

Linda H. Doerrer, Andrew J. Graham, Daniel Haussinger and Malcolm L. H. Green*

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

Received 29th October 1999, Accepted 14th January 2000 Published on the Web 9th February 2000

The syntheses of the new compounds $[W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_2R\})H_3]$, where $R = (C_6F_5) \mathbf{1}$, Ph **2**, H **3** or Cl **4**, $[Mo(\eta-C_5H_5)_2(H)(\eta^1-HB(C_6F_5)_3)] \mathbf{5}$, $[Mo(\eta-C_5H_5)_2(H)(\eta^1-H_2B(C_6F_5)_2)] \mathbf{6}$, $[Mo(\eta-C_5H_4Me)_2(H)(\eta^1-HB(C_6F_5)_3)] \mathbf{7}$, $[Re(\eta-C_5H_5)(\eta-C_5H_4B(C_6F_5)_3)H_2]\cdot 0.5C_6H_5Me \mathbf{8}$, $[Ta(\eta-C_5H_5)_2(H)_2(\eta^1-HB(C_6F_5)_3)] \mathbf{9}$ and $[Re(\eta-C_5H_5)(\eta-C_5H_4-\{B(C_6F_5)_2\})(C_6F_5)] \mathbf{10}$ are described. The crystal structures of compounds **4** and **10** have been determined. Initial electrophilic addition of the Lewis acid $B(C_6F_5)_3$ occurs either by *exo*-addition to a carbon of a η -cyclopentadienyl ring with formation of an *exo*-{ $(C_6F_5)_3B\}C_5H_5$, or by formation of an $M-\mu$ -H–B two-electron three-centre bond.

The strong Lewis acid $B(C_6F_5)_3$ has been shown to add to metal–alkyl and metal–hydrogen bonds to form two-electron three-center systems such as M– μ -Me– $B(C_6F_5)_3^1$ and M– μ -H– $B(C_6F_5)_3^2$. We have recently explored the addition reactions of $B(C_6F_5)_3$ to transition metal-oxo³ and -nitrido⁴ compounds. The compound $B(C_6F_5)_3$ also reacts in an unexpected manner with the compounds $[M(\eta-C_5H_5)(CO)_mMe]$, where M = Fe and n = 2 or M = Mo, W and n = 3, and in these cases transfer of a fluoroaryl group occurs.⁵ Other related transfer reactions have also been described.⁶

Since there are relatively few systematic studies of the reactions of Lewis acid molecules with transition metal compounds and since the organo-borane $B(C_6F_5)_3$ is a readily available^{5b,7} thermally stable crystalline compound, we have set out to explore its reactions more widely. Here we report the reactivity of the Lewis acids $B(C_6F_5)_2R$ [$R = (C_6F_5)$, Ph, H or Cl] towards a selection of metallocene hydrides of Groups 5, 6 and 7.

Results and discussion

Treatment of the compound $[W(\eta-C_5H_5)_2H_2]$ in toluene at -78 °C with B(C₆F₅)₃ gave a deep purple solution which, on warming to ca. -50 °C, gradually became pale yellow. This final product contained substantial quantities of starting dihydride as well as several other species and no tractable products could be obtained. However, the reaction between $[W(\eta-C_5H_5)_2H_2]$ and the boranes $B(C_6F_5)_2R$, where $R = (C_6F_5)$, Ph, H or Cl, in an aliphatic solvent at ambient temperature follows an entirely different course. On addition of these boranes to $[W(\eta-C_5H_5)_2H_2]$ in petroleum ether (bp 100–120 °C), a flocculent white precipitate separated immediately. After stirring for one hour, the products were isolated by filtration and washed thoroughly with petroleum ether to remove remaining traces of $[W(\eta-C_5H_5)_2H_2]$ and $B(C_6F_5)_2R$. The zwitterionic compounds $[W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_2R\})H_3],$ where $R = (C_6F_5) \mathbf{1}$, Ph 2, H 3 or Cl 4, were obtained analytically pure in high yield, as white or off-white powdery air- and moisture-sensitive solids which are moderately soluble in aromatic solvents and dichloromethane. Donating solvents such as tetrahydrofuran were found to cause decomposition. Full characterising data for compounds 1-4 are given in Table 1.

Previously, Braunschweig and Wagner have described the closely related zwitterionic trihydride compounds $[W(\eta-C_sH_s)-$

 $(\eta-C_5H_4\{BRCl_2\})H_3]$ where $R = Pr^i$ or Bu^t which were formed by the reaction of $[W(\eta-C_5H_5)_2H_2]$ with BRCl₂.⁸ The ¹H NMR spectroscopic data and coupling constants obtained for the compounds 1–4 are closely similar to those obtained for Braunschweig's complexes.

The ¹H NMR spectra in the region δ -6.26 to -6.7 showed a doublet and a triplet (integrating in the ratio 1:2) with additional ¹⁸³W satellite peaks, a typical pattern for an AB₂X spin system. The H–H coupling constants for the WH₃ hydrogens in compounds **1** to **3** lie in the region 4.8–9.6 Hz, consistent with data reported for [W(η -C₅H₅)₂H₃]Cl.⁹ The value of ²J_{HH} for compound **2** in CD₂Cl₂ is lower (4.8 Hz), and is comparable with that observed in the compound [W(η -C₅Me₅)₂H₃][BPh₄].¹⁰ The one bond ¹⁸³W–H coupling constant (where it could be determined) is of a similar magnitude to that found in the previously cited compounds⁸⁻¹⁰ with coupling to the central hydride being greater than that to the outer ones.

The ¹¹B-{¹H} NMR spectra for compounds 1–4 showed single sharp resonances in the range δ *ca.* -7 to -25, consistent with fourfold coordinated boron. For compound 3, a doublet with ¹J_{BH} = 86 Hz was observed in the proton-coupled ¹¹B NMR spectrum. Selected infrared spectral data are listed in Table 1. All the compounds 1–4 display a weak, broad band at *ca.* 1940–1990 cm⁻¹ which may be assigned to v(W-H).⁸

Single crystals of **4** suitable for analysis by X-ray crystallography were grown by slow evaporation of a solution in benzene at ambient temperature. The molecular structure of compound **4** is given in Fig. 1 and selected bond angles and distances are summarised in Table 2. The structure is essentially similar to that of the compound $[W(\eta-C_5H_5)-(\eta-C_5H_4\{BPr^iCl_2\})H_3]$.⁸ The W–H bonds in compound **4** are slightly shorter (1.41–1.52 Å) than those of the Pr^iBCl_2 analogue (1.51–1.58 Å) and the H_{outer} –W– H_{outer} angle much tighter (115.6 vs. 141.0°).

