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Electrophilic addition reactions of the Lewis acids $B(C_6F_5)_2R$ [$R = C_6F_5$, Ph, H or Cl] with the metallocene hydrides [$M(\eta\text{-}C_5H_5)_2H_2$] (M = Mo or W), [$Re(\eta\text{-}C_5H_5)_2H$] and [$Ta(\eta\text{-}C_5H_5)_2H_3$]

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The syntheses of the new compounds [$W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2R\})H_3$], where R = ($C_6F_5$) **1**, Ph **2**, H **3** or Cl **4**, [$Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)$] **5**, [$Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}H_2B(C_6F_5)_2)$] **6**, [$Mo(\eta\text{-}C_5H_4Me)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)$] **7**, [$Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4B(C_6F_5)_3)H_2$]·$0.5C_6H_5Me$ **8**, [$Ta(\eta\text{-}C_5H_5)_2(H)_2(\eta^1\text{-}HB(C_6F_5)_3)$] **9** and [$Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\text{-}\{B(C_6F_5)_2\})(C_6F_5)$] **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–μ-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-oxo [3] and -nitrido [4] compounds. The compound $B(C_6F_5)_3$ also reacts in an unexpected manner with the compounds [$M(\eta\text{-}C_5H_5)(CO)_nMe$], 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 [$W(\eta\text{-}C_5H_5)_2H_2$] in toluene at −78 °C with $B(C_6F_5)_3$ 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 [$W(\eta\text{-}C_5H_5)_2H_2$] 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 [$W(\eta\text{-}C_5H_5)_2H_2$] 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 [$W(\eta\text{-}C_5H_5)_2H_2$] and $B(C_6F_5)_2R$. The zwitterionic compounds [$W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2R\})H_3$], where R = ($C_6F_5$) **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 [$W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{BRCl_2\})H_3$] where R = Pr^i or Bu^t which were formed by the reaction of [$W(\eta\text{-}C_5H_5)_2H_2$] with $BRCl_2$.[8] The ^{1}H NMR spectroscopic data and coupling constants obtained for the compounds **1**–**4** are closely similar to those obtained for Braunschweig's complexes.

The ^{1}H 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 ^{183}W satellite peaks, a typical pattern for an AB_2X spin system. The H–H coupling constants for the WH_3 hydrogens in compounds **1** to **3** lie in the region 4.8–9.6 Hz, consistent with data reported for [$W(\eta\text{-}C_5H_5)_2H_3$]Cl.[9] The value of $^2J_{HH}$ for compound **2** in CD_2Cl_2 is lower (4.8 Hz), and is comparable with that observed in the compound [$W(\eta\text{-}C_5Me_5)_2H_3$][$BPh_4$].[10] The one bond ^{183}W–H coupling constant (where it could be determined) is of a similar magnitude to that found in the previously cited compounds [8–10] with coupling to the central hydride being greater than that to the outer ones.

The ^{11}B-{^{1}H} 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 ^{11}B 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 ν(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 [$W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{BPr^iCl_2\})H_3$].[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 ^{1}H NMR spectra of initially pure samples of compounds **1**–**4** showed a slow appearance of a small quantity of [$W(\eta\text{-}C_5H_5)_2H_2$] 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 = NEt_3, PMe_3, 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

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Table 1 Analytical and spectroscopic data for compounds **1**–**9**

