kα X-radiation on a single crystal mounted in a thin-walled glass capillary under N<sub>2</sub>. Cell dimensions were determined from the setting angle values of 14 centred reflections. A total of 2980 diffracted intensities (including checks) were measured in a unique hemisphere of reciprocal space for 4.0 < 2θ < 55.0° by Wyckoff ω scans. Three check reflections remeasured after every 50 ordinary data showed no decay and *ca.* 2% variation over the period of data collection. Of the non-check intensity data collected, 2829 unique observations remained after averaging of

duplicate and equivalent measurements and deletion of systematic absences, of these 2054 with *I* > 2σ(*I*) were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 374 azimuthal scan data, maximum and minimum transmission coefficients were 0.524 and 0.130 respectively. Lorentz and polarization corrections were applied. The structure was solved by heavy-atom (Patterson and Fourier difference) methods, and refined by full-matrix least squares against *F*. The two unique tungsten atoms lie at sites of crystallographic inversion symmetry at (0,0,0) and (0.5,0.5,0.5), there being two distinct half-molecules per asymmetric unit. All atoms were assigned anisotropic displacement parameters and an extinction parameter χ refined [χ = 0.0050(4) where *F*\* = *F*(1 + 0.002χ*F*<sup>2</sup>/sin2θ)<sup>-0.25</sup>]. Refinement of the 230 least-squares variables converged smoothly to residual indices *R* = 0.042, *R*' = 0.057, *S* = 1.97.†

Weights, *w*, were set equal to [σ<sub>c</sub><sup>2</sup>(*F*<sub>o</sub>) + *gF*<sub>o</sub><sup>2</sup>]<sup>-1</sup> where σ<sub>c</sub><sup>2</sup>(*F*<sub>o</sub>) is the variance in *F*<sub>o</sub> due to counting statistics and *g* = 0.0007 was chosen to minimize the variation in *S* as a function of *F*<sub>o</sub>. Final difference electron density maps showed no features outside the range +2.0 to -2.35 e Å<sup>-3</sup> the largest of which were within 1 Å of the metal atoms. Table 4 reports the atomic positional parameters.

Additional material available from the Cambridge Crystallographic Data centre comprises thermal parameters and remaining bond lengths and angles.

All calculations were made with programs of the SHELXTL PLUS<sup>12</sup> system as implemented on a Siemens R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 13.

**Specific Reactions.**—*Tungsten + hexafluorobenzene.* Tungsten atoms (2.03 g, 11 mmol) were condensed with 55.6 g (300 mmol) C<sub>6</sub>F<sub>6</sub> in 2 h; the unreacted C<sub>6</sub>F<sub>6</sub> (52.1 g, 280 mmol) was pumped out at 0 °C and then 1 was pumped out at 30 °C. Yield 0.155 g (0.028 mmol), 2.5%, of a pale yellow, quite volatile solid, *T*<sub>decomp</sub> 180 °C (air or N<sub>2</sub>); *m/z* 554 (100%, *M*<sup>+</sup>), 368 (5, *M* - C<sub>6</sub>F<sub>6</sub>), 349 (24, *M* - C<sub>6</sub>F<sub>6</sub> - F), 330 (6, *M* - C<sub>6</sub>F<sub>6</sub> - 2F), 318 (19, *M* - C<sub>6</sub>F<sub>6</sub> - CF<sub>2</sub>), 306 (7, *M* - C<sub>6</sub>F<sub>6</sub> - C<sub>2</sub>F<sub>2</sub>), 258 (72, WF<sub>4</sub><sup>+</sup>), 239 (28, WF<sub>3</sub><sup>+</sup>), 186 (21, C<sub>6</sub>F<sub>6</sub><sup>+</sup>) and 110 (76, C<sub>6</sub>F<sub>2</sub><sup>+</sup>). A crystal suitable for X-ray was grown from a cooled hexane solution.

A dark brown, air-sensitive solid remained in the reactor after 1 was pumped out. From a mass balance on the tungsten and hexafluorobenzene used in the reaction and by analysis on the solid, its composition was determined as close to WC<sub>6</sub>F<sub>6</sub>.

*Tungsten + hexafluorobenzene and benzene.* Tungsten (0.82 g, 4.5 mmol) evaporated over 2 h with the magnetic deflection electron gun was condensed at -196 °C with a mixture of C<sub>6</sub>F<sub>6</sub> (9.7 g, 52 mmol) and C<sub>6</sub>H<sub>6</sub> (4.1 g, 52 mmol). Washing out at room temperature with methylcyclohexane and purification gave 3 contaminated by a trace (<2%) of 1. Yield 70 mg (0.16 mmol), 3.5%, of a yellow-green air-stable solid; *m/z* 446 (23.5%, *M*<sup>+</sup>), 368 (13.6, *M* - C<sub>6</sub>H<sub>6</sub>), 349 (1.4, *M* - C<sub>6</sub>F<sub>6</sub> - F), 317 (2.9, *M* - C<sub>6</sub>H<sub>6</sub> - CF<sub>2</sub>), 296 (1.2, *M* - C<sub>6</sub>F<sub>4</sub>), 277 (1.4, *M* - C<sub>6</sub>F<sub>5</sub>), 258 (11.2, *M* - C<sub>6</sub>F<sub>6</sub>), 186 (5.0, C<sub>6</sub>F<sub>6</sub><sup>+</sup>), 110 (30.0, C<sub>6</sub>F<sub>2</sub><sup>+</sup>) and 78 (100, C<sub>6</sub>H<sub>6</sub><sup>+</sup>).