The ¹H NMR spectra of initially pure samples of compounds 1–4 showed a slow appearance of a small quantity of $[W(\eta-C_5H_5)_2H_2]$ but the intensity of these signals did not increase after about 12 hours. This observation suggested there was a slow equilibrium dissociation of the $B(C_6F_5)_2R$ groups. Hence, compound 1 was reacted with a series of competing Lewis bases, L = NEt₃, PMe₃, THF, in the expectation that they would trap the free borane. In a typical experiment, *ca.* 20 mg of 1 was dissolved in toluene and an excess of the

	Compound ^{<i>a</i>}	NMR data ^b
1	$\begin{split} & [W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_3\})H_3] \\ & White \\ & C, 40.7 (40.6); H, 1.1 (1.5); B, 1.05 (1.3) \\ & Mass: 851, [M + Na]^+; 828, [M]^+; 660, \\ & [M - (C_6F_5) - H]^+; 316, [M - B(C_6F_5)_3]^+ \\ & IR: 1939w \ (\nu(W-H)), 1768w, 1645w, \end{split}$	¹ H: -6.38 (d, 2H, ² J_{HH} = 9.6, WH _{outer}), -6.27 (t, 1H, ² J_{HH} = 9.6, WH _{centre}), 5.23 (s, 5H, C ₅ H ₅), 5.52 and 5.56 (s, 2H, each, C ₅ H ₄ B) ¹¹ B-{ ¹ H}: -15.6 (s) ¹³ C-{ ¹ H}: 83.30 and 84.18 (s, C ₅ H ₄ B), 87.11 (br s, C ₅ H ₄ B, C _{ipso}), 96.93 (s, C ₅ H ₅), 130.46 (d, ¹ J_{CF} = 251, B(C ₆ F ₅), C _m), 137.60 (d, ¹ J_{CF} = 253, B(C ₆ F ₅), C _p), 148.46 (d, ¹ J_{CF} = 249, B(C ₆ F ₅), C _o) ^c
2	1516m, 1262s, 1089s, 975m, 833m, 800s $[W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_2(C_6H_5)\})H_3]$ Off-white C, 45.6 (45.6); H, 2.1 (2.3); B, 1.7 (1.5) Mass: 316, $[M - B(C_6F_5)_2(C_6H_5)]^+$ IR: 3551m (aromatic $v(C-H)$), 1951w (v(W-H)), 1645m, 1518m, 1103m, 1082s, 981s (81s (br)	¹ H: -6.48 (d, 2H, ${}^{2}J_{HH} = 4.8$, WH _{outer}), -6.38 (t, 1H, ${}^{2}J_{HH} = 4.8$, WH _{centre}), 4.94 and 5.38 (s, 2H each, C ₅ H ₄ B), 5.10 (s, 5H, C ₅ H ₅), 7.1–7.3 (m, 5H, C ₆ H ₅) ¹¹ B-{ ¹ H}: -13.1 (s) ¹³ C-{ ¹ H}: 71.60 and 84.03 (s, C ₅ H ₅ B), 83.42 (s, C ₅ H ₅), 87.24 (br s, C ₅ H ₄ B, C _{ipso}), 96.91 (br s, B(C ₆ H ₅), C _{ipso}), 112.60 (br s, B(C ₆ F ₅), C _{ipso}), 124.80 (s, B(C ₆ H ₅), C _m), 126.41 (s, B(C ₆ H ₅), C _p), 133.91 (s, B(C ₆ H ₅), C _p), 137.16 (d, ¹ J _{CF} = 258, B(C ₆ F ₅), C _m), 138.46 (d, ¹ J _{CF} = 239, B(C ₆ F ₅), C _p), 148.21 (d) ¹ J _{CF} = 220 B(C ₅ E), C ₁)
3	[W(η -C ₅ H ₅)(η -C ₅ H ₄ {B(C ₆ F ₅) ₂ H})H ₃] Off-white C, 39.9 (39.9); H, 1.7 (2.0); B, 1.6 (1.6) IR: 1991w (ν (W–H)), 1636w, 1510m, 1275m, 1108m, 1087m, 1073m, 1023w,	¹¹ H: -6.71 (d, $2F_{CF}^{-22.0}$, $B(C_{6}^{+}, 5)$, C_{o}^{-1}) ¹ H: -6.71 (d, $2H, {}^{2}J_{HH} = 7.6, {}^{1}J_{WH} = 4.60$, WH_{outer}), -6.44 (t, $1H, {}^{2}J_{HH} = 7.6, {}^{1}J_{WH} = 66.6$, WH_{centre}), 4.5 (br s, BH), 5.25 and 5.29 (m, $2H$, each, $C_{5}H_{4}B$), 5.33 (s, $5H, C_{5}H_{5}$) ¹¹ B: -123.4 (s) ¹¹ B: -23.4 (d, ${}^{1}J_{BH} = 86$) ¹³ C-{ ¹ H}: 71.77 and 82.67 (s, $C_{5}H_{4}B$), 84.71 (s, $C_{5}H_{5}$), 89.50 (br s, $C_{5}H_{4}B, C_{ipso}$), 136.88 (d,
4	964s (br) [W(η-C ₅ H ₃)(η-C ₅ H ₄ {B(C ₆ F ₅) ₂ Cl})H ₃] Grey-white C, 39.25 (37.9); H, 2.5 (1.7); B, 1.2 (1.55); Cl, 5.5 (5.1)	$\label{eq:constraint} \begin{array}{l} {}^{1}J_{CF} = 242, \ B(C_{6}F_{5}), \ C_{m}), \ 138.55 \ (d, \ {}^{1}J_{CF} = 242, \ B(C_{6}F_{5}), \ C_{p}), \ 148.24 \ (d, \ {}^{1}J_{CF} = 293, \ B(C_{6}F_{5}), \ C_{o}) \\ {}^{1}H: \ -6.37 \ (d, \ 2H, \ {}^{2}J_{HH} = 7.8, \ {}^{1}J_{WH} = 46.2, \ WH_{outer}), \ -6.26 \ (t, \ 1H, \ {}^{2}J_{HH} = 7.8, \ {}^{1}J_{WH} = 66.2, \\ WH_{centre}), \ 5.20 \ and \ 5.52 \ (s, \ 2H, \ each, \ C_{5}H_{4}B), \ 5.40 \ (s, \ 5H, \ C_{5}H_{5}) \\ {}^{11}B_{-}\{^{1}H\}: \ -6.7 \ (s) \\ {}^{13}C_{-}\{^{1}H\}: \ 83.71 \ (s, \ C_{5}H_{5}), \ 84.66^{d} \ (s, \ C_{5}H_{4}B), \ 87.70 \ (br \ s, \ C_{5}H_{4}B, \ C_{ipso}), \ 123.0 \ (br \ s, \ B(C_{6}F_{5}), \ C_{ipso}), \\ \end{array}$
5	IR: 1941w (ν (W–H)), 1645m, 1516m, 1280m, 1089s (br), 1019w, 974s [Mo(η -C ₅ H ₅) ₂ (H)(η ¹ -HB(C ₆ F ₅) ₃)] Blue C, 45.2 (45.4); H, 2.2 (1.6) W 2125 (10.1470)	137.16 (d, ${}^{1}J_{CF} = 264$, B(C ₆ F ₅), C _m), 139.26 (d, ${}^{1}J_{CF} = 269$, B(C ₆ F ₅), C _p), 147.54 (d, ${}^{1}J_{CF} = 239$, B(C ₆ F ₅), C _o) ¹ H: -17.5 (br s, Mo–H–B), -6.21 (s, 1H, MoH), 4.95 (s, 10H, C ₅ H ₅) ¹¹ B-{}^{1}H}: -25.8 (s) ¹¹ B: -25.8 (d, {}^{1}J_{BH} = 87) ¹³ C (1H), 25(C C, L), 127.0 (d, L), 27.0 (d,
6	IR: 2135m (ν(B–H)), 1550m, 1470s [Mo(η-C ₅ H ₅) ₂ (H)(η ¹ -H ₂ B(C ₆ F ₅) ₂)] Blue C, 44.5 (46.0); H, 1.75 (2.3); B, 1.6 (1.8) IR: ^e 3600w, 3130w, 2964w, 2930w, 2866w, 2390w, 1724w, 1645m, 1516s, 1470s,	¹¹ C-{ ¹ H}: 83.6 (s, C ₅ H ₅), 127.0 (br s, B(C ₆ F ₅), C _{ipso}), 136.65 (d, ${}^{7}J_{CF} = 256$, B(C ₆ F ₅), C _m), 138.02 (d, ${}^{1}J_{CF} = 237$, B(C ₆ F ₅), C _p), 148.36 (d, ${}^{1}J_{CF} = 229$, B(C ₆ F ₅), C _o) ¹¹ H: ${}^{f}-18.2$ (br s, Mo–H–B), -13.56 (s, 1H, MoH), 4.18 (s, 10H, C ₅ H ₅), 4.6 (br s, 1H, BH) ¹¹ B-{ ¹ H}: {}^{f}-12.1 (s) ¹³ C-{ ¹ H}: {}^{f}-63.1 (s, C ₅ H ₅). Remaining resonances not detected
7	1405m, 1340m, 1308m, 1102s, 984s $[Mo(\mu-C_{5}H_{4}Me)_{2}(H)(\eta^{1}-HB(C_{6}F_{5})_{3})]$ Blue	¹ H: ^{<i>g</i>} – 17.8 (br s, Mo–H–B), –7.01 (s, 1H, MoH), 1.27 and 1.45 (s, 3H, each, CH ₃), 3.73, 3.92, 4.04 and 4.23 (s, 2H each, C ₅ H_4 CH ₃)
8	C, 47.1 (46.9); H, 2.5 (2.1) $[\text{Re}(\eta-\text{C}_{5}\text{H}_{5})(\eta-\text{C}_{5}\text{H}_{4}\text{B}(\text{C}_{6}\text{F}_{5})_{3})\text{H}_{2}]^{h}$ Light brown C, 43.4 (43.2); H, 2.0 (1.7); B, 0.9 (1.2) Mass: 852, $[M + \text{Na}]^{+}$; 829, $[M]^{+}$; 828, $[M - \text{H}]^{+}$; 662, $[M - (\text{C}_{6}\text{F}_{5})]^{+}$; 512, $[\text{B}(\text{C}_{6}\text{F}_{5})_{3}]^{+}$; 318, $[M + \text{H} - \text{B}(\text{C}_{6}\text{F}_{5})_{3}]^{+}$; 317, $[M - \text{B}(\text{C}_{6}\text{F}_{5})_{3}]^{+}$; 167, $[(\text{C}_{6}\text{F}_{5})]^{+}$ IR: 2727m, 1644s, 1515s, 1456s, 1273s, 1000-077-858 m.	¹ H: -13.87 (s, 2H, ReH), 2.34 (s, 1.5H, $H_3CC_6H_5$), 4.98 (s, 5H, C_5H_5), 5.07 and 5.16 (br s, 2H each, C_5H_4B), 7.0–7.3 (m, 2.5H, $H_3CC_6H_5$) ¹ B-{ ¹ H}: -15.8 (s) ¹³ C-{ ¹ H}: 74.63 and 77.60 (s, C_5H_4B), 76.63 (s, C_5H_5), 84.10 (br s, C_5H_4B , C_{ipso}), 134.71 (d, ¹ $J_{CF} = 232$, B(C_6F_5), C_m), 136.76 (d, ¹ $J_{CF} = 243$, B(C_6F_5), C_p), 148.20 (d, ¹ $J_{CF} = 222$, B(C_6F_5), C_o) ^c
9	[1895, 96/s, 858m] $[Ta(\eta-C_5H_5)_2(H)_2(\eta^1-HB(C_6F_5)_3)]$ Light orange C, 40.7 (40.7); H, 1.7 (1.6); B, 1.5 (1.3)	¹ H: ^{<i>g</i>} -4.1 (br s, fwhh <i>ca</i> . 200 Hz, TaH ₂), 4.65 (s, 9H, C ₅ H ₅), 5.08 (s, 23H, C ₅ H ₅) ¹¹ B-{ ¹ H}: ^{<i>g</i>} -0.2 (s) Selected ¹³ C-{ ¹ H}: ^{<i>g</i>} 91.60 (s, C ₅ H ₅), 106.44 (s, C ₅ H ₅) ^{<i>i</i>}
^a Ai Nu	nalytical data given as found (calculated) in $\%$.	Mass spectral data (fast atom bombardment) given as m/z (assignment), selected IR data (cm ⁻¹) as probe temperature. Data given as: chemical shift (δ) (multiplicity, relative intensity, J in Hz.