	Compound[a]	NMR data[b]
1	$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_3\})H_3]$ 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 (ν(W–H)), 1768w, 1645w, 1516m, 1262s, 1089s, 975m, 833m, 800s	^1H: −6.38 (d, 2H, $^2J_{HH} = 9.6$, WH_{outer}), −6.27 (t, 1H, $^2J_{HH} = 9.6$, WH_{centre}), 5.23 (s, 5H, C_5H_5), 5.52 and 5.56 (s, 2H, each, C_5H_4B) $^{11}B\text{-}\{^1H\}$: −15.6 (s) $^{13}C\text{-}\{^1H\}$: 83.30 and 84.18 (s, C_5H_4B), 87.11 (br s, C_5H_4B, C_{ipso}), 96.93 (s, C_5H_5), 130.46 (d, $^1J_{CF} = 251$, $B(C_6F_5)$, C_m), 137.60 (d, $^1J_{CF} = 253$, $B(C_6F_5)$, C_p), 148.46 (d, $^1J_{CF} = 249$, $B(C_6F_5)$, C_o)[c]
2	$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2(C_6H_5)\})H_3]$ 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 ν(C–H)), 1951w (ν(W–H)), 1645m, 1518m, 1103m, 1082s, 981s, 811s (br)	^1H: −6.48 (d, 2H, $^2J_{HH} = 4.8$, WH_{outer}), −6.38 (t, 1H, $^2J_{HH} = 4.8$, WH_{centre}), 4.94 and 5.38 (s, 2H each, C_5H_4B), 5.10 (s, 5H, C_5H_5), 7.1–7.3 (m, 5H, C_6H_5) $^{11}B\text{-}\{^1H\}$: −13.1 (s) $^{13}C\text{-}\{^1H\}$: 71.60 and 84.03 (s, C_5H_5B), 83.42 (s, C_5H_5), 87.24 (br s, C_5H_4B, C_{ipso}), 96.91 (br s, $B(C_6H_5)$, C_{ipso}), 112.60 (br s, $B(C_6F_5)$, C_{ipso}), 124.80 (s, $B(C_6H_5)$, C_m), 126.41 (s, $B(C_6H_5)$, C_p), 133.91 (s, $B(C_6H_5)$, C_o), 137.16 (d, $^1J_{CF} = 258$, $B(C_6F_5)$, C_m), 138.46 (d, $^1J_{CF} = 239$, $B(C_6F_5)$, C_p), 148.21 (d, $^1J_{CF} = 220$, $B(C_6F_5)$, C_o)
3	$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2H\})H_3]$ 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, 964s (br)	^1H: −6.71 (d, 2H, $^2J_{HH} = 7.6$, $^1J_{WH} = 4.60$, WH_{outer}), −6.44 (t, 1H, $^2J_{HH} = 7.6$, $^1J_{WH} = 66.6$, WH_{centre}), 4.5 (br s, BH), 5.25 and 5.29 (m, 2H, each, C_5H_4B), 5.33 (s, 5H, C_5H_5) $^{11}B\text{-}\{^1H\}$: −23.4 (s) ^{11}B: −23.4 (d, $^1J_{BH} = 86$) $^{13}C\text{-}\{^1H\}$: 71.77 and 82.67 (s, C_5H_4B), 84.71 (s, C_5H_5), 89.50 (br s, C_5H_4B, C_{ipso}), 136.88 (d, $^1J_{CF} = 242$, $B(C_6F_5)$, C_m), 138.55 (d, $^1J_{CF} = 242$, $B(C_6F_5)$, C_p), 148.24 (d, $^1J_{CF} = 293$, $B(C_6F_5)$, C_o)
4	$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2Cl\})H_3]$ Grey-white C, 39.25 (37.9); H, 2.5 (1.7); B, 1.2 (1.55); Cl, 5.5 (5.1) IR: 1941w (ν(W–H)), 1645m, 1516m, 1280m, 1089s (br), 1019w, 974s	^1H: −6.37 (d, 2H, $^2J_{HH} = 7.8$, $^1J_{WH} = 46.2$, WH_{outer}), −6.26 (t, 1H, $^2J_{HH} = 7.8$, $^1J_{WH} = 66.2$, WH_{centre}), 5.20 and 5.52 (s, 2H, each, C_5H_4B), 5.40 (s, 5H, C_5H_5) $^{11}B\text{-}\{^1H\}$: −6.7 (s) $^{13}C\text{-}\{^1H\}$: 83.71 (s, C_5H_5), 84.66[d] (s, C_5H_4B), 87.70 (br s, C_5H_4B, C_{ipso}), 123.0 (br s, $B(C_6F_5)$, C_{ipso}), 137.16 (d, $^1J_{CF} = 264$, $B(C_6F_5)$, C_m), 139.26 (d, $^1J_{CF} = 269$, $B(C_6F_5)$, C_p), 147.54 (d, $^1J_{CF} = 239$, $B(C_6F_5)$, C_o)