A crystal suitable for crystallography was grown from a cooled pentane solution but X-ray analysis showed it to be disordered.

*Tungsten + hexafluorobenzene + 1,3,5-trimethylbenzene.* Tungsten atoms (1.33 g, 7.3 mmol) were condensed over 40 min with a mixture of C<sub>6</sub>F<sub>6</sub> (10 g, 53 mmol) and C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>-1,3,5 (6.5 g, 53 mmol) at -196 °C. Washing out with hexane and sublimation gave pure 6. Yield 77 mg, 2.2%, of a yellow-orange solid which decomposed on standing in air; *m/z* 488 (100%,

† *R* = Σ|Δ|/Σ|*F*<sub>o</sub>|, *R*' = [Σ*w*Δ<sup>2</sup>/Σ*wF*<sub>o</sub><sup>2</sup>]<sup>1/2</sup>, *S* = [Σ*w*Δ<sup>2</sup>/(*N*<sub>o</sub> - *N*<sub>v</sub>)]<sup>1/3</sup> where Δ = *F*<sub>o</sub> - *F*<sub>c</sub> and *N*<sub>o</sub> and *N*<sub>v</sub> are the number of observations and variables respectively.

$M^+$ ), 368 (25,  $M - C_9H_{12}$ ), 318 (7,  $M - C_9H_{12} - CF_2$ ) and 302 (5,  $M - C_6F_6$ ) {only tungsten containing peaks are listed, with the parent ion assigned as base peak, because part of the non-tungsten containing ions appeared to arise through thermal decomposition}.

**Tungsten + 1,3,5-trifluorobenzene.** Tungsten atoms (0.43 g, 2.4 mmol), formed in an electrostatically focussed electron gun at 600 W) were condensed at  $-196^\circ C$  over 2 h with  $C_6H_3F_3-1,3,5$  (18 g, 136 mmol). Washing with pentane at room temperature followed by purification gave **8**. Yield 13 mg (0.035 mmol), 1.5%, of a brick-red, air-stable solid;  $T_{\text{explosion}}$   $137^\circ C$  air,  $150^\circ C$   $N_2$ ;  $m/z$  446 (100%,  $M^+$ ), 314 (26,  $M - C_6H_3F_3$ ), 294 (25,  $M - C_6H_3F_3 - HF$ ), 288 (32,  $WC_4F_3H^+$ ), 264 (53,  $WC_5H_3F^+$ ), 239 (17,  $WF_3^+$ ) and 220 (9,  $WF_2^+$ ).

**Tungsten + hexafluorobenzene and 1,3,5-trifluorobenzene.** Tungsten (0.85 g, 5.1 mmol) evaporated over 2 h with the magnetic deflection electron gun was condensed at  $-196^\circ C$  with a mixture of  $C_6F_6$  (8.8 g, 4.7 mmol) and  $C_6H_3F_3-1,3,5$  (6.0 g, 4.5 mmol). Washing out at room temperature with toluene gave 15 mg of a yellow-orange solid, shown by  $^{19}F$  NMR spectroscopy to contain a mixture of **1**, **8** and **10** and 1:4:8 mole ratio.

**Molybdenum + hexafluorobenzene.** Molybdenum atoms (0.60 g, 6.3 mmol) were condensed in 20 min with  $C_6F_6$  (16 g, 86 mmol) at  $-196^\circ C$ . The product was washed out with pentane at room temperature and purified by recrystallization to give **2**. Yield 20 mg (0.042 mmol), 0.7%, of a yellow, volatile solid,  $T_{\text{decomp}}$   $135^\circ C$  (air),  $180^\circ C$  ( $N_2$ );  $m/z$  464 (64%,  $M^+$ ), 445 (4,  $M - F$ ), 278 (6,  $M - C_6F_6$ ), 257 (11,  $M - C_6F_6 - F$ ), 186 (5,  $C_6F_6^+$ ), 149 (13,  $MoF_3^+$ ), 130 (15,  $MoF_2^+$ ), 129 (8,  $C_6F_3^+$ ), 111 (18,  $MoF^+$ ), 110 (20,  $C_6F_2^+$ ), 92 (100,  $Mo^+$ ) and 79 (17,  $C_5F^{+?}$ ).