^a Analytical data given as found (calculated) in %. Mass spectral data (fast atom bombardment) given as *miz* (assignment), selected IR data (cm⁻) as Nujol mulls except where stated otherwise. ^b At probe temperature. Data given as: chemical shift (δ) (multiplicity, relative intensity, *J* in Hz, assignment). Data obtained in CD₂Cl₂ except where stated otherwise. ^c B(C₆F₅), C_{ipso} resonance not detected. ^d Two coincident peaks. ^e KBr disc. ^f Data obtained in D₃CC₆D₅. ^g Data obtained in C₆D₆. ^h Obtained with one half an equivalent of co-crystallised toluene. ⁱ Peaks in *ca*. 3:1 ratio.

Lewis base added either neat (THF or NEt₃) or as a solution in petroleum ether (PMe₃). In all three cases, the solution quickly became yellow and, where $L = PMe_3$, there was precipitation of poorly soluble Me₃P·B(C₆F₅)₃. After 1 hour stirring, volatiles, including any excess of the Lewis base, were removed under vacuum and the reaction residues dissolved in C₆D₆ for analysis by ¹H and ¹¹B-{¹H} NMR spectroscopy.

For all three Lewis bases (L) almost total reaction of 1 to give $[W(\eta-C_5H_5)_2H_2]$ and the adducts $L\cdot B(C_6F_5)_3$ had occurred. The adducts were independently synthesised from $B(C_6F_5)_3$ and L and characterised for the purpose of comparison. The reaction between $[Mo(\eta-C_5H_5)_2H_2]$ and $B(C_6F_5)_3$ in either toluene or petroleum ether yields a dark blue solid **5** even at -78 °C. The product **5** was difficult to investigate owing to its extreme insolubility in toluene and petroleum ether. Dichloromethane causes fairly rapid decomposition of the product to an intractable green solution but it was possible to obtain NMR spectra. These strongly suggested that **5** could be formulated as an adduct of the form $[Mo(\eta-C_5H_5)_2(H)(\eta^1-HB-(C_6F_5)_3)]$ **5**, since two resonances were observed in the hydride region of the ¹H NMR spectrum; a sharp peak at δ -6.21 in the region expected for a molybdenum-bound hydride and a very broad signal at δ -17.5. The latter signal is assigned to a Mo-H-B bridging hydride rather than abstracted $[HB(C_6F_5)_3]^-$ since the ¹H NMR spectral shift of this anion is known to occur at δ 3.98.^{2a} Also, the proton-coupled ¹¹B NMR spectrum shows a doublet with ¹J_{BH} = 87 Hz, consistent with other reported M-H-B bridging units.¹¹ Infrared and microanalytical data for **5** are also consistent with the proposed formulation.

The Lewis base 4-methylpyridine was added to **5** in order to support the proposal that it was a simple adduct (the $(C_6F_5)_{3}$ -

Table 2	Selected bond	distances ((Å)	and angles	(°)	for comp	ound	4
---------	---------------	-------------	-----	------------	-----	----------	------	---

W(1)-H(202)	1.49(5)	B(1)–Cl(1)	1.915(5)
W(1)-H(203)	1.52(5)	B(1)-C(20)	1.652(6)
W(1)-H(204)	1.41(6)	B(1) - C(30)	1.648(5)
$Cp_{cent} - W(1)$	1.98	B(1)-C(1)	1.637(6)
Cp'_{cent} -W(1)	1.97		
Cp _{cent} -W-Cp' _{cent}	145.9	H(203)-W-H(204)	60.8(30)
H(202)–W–H(203)	54.8(27)	H(202)-W-H(204)	115.6(33)
$Cp_{cent} = centroid of$	$(\eta^5-C_5H_5)$ ring	g; $Cp'_{cent} = centroid of$	$(\eta^{5}-C_{5}H_{4}B-$
$(C_6F_5)_3$ Cl) ring			



Fig. 1 Molecular structure of compound $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\text{-}\{B(C_6F_5)_2Cl\})H_3]$ 4.