5	$[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ Blue C, 45.2 (45.4); H, 2.2 (1.6) IR: 2135m (ν(B–H)), 1550m, 1470s	^1H: −17.5 (br s, Mo–H–B), −6.21 (s, 1H, MoH), 4.95 (s, 10H, C_5H_5) $^{11}B\text{-}\{^1H\}$: −25.8 (s) ^{11}B: −25.8 (d, $^1J_{BH} = 87$) $^{13}C\text{-}\{^1H\}$: 83.6 (s, C_5H_5), 127.0 (br s, $B(C_6F_5)$, C_{ipso}), 136.63 (d, $^1J_{CF} = 256$, $B(C_6F_5)$, C_m), 138.02 (d, $^1J_{CF} = 237$, $B(C_6F_5)$, C_p), 148.36 (d, $^1J_{CF} = 229$, $B(C_6F_5)$, C_o)
6	$[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$ 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, 1405m, 1340m, 1308m, 1102s, 984s	^1H:[f] −18.2 (br s, Mo–H–B), −13.56 (s, 1H, MoH), 4.18 (s, 10H, C_5H_5), 4.6 (br s, 1H, BH) $^{11}B\text{-}\{^1H\}$:[f] −12.1 (s) $^{13}C\text{-}\{^1H\}$:[f] 63.1 (s, C_5H_5). Remaining resonances not detected
7	$[Mo(\mu\text{-}C_5H_4Me)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ Blue C, 47.1 (46.9); H, 2.5 (2.1)	^1H:[g] −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, $C_5\mathit{H}_4CH_3$)
8	$[Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4B(C_6F_5)_3)H_2]$[h] Light brown C, 43.4 (43.2); H, 2.0 (1.7); B, 0.9 (1.2) Mass: 852, $[M + Na]^+$; 829, $[M]^+$; 828, $[M - H]^+$; 662, $[M - (C_6F_5)]^+$; 512, $[B(C_6F_5)_3]^+$; 318, $[M + H - B(C_6F_5)_3]^+$; 317, $[M - B(C_6F_5)_3]^+$; 167, $[(C_6F_5)]^+$ IR: 2727m, 1644s, 1515s, 1456s, 1273s, 1089s, 967s, 858m	^1H: −13.87 (s, 2H, ReH), 2.34 (s, 1.5H, $\mathit{H}_3CC_6H_5$), 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, $H_3CC_6\mathit{H}_5$) $^{11}B\text{-}\{^1H\}$: −15.8 (s) $^{13}C\text{-}\{^1H\}$: 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, $^1J_{CF} = 232$, $B(C_6F_5)$, C_m), 136.76 (d, $^1J_{CF} = 243$, $B(C_6F_5)$, C_p), 148.20 (d, $^1J_{CF} = 222$, $B(C_6F_5)$, C_o)[c]
9	$[Ta(\eta\text{-}C_5H_5)_2(H)_2(\eta^1\text{-}HB(C_6F_5)_3)]$ Light orange C, 40.7 (40.7); H, 1.7 (1.6); B, 1.5 (1.3)	^1H:[g] −4.1 (br s, fwhh *ca.* 200 Hz, TaH_2), 4.65 (s, 9H, C_5H_5), 5.08 (s, 23H, C_5H_5) $^{11}B\text{-}\{^1H\}$:[g] −0.2 (s) Selected $^{13}C\text{-}\{^1H\}$:[g] 91.60 (s, C_5H_5), 106.44 (s, C_5H_5)[i]