**Molybdenum + hexafluorobenzene + benzene.** Molybdenum atoms (1.7 g, 18 mmol) were condensed in 2 h with a mixture of  $C_6F_6$  (14.5 g, 78 mmol) and  $C_6H_6$  (6.1 g, 78 mmol) at  $-196^\circ C$ . The only sublimable product in the pentane wash was **3**. Yield 80 mg (0.22 mmol), 1.2%, of greenish-yellow crystals, unstable in air above  $35^\circ C$ ,  $T_{\text{decomp}}$  ( $N_2$ )  $130^\circ C$ ;  $m/z$  356 (100%,  $M^+$ ), 278 (14,  $M - C_6H_6$ ), 170 (99,  $M - C_6F_6$ ), 110 (9,  $C_6F_2^+$ ), 92 (53,  $Mo^+$ ) and 78 (23,  $C_6H_6^+$ ).

**Molybdenum + 1,3,5-trifluorobenzene.** Molybdenum atoms (1.2 g, 12.5 mmol) were condensed in 1 h with  $C_6H_3F_3-1,3,5$  (12.0 g, 91 mmol) at  $-196^\circ C$ . Washing out with pentane, followed by sublimation gave **7**. Yield 37 mg (0.1 mmol), 0.8%, of vermilion crystals,  $T_{\text{explosion}}$   $135^\circ C$  (air),  $176^\circ C$  ( $N_2$ );  $m/z$  356 (100%,  $M^+$ ), 224 (36,  $M - C_6H_3F_3$ ), 294 (17,  $M - C_6H_3F_3 - HF$ ), 132 (5,  $C_6H_3F_3^+$ ), 130 (16,  $MoF_2^+$ ), 113 (4,  $C_6H_2F_3^+$ ), 111 (15,  $MoF^+$ ) and 92 (99,  $Mo^+$ ).

**Molybdenum + hexafluorobenzene + 1,3,5-trifluorobenzene.** Molybdenum atoms (0.83 g, 8.6 mmol) were evaporated in 2 h with the magnetic electron gun and the vapour was condensed with  $C_6H_6$  (8.5 g, 46 mmol) and  $C_6H_3F_3-1,3,5$  (6.0 g, 45 mmol) at  $-196^\circ C$ . Only a few milligrams of toluene-soluble product were obtained, which was shown by MS to be a mixture of **7** and **9** in a mole ratio, determined by NMR spectroscopy, of about 2:1.

**Molybdenum + hexafluorobenzene + 1,3,5-trimethylbenzene.** Molybdenum atoms (0.78 g, 8 mmol) were condensed in 25 min with a mixture of  $C_6F_6$  (4.9 g, 26 mmol) and  $C_6H_3Me_3-1,3,5$  (3.1 g, 26 mmol) at  $-196^\circ C$ . Washing with pentane and sublimation gave pure **5**. Yield 218 mg (0.54 mmol), 6.7%, of orange-brown crystals;  $m/z$  398 (100%,  $M^+$ ), 212 (87,  $M - C_6F_6$ ), 119 (48,  $C_9H_{11}^+$ ) and 92 (11,  $Mo^+$ ).

### Acknowledgements

We are grateful to the SERC for research support and for studentships to J. J. B. and A. J. S., to ICI for supplementing the studentship to A. J. S., and to Dr. M. Murray for help with the NMR data.

### References

- 1 R. Middleton, J. R. Hull, S. R. Simpson, C. H. Tomlinson and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1973, 120.
- 2 T. S. Tan and M. J. McGlinchey, *J. Am. Chem. Soc.*, 1976, **98**, 2271.
- 3 V. Graves and J. J. Lagowski, *Inorg. Chem.*, 1976, **15**, 577.
- 4 K. J. Klabunde and H. F. Efnér, *J. Fluorine Chem.*, 1974, **4**, 114.
- 5 M. P. Andrews, S. M. Mattar and G. A. Ozin, *J. Phys. Chem.*, 1986, **90**, 744.
- 6 W. D. Jones, M. G. Partridge and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1991, 264; T. W. Bell, M. Helliwell, M. G. Partridge and R. N. Perutz, *Organometallics*, 1992, **11**, 1911.
- 7 S. T. Belt, M. Helliwell, W. D. Jones, M. G. Partridge and R. N. Perutz, *J. Am. Chem. Soc.*, 1993, **115**, 1429.
- 8 K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F. Ming Miao and J. Woolcock, *Acta Crystallogr., Sect. B*, 1982, **38**, 456.
- 9 W. Gausling and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 186; H. Bonneman and B. Karoll, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1490.
- 10 P. L. Timms, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 272; M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119.
- 11 P. L. Timms, *J. Chem. Soc. A*, 1970, 2526.
- 12 G. M. Sheldrick, SHELXTL PLUS Revision 2.4, Göttingen, 1988.
- 13 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 5th July 1993; Paper 3/03875K