 $B \cdot NC_5H_4(CH_3)$ adduct had been independently synthesised and characterised).¹² Excess 4-methylpyridine was added to a suspension of the blue adduct 5 in toluene and, over the course of 2 days, the blue solid had vanished and the solution phase became golden yellow. The NMR spectrum of this solution revealed it to contain a mixture of $[Mo(\eta-C_5H_5)_2H_2]$ and $(C_6F_5)_3B \cdot NC_5H_4(CH_3)$. The long reaction period may be attributed to the low solubility of compound 5 in toluene.

The reaction between $[Mo(\eta-C_5H_5)_2H_2]$ and bis(pentafluorophenyl)borane HB(C₆F₅)₂ in toluene at -78 °C gave an immediate colour change from yellow to red *via* orange. Upon warming to ambient temperature and removal of volatiles *in vacuo*, an olive-green oily solid was obtained which, after washing thoroughly with petroleum ether (bp 40–60 °C), afforded a blue powder $[Mo(\eta-C_5H_5)_2(H)(\eta^1-H_2B(C_6F_5)_2)]$, **6** in 35% yield. Compound **6** could be crystallised from toluene at -80 °C as needles which were not suitable for study by X-ray diffraction.

The blue compound **6** shared many characteristics with the product formed from $[Mo(\eta-C_5H_5)_2H_2]$ and $B(C_6F_5)_3$ (**5**), being unstable both thermally and to air. The high airsensitivity precluded the acquisition of entirely satisfactory microanalytical or mass spectral data. The solubility of **6** was somewhat greater than that of compound **5** and so NMR spectra were obtained in d₈-toluene. A single (C_5H_5) resonance was observed in both the ¹H and ¹³C-{¹H} NMR spectra, indicating that the Lewis acid had not added to a cyclopentadienyl ring. Two ¹H NMR spectroscopic resonances appeared in the high field region of the spectrum, a sharp signal at δ -13.56, which was assigned to a Mo–H moiety, and a broad resonance at δ -18.2 attributed to a bridging Mo–H–B unit. The other hydrogen bound to boron was observed at δ 4.59, close to its position in the free borane (δ 4.5, fwhh = 25 Hz¹³) but having a sharper appearance.

The ¹¹B-{¹H} NMR spectrum shows a single peak at δ –12.1 in the region typical for fourfold coordination of boron. No splitting ascribable to protons appears on removal of proton-decoupling; although it may be that the relatively large line width of the signal precludes its observation. Unfortunately, the solubility of **6** was too low to permit the weak (C₆F₅) resonances to be observed in the ¹³C-{¹H} NMR spectrum and a sample in CD₂Cl₂ decomposed before spectra could be acquired.

An infrared spectrum of **6** showed several strong bands in the range 950–1500 cm⁻¹ due to C–F absorptions; a broad band at 1724 cm⁻¹ is assigned to v(Mo-H). The B–H_{bridge} stretch is predicted to appear at around 2000 cm⁻¹;¹¹ however no peak is observed in this region, it is possibly broadened into the baseline. A weak absorption at 2390 cm⁻¹ can be assigned to the B–H_{terminal} stretch.

In view of the low solubility of both compounds 5 and 6 it was decided to study the reactions of $B(C_6F_5)_3$ with the alkyl-cyclopentadienyl compounds [Mo(η-C5H4R)2H2], where R = Me, Pr^{i} or Bu^{n} . The reaction between $[Mo(\eta-C_{5}H_{4}Me)_{2} H_2$ ¹⁴ and $B(C_6F_5)_3$ gave a blue product $[Mo(\eta-C_5H_4Me)_2 (H)(\eta^1 - HB(C_6F_5)_3)$] 7 which was more soluble in benzene than was 5; however the improvement in solubility was insufficient to obtain meaningful ¹³C-{¹H} NMR spectral data. The isopropyl derivative, [Mo(η-C₅H₄Prⁱ)₂H₂], was synthesised from [MoCl₄·dme], Na[C₅H₄Prⁱ] and LiAlH₄ following the method of Persson and Andersson.¹⁵ Reaction with B(C₆F₅)₃ in toluene was slow, even on warming and although a different compound was obtained, it was oily and could not be purified. No reaction at all was observed between $[Mo(\eta-C_5H_4Bu^n)_2H_2]$ and $B(C_6F_5)_3$. It is clear that adding longer chain alkyl substituents to the cyclopentadienyl rings, although improving the solubility of the adduct, also hinders the reaction considerably and increases the oiliness of the products, so this approach was abandoned.

Lewis acid adducts of the d⁴ compound [Re(η -C₅H₅)₂H] with BF₃¹⁶ and with AlX₃ (X = Cl or Br) or AlHCl₂¹⁷ have been described and have been assigned a structure where the Lewis acid is attached to one of the two lone pairs on the rhenium centre. However, in view of the reactivity of [W(η -C₅H₅)₂H₂] with B(C₆F₅)₃, attack at a cyclopentadienyl ring was anticipated.

The hydride $[\text{Re}(\eta-\text{C}_5\text{H}_5)_2\text{H}]$ in petroleum ether (bp 100–120 °C) was treated with one equivalent of $B(\text{C}_6\text{F}_5)_3$. A light brown precipitate formed immediately and was isolated by filtration after 1 hour of stirring. Washing with petroleum ether to remove excess starting materials failed to render the product entirely pure so it was crystallised from toluene by slow cooling to -80 °C which yielded brown microcrystals of the zwittionic compound $[\text{Re}(\eta-\text{C}_5\text{H}_5)(\eta-\text{C}_5\text{H}_4\{B(\text{C}_6\text{F}_5)_3\})\text{H}_2]\cdot 0.5\text{C}_6\text{H}_5\text{Me} \ 8$ in 65% yield.

The ¹H NMR spectrum of **8** in CD₂Cl₂ showed a typical pattern in the cyclopentadienyl region expected for the proposed structure including a sharp resonance of relative intensity 5 at δ 4.98, ascribable to the unsubstituted (η -C₅H₅) ligand, and two broader signals, each of intensity 2, downfield of this which are assigned to the (η -C₅H₄{B(C₆F₅)₃}) ligand. Only a single upfield resonance is observed, at δ –13.87, with a relative intensity 2 and this may be assigned to the two identical hydrides of an ReH₂ group. Unlike the analogous tungsten compound **1** compound **8** is stable in solution, and thus no hydride resonance due to the starting material at δ –12.90 was observed. Note that in the report of the [Re(η -C₅H₅)₂H₂]⁺ cation in the literature¹⁸ the hydride also moves upfield when compared to the starting monohydride, although not to such a great extent as is observed here. Toluene is also observed

in the spectrum and integration of both the methyl peak and the phenyl region indicates that there is one half an equivalent of solvent present; this was supported by the microanalytical data.

The ¹¹B-{¹H} NMR spectrum of **8** showed a single sharp peak at δ -15.8 which remains a singlet in the absence of decoupling, providing further evidence that the borane has not added to a Re–H bond.

The ¹³C-{¹H} NMR spectrum of **8** showed the resonances expected except that of the *ipso-C*₆F₅ signal which was presumed either to be too weak or too broad to be located. As is the case with compounds **1** to **4**, assignment is straightforward with similar patterns being observed in both the cyclopentadienyl and pentafluorophenyl regions in all five complexes.

The infrared spectrum of compound **8** showed no bands between 1650 cm⁻¹ and 2400 cm⁻¹ assignable to Re–H groups. However, the infrared spectrum of the $[\text{Re}(\eta-\text{C}_5\text{H}_5)_2\text{H}_2]^+$ cation showed, at best, only very weak bands around 2000 cm⁻¹ for the Re–H stretch¹⁸ and later solution and matrix isolation studies found no infrared-active Re–H stretch.¹⁹ A fast atom bombardment mass spectrum of **8** showed several peaks assignable to expected fragments of **8** and a weak peak for the parent ion was observed at m/z = 829. Treatment of compound **8** with an excess of PMe₃ in toluene gave only an extremely small peak at $\delta - 3.9$ in the ¹¹B-{¹H} NMR spectrum due to (C₆F₅)₃B·PMe₃ and the resulting ¹H NMR spectrum was essentially that of **8**.

The metallocene trihydride $[Ta(\eta-C_5H_5)_2H_3]$ was treated with one equivalent of $B(C_6F_5)_3$ in toluene at room temperature. A slow colour change from pale yellow to dark orange was observed over 3 hours and then the volatiles were removed under vacuum to yield an orange oil. Sonication in petroleum ether for 15 minutes rendered a light orange powder of $[Ta(\eta-C_5H_5)_2(H)_2(\eta^1-HB(C_6F_5)_3)]$ 9. Microanalytical data were correct for a 1:1 adduct, but unfortunately NMR spectroscopy failed to confirm unambiguously that adduct formation had occurred. The ¹¹B-{¹H} NMR spectrum showed a fairly sharp resonance at δ –0.2 in the region expected for four-coordinate boron, however there was no splitting visible on removal of decoupling and the line width was of a sufficiently low magnitude to lead one to expect that proton coupling should be observable if a B–H unit existed.

Previous studies of the reaction of $[Ta(\eta-C_5H_5)_2H_3]$ with Lewis acids have found that attack occurs at the central hydride ligand *e.g.* the reaction with triethylaluminium described by Tebbe.²⁰ In accord with this, one might therefore expect that ¹H NMR spectroscopy of the product from the reaction with $B(C_6F_5)_3$ would show a more or less unaltered B_2 component and a shifted and broadened A component in the hydride region of the spectrum. In actual fact, the only observed upfield resonance is an extremely broad (fwhh = *ca*. 200 Hz), very weak signal centred at δ -4.1 which could possibly correspond to the borane rapidly hopping between all three hydrides.

In conclusion, selected new compounds and their reactions are shown in Schemes 1 and 2. Addition of the Lewis acid $B(C_6F_5)_3$ to metallocene hydrides occurs either at the M–H bond or by initial *exo*-addition to a carbon of an η -cyclopentadienyl ring. In the latter reaction this would result in a η -cyclopentadiene ring, *i.e.* (η -C₅H₅{BR₃}), and the compound would have a formal electron count of 16-electrons. These compounds are not observed and the isolated product results from oxidative addition of the *endo*-C–H group of the (η -C₅H₅-{BR₃}) ligand to the metal centre resulting in the formation of a zwiterrionic 18-electron compound. This reaction sequence is illustrated in Scheme 1. The fact that [Mo(η -C₅H₅)₂H₂] adds B(C₆F₅)₃ to the Mo–H bond whilst for [W(η -C₅H₅)₂H₂] the reaction with B(C₆F₅)₃ proceeds *via* addition to the η -cyclopentadienyl ring may be associated with the greater ease of



Scheme 1 i $B(C_6F_5)_2R$ (where $R = (C_6F_5)$, Ph, H or Cl) in petroleum ether (bp 100–120 °C) at room temperature; ii add L (where $L = Et_3N$, PMe₃ or THF).



Scheme 2 i $B(C_6F_5)_3$ in toluene at -78 °C, then triturate with petroleum ether (bp 40–60 °C); ii 4-methylpyridine (L) in toluene for 2 days at room temperature; iii $B(C_6F_5)_3$ in petroleum ether (bp 100–120 °C) at room temperature; iv $B(C_6F_5)_3$ in toluene at room temperature.

oxidation of 6d transition metals compared with that for the corresponding 5d metals. The tantalum trihydride is a d⁰ compound so further oxidation is not possible; thus addition to the Ta–H bonds is the only option. For the d⁴ compound [$\text{Re}(\eta-\text{C}_{5}\text{H}_{5})_{2}\text{H}$] the observation that the product is formed by *exo*-addition to the η -cyclopentadienyl ring followed by proton



Fig. 2 Molecular structure of compound $[Re(\eta-C_5H_5)(\eta-C_5H_4-\{B(C_6F_5)_2\})(C_6F_5)]$ 10.

migration to the metal is consistent with the analogous reaction of $[W(\eta-C_5H_5)_2H_2]$.

The reaction between $[Re(\eta-C_5H_5)_2CH_3]$ and $B(C_6F_5)$ in dichloromethane was monitored by the ¹H NMR spectra at intervals of 10 °C from -80 to -10 °C. The ¹H NMR spectrum changed only slightly over the temperature range and the main peaks observed initially showed only one resonance in the C_5H_5 region (δ 4.25) together with one signal assignable to a CH₃-moiety (at δ 0.30). We note that the compound [Re- $(\eta$ -C₅H₅)₂CH₃] in CD₂Cl₂ has two peaks, at δ 4.27 (η -C₅H₅) and 0.39 (CH₃). The ¹¹B-{¹H} NMR spectrum shows a strong, sharp peak at δ -15, its intensity dropped as the temperature rose from -80 to -10 °C. The data are consistent with an initial equilibrium between a mixture of $[Re(\eta-C_5H_5)_2(CH_3)] +$ $B(C_6F_5)_3$ and the adduct $[Re(\eta-C_5H_5)_2(CH_3\cdot B(C_6F_5)_3)]$. Unfortunately the ¹⁹F NMR spectra were broad and complex, possibly due to hindered rotation and the sample was too dilute to give meaningful ¹³C-{¹H} NMR spectra. At -30 °C the sample was still yellow but a yellow precipitate had formed and it is this which accounts for the weakness of the ${}^{13}C-{}^{1}H$ NMR spectrum.

As the sample was warmed from -10 to +25 °C, the reaction mixture changed steadily from yellow via orange to bright red and gas evolution was observed. At the same time the ¹H NMR spectra developed two weak Re-hydride resonances, at δ -12.32 and -11.83, whilst the C₅H₅ region showed 6 clear peaks. The initially single bands attributed to the Re-methyl group first split into two bands and these then broadened and then disappeared. These changes in the methyl region were accompanied by the development of unusually sharp bands in the ¹H NMR spectrum at δ –0.21 and for ¹³C-{¹H} NMR at δ -2. These latter bands can be assigned unambiguously to CH₄. After room temperature was reached these bands assigned to CH₄ had reduced in intensity due to the diminished solubility of CH₄ in CD₂Cl₂ with the increase of temperature. This was confirmed by recooling the sample, which restored the original intensity of the CH4 signal. After standing at room temperature red crystals of 10 separated from the reaction mixture and the crystal structure was determined. The molecular structure of the compound 10 is shown in Fig. 2 and selected distances and angles are given in Table 3. The structure shows that the compound 10 has a $Re-C_6F_5$ group and a $B(C_6F_5)_2$ group. The distance F(31)-C(31) is at 1.361(2) Å significantly longer than F(45)–C(45) at 1.347(3) Å. Similar elongation is seen for the bond F(35)-C(35) when compared to F(41)–C(41).

A possible mechanism for the formation of **10** is shown in Scheme 3.

In conclusion, the new reactions and compounds 1-10 are shown in Schemes 1-3.

Table 3 Selected bond lengths (Å) and angles (°) for compound 10

$Re(1)-C(30)$ $Re(1)-Cp_{cent}$ $Re(1)-Cp'_{cent}$	2.174(3) 1.90 1.88	C(1)–B(1) B(1)–C(40) B(1)–C(50)	1.526(3) 1.581(3) 1.602(3)
C(1)–B(1)–C(40) C(1)–B(1)–C(50)	126.7(2) 115.2(2)	C(40)-B(1)-C(50)	115.70(18)



Scheme 3 Mechanism proposed for the formation of 10.

Experimental

All preparations and manipulations of air and/or moisture sensitive materials were carried out under an atmosphere of dinitrogen using standard Schlenk line techniques or in an inertatmosphere glove-box containing dinitrogen. Dinitrogen was purified before use by passage through a drying column filled with activated molecular sieves (4 Å) and a de-oxygenating column filled with either manganese(II) oxide suspended on vermiculite (Schlenk line) or BASF catalyst (glove-box). Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from sodium (petroleum ether (bp 100-120 °C) and toluene), sodium/potassium alloy (pentane and petroleum ether (bp 40-60 °C)) or potassium (THF) under a slow continuous stream of dinitrogen. Deuterated solvents for NMR spectroscopy were dried over calcium hydride (dichloromethane) or potassium (benzene and toluene) and de-oxygenated by three freeze-pump-thaw cycles.

NMR spectra were recorded on a Bruker AM300 spectrometer (¹H, ¹¹B and ¹³C NMR spectra were recorded at 300.13, 96.25 and 75.5 MHz respectively). The spectra were referenced internally using the residual protio-solvent (1H) and solvent (13C) resonances and measured relative to tetramethylsilane ($\delta = 0$); or referenced externally to BF₃·Et₂O (¹¹B, $\delta = 0$). Chemical shifts are quoted in δ (ppm); a positive sign indicates a downfield shift relative to the standard. Coupling constants are given in Hz. Fast atom bombardment mass spectra were obtained by the EPSRC Mass Spectrometry Service at the University College of Swansea under the supervision of Dr J. A. Ballantine. Infrared spectra were recorded as Nujol mulls between NaCl plates or as KBr discs on a Perkin-Elmer 1710 FTIR spectrometer in the range 400 to 4000 cm⁻¹. Elemental analyses were obtained by the microanalytical department of the Inorganic Chemistry Laboratory. 4-Methylpyridine (99%) and NEt₃ (99%) were purchased from Aldrich and pre-dried before use over activated 4 Å molecular sieves. $[W(\eta-C_5H_5)_2-$ H₂],¹⁵ PMe₃,²¹ [Mo(η -C₅H₅)₂H₂],¹⁴ [Mo(η -C₅H₄Me)₂H₂],¹⁴ [Mo(η -C₅H₄Pri)₂H₂],¹⁵ [Mo(η -C₅H₄Buⁿ)₂H₂],¹⁵ [Re(η -C₅H₅)₂H],²² [Ta(η -C₅H₅)₂H₃],²³ B(C₆F₅)₃,⁵⁷ PhB(C₆F₅)₂,²⁴ ClB(C₆F₅)₂)²⁵ and $HB(C_6F_5)_2^{13}$ were prepared by literature methods.

Preparations

 $[W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_3\})H_3]$ 1. To a stirred solution

of $[W(\eta-C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm³) a solution of B(C₆F₅)₃ (0.530 g, 1.04 mmol) in petroleum ether (bp 100–120 °C) (10 cm³) was added dropwise. Immediate precipitation of a flocculant white solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for one hour after which time the product was isolated by filtration, washed with petroleum ether (bp 40–60 °C) (2 × 20 cm³) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.750 g (91%).

[W(η-C₅H₅)(η-C₅H₄{B(C₆F₅)₂(C₆H₅)})H₃] 2. To a stirred solution of $[W(η-C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (30 cm³) was added dropwise a solution of B(C₆F₅)₂(C₆H₅) (0.430 g, 1.02 mmol) in petroleum ether (bp 100–120 °C) (15 cm³). Immediate precipitation of a flocculent off-white solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for thirty minutes after which time the product was isolated by filtration, washed with petroleum ether (bp 100–120 °C) (2 × 20 cm³) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.550 g (75%).

[W(η-C₅H₅)(η-C₅H₄{B(C₆F₅)₂**H**})**H**₃] **3.** To a stirred solution of [W(η-C₅H₅)₂H₂] (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm³) was added dropwise a solution of HB(C₆F₅)₂ (0.355 g, 1.03 mmol) in petroleum ether (bp 100– 120 °C) (20 cm³). Rapid precipitation of a flocculent off-white solid was observed and the solution lost its yellow colour. After stirring for one hour, the product was isolated by filtration, washed with petroleum ether (bp 100–120 °C) (30 cm³) then petroleum ether (bp 40–60 °C) (2 × 30 cm³) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.470 g (72%).

[W(η-C₅H₅)(η-C₅H₄{B(C₆F₅)₂Cl})H₃] 4. To a stirred solution of [W(η-C₅H₅)₂H₂] (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (20 cm³) was added dropwise a solution of ClB(C₆F₅)₂ (0.400 g, 1.05 mmol) in petroleum ether (bp 100– 120 °C) (10 cm³). Immediate precipitation of a flocculent greywhite solid was observed and the solution rapidly lost its yellow colour. Stirring was maintained for one hour after which time the product was isolated by filtration, washed with petroleum ether (bp 100–120 °C) (3 × 10 cm³) and dried *in vacuo* overnight. Single crystals suitable for analysis by X-ray diffraction were grown by slow evaporation at room temperature from a solution of **4** (20 mg) in benzene (15 cm³) under a flow of dinitrogen. Yield: 0.450 g (65%).

[Mo(η-C₅H₅)₂(H)(η¹-HB(C₆F₅)₃)] 5. To a cold $(-78 \,^{\circ}\text{C})$ solution of [Mo(η-C₅H₅)₂H₂] (0.550 g, 2.41 mmol) in toluene (30 cm³) was added dropwise B(C₆F₅)₃ (1.240 g, 2.42 mmol) in toluene (30 cm³). A deep blue suspension formed immediately and stirring was maintained while the reaction mixture was allowed to reach ambient temperature. The solvent was removed under vacuum and the resulting dark blue oily solid triturated with petroleum ether (bp 40–60 °C) (3 × 30 cm³) to yield the product as a blue powder which was dried overnight *in vacuo*. Yield: 1.1 g (62%).

[Mo(η-C₅H₅)₂(H)(η¹-H₂B(C₆F₅)₂)] 6. To a cold $(-78 \,^{\circ}\text{C})$ solution of [Mo(η-C₅H₅)₂H₂] (0.228 g, 1.00 mmol) in toluene (25 cm³) a solution of HB(C₆F₅)₂ (0.346 g, 1.00 mmol) in toluene (30 cm³) was slowly added with stirring. The solution gradually darkened from yellow through orange to red and was allowed to reach ambient temperature. Removal of volatiles under vacuum yielded an olive-green oily solid which afforded a blue powder after trituration with petroleum ether (bp 40–60 °C) (30 cm³). The product was crystallised from toluene (-80 °C) as blue needles. Yield: 0.2 g (35%).

[Mo(η-C₅H₄Me)₂(H)(η¹-HB(C₆F₅)₃)] 7. To a cold (-78 °C) solution of [Mo(η-C₅H₄Me)₂H₂] (0.310 g, 1.21 mmol) in toluene (20 cm³) was added a solution of B(C₆F₅)₃ (0.620 g, 1.21 mmol) in toluene (20 cm³) with stirring. An immediate colour change to dark blue was observed and the reaction was allowed to warm to ambient temperature. Removal of volatiles under vacuum afforded a blue oily solid which yielded a blue powder after trituration with petroleum ether (bp 40–60 °C) (2 × 30 cm³). The product purity was confirmed by microanalysis. Yield 0.5 g (54%).

[Re(η-C₅H₅)(η-C₅H₄{B(C₆F₅)₃)H₂] 8. To a stirred solution of [Re(η-C₅H₅)₂H] (0.317 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm³) was slowly added a solution of B(C₆F₅)₃ (0.530 g, 1.04 mmol) in petroleum ether (bp 100–120 °C) (10 cm³). Immediate formation of a light brown precipitate was observed and after 1 hour of stirring this was isolated by filtration. The product was washed with petroleum ether (bp 40–60 °C) (3 × 20 cm³) and recrystallised from toluene as a brown microcrystalline solid at -80 °C. Purity as 8·0.5C₆H₅Me was confirmed by microanalysis and NMR spectroscopy. Yield: 0.53 g (65%).

[Ta(η-C₅H₅)₂(H)₂(η¹-HB(C₆F₅)₃)] 9. To a stirred solution of [Ta(η-C₅H₅)₂H₃] (0.314 g, 1.00 mmol) in toluene (20 cm³) was added a solution of B(C₆F₅)₃ (0.512 g, 1.00 mmol) in toluene (15 cm³). Over the course of 3 hours stirring, a slow colour change from pale yellow to dark orange was observed. After this time, volatiles were removed *in vacuo* to yield an orange oil. Sonication of this compound in petroleum ether (bp 40–60 °C) (20 cm³) for 15 minutes yielded the product as a light orange powder which was isolated by filtration and dried overnight under vacuum. Microanalysis confirmed that this compound could be formulated as a 1:1 adduct of the two starting materials; however, NMR spectroscopic data were not straightforward. No further purification could be achieved by crystallisation from toluene at -80 °C.

[Re(η-C₅H₅)(η-C₅H₄{B(C₆F₅)₂)(C₆F₅)] 10. In an NMR tube, a mixture of [Re(η-C₅H₅)₂CH₃] (0.016 g, 48 mmol) and B(C₆F₅)₃ (0.025 g, 49 mmol) was quickly cooled to liquid nitrogen temperature. CD₂Cl₂ (0.8 cm³) was condensed onto the mixture and the tube was flame-sealed. The sample was then warmed to -80 °C, giving a yellow solution. The NMR tube was transferred to the precooled (-80 °C) NMR spectrometer and allowed to warm slowly to room temperature. At intervals of 10 °C, the ¹H NMR spectrum was recorded at each temperature. After the sample reached room temperature bright red microcrystals of 10 precipitated in the NMR tube. The compound 10 is very sensitive to moisture, only sparingly soluble in CH₂Cl₂ and almost insoluble in toluene and other hydrocarbons. It reacts readily with donor atom solvents like THF or DMSO, presumably to give the simple adducts.

Single crystals of **10** suitable for X-ray diffraction analysis were grown by layering a solution of $[\text{Re}(\eta-\text{C}_5\text{H}_5)_2\text{CH}_3]$ (0.050 g, 0.15 mmol) in CH₂Cl₂ (0.8 cm³) with neat CH₂Cl₂ (2.0 cm³) followed by careful addition of a solution of B(C₆F₅)₃ (0.075 g, 0.15 mmol) in CH₂Cl₂ (0.5 cm³) in an NMR tube fitted with a Young's tap. Crystallisation occurred on standing at room temperature over one week to give dark red blocks. Estimated yield *ca.* 50%.

Reactions

Between $[W(\eta-C_5H_5)(\eta-C_5H_4\{B(C_6F_5)_3\})H_3]$ 1 and L [where L = THF, NEt₃ or PMe₃]. To a solution of $[W(\eta-C_5H_5)(\eta-C_5H_4B(C_6F_5)_3)H_3]$ 1 (20 mg, 0.024 mmol) in toluene (10 cm³) was added an excess of the Lewis base L; either THF (3 drops), NEt₃ (3 drops) or PMe₃ (1 cm³ of a 0.105 M solution in petroleum ether (bp 40–60 °C)). The solutions rapidly became

	4	10
Molecular formula	WClF ₁₀ C ₂₂ H ₁₂ B	ReC ₂₈ H ₉ F ₁₅ B
Formula weight	696.43	827.36
Crystal system	Triclinic	Orthorhombic
a/Å	8.470(4)	15.427(3)
b/Å	10.106(4)	15.619(4)
c/Å	13.403(3)	19.877(2)
a/°	80.26(3)	90.00
βl°	74.88(3)	90.00
y/°	67.53(2)	90.00
V/Å ³	1020.4	4789.4
Space group	$P\bar{1}$	Pbca
Ź	2	8
T/K	125	125
μ/mm^{-1}	6.01	5.21
Total data collected	5082	4766
Unique data	3795	3940
Merging R	0.00	0.02
R	0.0264	0.0238
R _w	0.0296	0.0247

yellow in colour and after the reactions had been allowed to proceed for 1 hour, the volatiles were removed *in vacuo* and the residues were dried for a further 2 hours. The products were analysed by ¹H and ¹¹B-{¹H} NMR spectroscopy and showed that all three experiments gave virtually quantitative formation of $[W(\eta-C_5H_5)_2H_2]$ and $(C_6F_5)_3B\cdot L$ [L = THF, NEt₃ or PMe₃]. In the case where L = THF, a small amount (*ca.* 10%) of $[W(\eta-C_5H_5)(\eta-C_5H_4B(C_6F_5)_3)H_3]$ remained. Where L = PMe₃, some of the residue proved to be insoluble in C₆D₆ and this was identified as $(C_6F_5)_3B\cdot PMe_3$ and an independent synthesis of this adduct confirmed its insolubility in benzene.

NMR data for $(C_6F_5)_3$ B·NEt₃ $(C_6D_6, 298 \text{ K})$: ¹H, δ 0.51 (m, 9H, NCH₂CH₃), 1.62 (m, 6H, NCH₂CH₃); ¹¹B-{¹H}, δ -3.9 (s).

NMR data for $(C_6F_5)_3$ B•THF $(C_6D_6, 298 \text{ K})$: ¹H, δ 1.42 (m, 4H, C₄H₈O), 3.55 (m, 4H, C₄H₈O); ¹¹B-{¹H}, δ -3.7 (s).

Between $[Mo(\eta-C_5H_5)_2(H)(\eta^1-HB(C_6F_5)_3)]$ 5 and 4-methylpyridine. To a suspension of $[Mo(\eta-C_5H_5)_2(H)(\eta^1-HB(C_6F_5)_3)]$ 5 (45 mg, 0.061 mmol) in toluene (5 cm³), excess 4-methylpyridine (3 drops) was added. Over the course of 2 days' stirring, the blue solid disappeared and the solution phase became golden yellow. The volatiles were removed, the residue dried overnight *in vacuo* and analysis by NMR spectroscopy in C₆D₆ was undertaken. This allowed the products to be identified as $[Mo(\eta-C_5H_5)_2H_2]$ and $(C_6F_5)_3B\cdot4$ -methylpyridine (which has been independently synthesised).

NMR data for $(C_6F_5)_3B$ ·NC₅H₄(CH₃) $(C_6D_6, 298 \text{ K})$: ¹H, δ 1.39 (s, 3H, NC₅H₄CH₃), 6.14 (d, 2H, ³J_{HH} = 6.5, NC₅H₄CH₃, H_m), 7.89 (d, 2H, ³J_{HH} = 6.5, NC₅H₄CH₃, H_o); ¹¹B-{¹H}, δ -4.0.

Between $[\text{Re}(\eta-\text{C}_5\text{H}_5)(\eta-\text{C}_5\text{H}_4\{\text{B}(\text{C}_6\text{F}_5)_3\})\text{H}_2]$ 8 and PMe₃. The compound $[\text{Re}(\eta-\text{C}_5\text{H}_5)(\eta-\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{H}_2]$ 8 (20 mg, 0.024 mmol) was dissolved in toluene (10 cm³) and PMe₃ (1 cm³ of a 0.105 M solution in petroleum ether (bp 40–60 °C), 0.105 mmol) was added with stirring. No immediate colour change was evident and, after 1 hour, volatiles were removed under vacuum and the residues were examined by NMR spectroscopy. This revealed that compound 8 was present unaltered.

Crystallography

Data were collected as previously described,²⁶ images were processed with the DENZO and SCALEPACK programs.²⁷ All solution, refinement and graphical calculations were performed using the CRYSTALS²⁸ and CAMERON^{29,30} software packages. The three hydrogens bound to tungsten in **4** were

located in the final difference map and their positions refined with isotropic thermal parameters. A Chebychev weighting scheme with the parameters 2.84, 0.362 and 2.06 was applied as well as an empirical absorption correction.³¹ This yielded R = 0.0264 and $R_w = 0.0296$ with maximum residual electron density of 1.76 e Å⁻³.

CCDC reference number 186/1803.

See http://www.rsc.org/suppdata/dt/a9/a908623d/ for crystallographic files in .cif format.

Acknowledgements

We thank St John's College, Oxford for a Junior Research Fellowship (to L. H. D.) and the EPSRC for a graduate award (to A. J. G.).

References

- X. Yang, C. L. Stern and T. J. Marks, J. Am. Chem. Soc., 1991, 113, 3623; J. Gillis, M.-J. Tudoret and M. C. Baird, J. Am. Chem. Soc., 1993, 115, 2543; M. Bochmann, S. J. Lancaster, M. B. Hursthouse and K. M. A. Malik, Organometallics, 1994, 13, 2235; Z. Guo, D. C. Swenson, A. S. Guram and R. F. Jordan, Organometallics, 1994, 13, 766; R. Gómez, M. L. H. Green and J. L. Haggitt, J. Chem. Soc., Chem. Commun., 1994, 2607; A. D. Horton, Organometallics, 1997, 527, 7; T. L. Tremblay, S. W. Ewart, M. J. Sarsfield and M. C. Baird, Chem. Commun., 1997, 831; J. D. Scollard, D. H. McConville and S. J. Rettig, Organometallics, 1997, 16, 1810; M. L. H. Green and J. Saßmannshausen, Chem. Commun., 1999, 115; W. E. Piers, Chem. Eur. J., 1988, 4, 13; V. Burlakov, S. I. Troyanov, A. V. Letov, E. T. Mysov, G. G. Furin and V. B. Sgur, Russ. Chem. Bull., 1999, 48, 1012.
- 2 (a) X. Yang, C. L. Stern and T. J. Marks, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1375; (b) D. Röttger, S. Schmuck and G. Erker, *J. Organomet. Chem.*, 1996, **508**, 263.
- J. R. Galsworthy, M. L. H. Green, M. Müller and K. Prout, J. Chem. Soc., Dalton Trans., 1997, 1309; J. R. Galsworthy, J. C. Green, M. L. H. Green and M. Müller, J. Chem. Soc., Dalton Trans., 1998, 15; L. H. Doerrer, J. R. Galsworthy, M. L. H. Green and M. A. Leech, J. Chem. Soc., Dalton Trans., 1998, 2483; L. H. Doerrer, J. R. Galsworthy, M. L. H. Green, M. A. Leech and M. Müller, J. Chem. Soc., Dalton Trans., 1998, 3191; M. L. H. Green, G. Barrado, L. H. Doerrer and M. A. Leech, J. Chem. Soc., Dalton Trans., 1999, 1061.
- 4 L. H. Doerrer, A. J. Graham and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1998, 3941.
- 5 (a) M. L. H. Green, J. Haggitt and C. P. Mehnert, J. Chem. Soc., Chem. Commun., 1995, 1853; (b) A. N. Chernega, A. J. Graham, M. L. H. Green, J. Haggitt, J. Lloyd, C. P. Mehnert, N. Metzler and J. Souter, J. Chem. Soc., Dalton Trans., 1997, 2293.
- 6 R. Gomez, M. L. H. Green and J. L. Haggitt, J. Chem. Soc., Dalton Trans., 1996, 939.
- 7 A. G. Massey and A. J. Park, J. Organomet. Chem., 1964, 2, 245.
- 8 H. Braunschweig and T. Wagner, Chem. Ber., 1994, 127, 1613.
- 9 D. M. Heinekey, J. Am. Chem. Soc., 1991, 113, 6074.
- 10 G. Parkin and J. E. Bercaw, Polyhedron, 1988, 7, 2053.
- 11 T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
- 12 A. J. Graham, Part II Thesis, University of Oxford, 1994.
- 13 D. J. Parks, R. E. v. H. Spence and W. E. Piers, Angew. Chem., Int. Ed. Engl., 1995, 34, 809.
- 14 N. D. Silavwe, M. P. Castellani and D. R. Tyler, *Inorg. Synth.*, 1992, 29, 204.
- 15 C. Persson and C. Andersson, Organometallics, 1993, 12, 2370.
- 16 M. P. Johnson and D. F. Shriver, J. Am. Chem. Soc., 1966, 88, 301.
- 17 V. M. Ishchenko, G. L. Soloveichik, B. M. Bulychev and T. A. Sokolova, *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.*), 1984, 29, 66.
- 18 M. L. H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc., 1958, 3916.
- 19 R. B. Girling, P. Grebenik and R. N. Perutz, *Inorg. Chem.*, 1986, 25, 31.
- 20 F. N. Tebbe, J. Am. Chem. Soc., 1973, 95, 5412.
- 21 M. L. Luetkens, A. P. Sattelberger, H. H. Murray, J. D. Basil and J. P. Fackler, *Inorg. Synth.*, 1989, **26**, 7.
- 22 D. M. Heinekey and G. L. Gould, Organometallics, 1991, 10, 2977.
- 23 M. L. H. Green, J. A. McCleverty, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

- 24 P. A. Deck, C. L. Beswick and T. J. Marks, J. Am. Chem. Soc., 1998, 120, 1772.
- 25 R. D. Chambers and T. Chivers, Organomet. Chem. Rev., 1966, 1, 279.
- 26 L. H. Doerrer, M. L. H. Green, D. Häußinger and J. Saβmannhausen, J. Chem. Soc., Dalton Trans., 1999, 2111.
- 27 Z. Otwinowski and W. Minor, in Methods in Enzymology, Academic
- Press, New York, 1996, vol. 276, p. 307.
 28 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide, Issue 10*, Chemical Crystallography Laboratory, University of Oxford, 1996.
- 29 D. J. Watkin, C. K. Prout and L. J. Pearce, CAMERON, Chemical
- D. J. Watkill, C. K. Plout and E. J. Feater, CAMEROFY, Chemical Crystallography Laboratory, University of Oxford, 1996.
 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, SIR92, Program for automatic solution of crystal structures by direct methods, J. Appl. Crystallogr., 1994, 27, 435.
- 31 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 1983, 39, 158.

Paper a908623d