[a] Analytical data given as found (calculated) in %. Mass spectral data (fast atom bombardment) given as *m*/*z* (assignment), selected IR data (cm^{-1}) 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 CD_2Cl_2 except where stated otherwise. [c] $B(C_6F_5)$, C_{ipso} resonance not detected. [d] Two coincident peaks. [e] KBr disc. [f] Data obtained in $D_3CC_6D_5$. [g] Data obtained in C_6D_6. [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 NEt_3) or as a solution in petroleum ether (PMe_3). In all three cases, the solution quickly became yellow and, where L = PMe_3, there was precipitation of poorly soluble $Me_3P\cdot B(C_6F_5)_3$. After 1 hour stirring, volatiles, including any excess of the Lewis base, were removed under vacuum and the reaction residues dissolved in C_6D_6 for analysis by ^1H and $^{11}B\text{-}\{^1H\}$ NMR spectroscopy.

For all three Lewis bases (L) almost total reaction of **1** to give $[W(\eta\text{-}C_5H_5)_2H_2]$ 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 $[Mo(\eta\text{-}C_5H_5)_2H_2]$ 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 $[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ **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 ^{11}B 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 compound **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 (η^5-C_5H_5) ring; Cp'_{cent} = centroid of (η^5-$C_5H_4B(C_6F_5)_2Cl$) ring

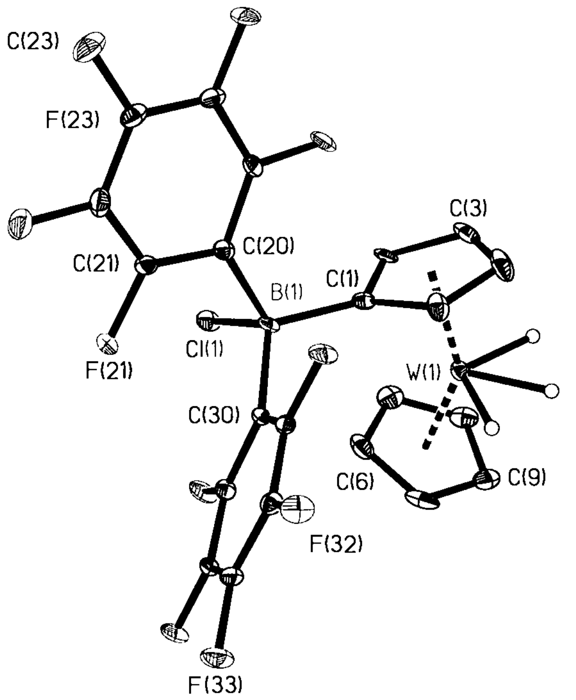


Fig. 1 Molecular structure of compound [W(η-C_5H_5)(η-C_5H_4-{$B(C_6F_5)_2Cl$})H_3] **4**.

B·$NC_5H_4(CH_3)$ 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(η-C_5H_5)$_2$$H_2$] and $(C_6F_5)_3B$·$NC_5H_4(CH_3)$. The long reaction period may be attributed to the low solubility of compound **5** in toluene.

The reaction between [Mo(η-C_5H_5)$_2$$H_2$] and bis(pentafluorophenyl)borane $HB(C_6F_5)_2$ 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(η-C_5H_5)$_2$(H)(η^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(η-C_5H_5)$_2$$H_2$] and $B(C_6F_5)_3$ (**5**), being unstable both thermally and to air. The high air-sensitivity 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 d_8-toluene. A single (C_5H_5) resonance was observed in both the ^1H and ^{13}C-{^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 Hz[13]) but having a sharper appearance.

The ^{11}B-{^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 (C_6F_5) resonances to be observed in the ^{13}C-{^1H} NMR spectrum and a sample in CD_2Cl_2 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 ν(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-C_5H_4R)$_2$$H_2$], where R = Me, Pr^i or Bu^n. The reaction between [Mo(η-C_5H_4Me)$_2$-H_2][14] and $B(C_6F_5)_3$ gave a blue product [Mo(η-C_5H_4Me)$_2$-(H)(η^1-$HB(C_6F_5)_3$)] **7** which was more soluble in benzene than was **5**; however the improvement in solubility was insufficient to obtain meaningful ^{13}C-{^1H} NMR spectral data. The isopropyl derivative, [Mo(η-$C_5H_4Pr^i$)$_2$$H_2$], was synthesised from [$MoCl_4$·dme], Na[$C_5H_4Pr^i$] and $LiAlH_4$ following the method of Persson and Andersson.[15] Reaction with $B(C_6F_5)_3$ 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(η-$C_5H_4Bu^n$)$_2$$H_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 d^4 compound [Re(η-C_5H_5)$_2$H] with BF_3[16] and with AlX_3 (X = Cl or Br) or $AlHCl_2$[17] 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-C_5H_5)$_2$$H_2$] with $B(C_6F_5)_3$, attack at a cyclopentadienyl ring was anticipated.

The hydride [Re(η-C_5H_5)$_2$H] in petroleum ether (bp 100–120 °C) was treated with one equivalent of $B(C_6F_5)_3$. 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 [Re(η-C_5H_5)(η-C_5H_4{$B(C_6F_5)_3$})H_2]·0.5C_6H_5Me **8** in 65% yield.

The ^1H NMR spectrum of **8** in CD_2Cl_2 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-C_5H_5) ligand, and two broader signals, each of intensity 2, downfield of this which are assigned to the (η-C_5H_4{$B(C_6F_5)_3$}) 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 ReH_2 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-C_5H_5)$_2$$H_2$]$^+$ cation in the literature[18] 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.

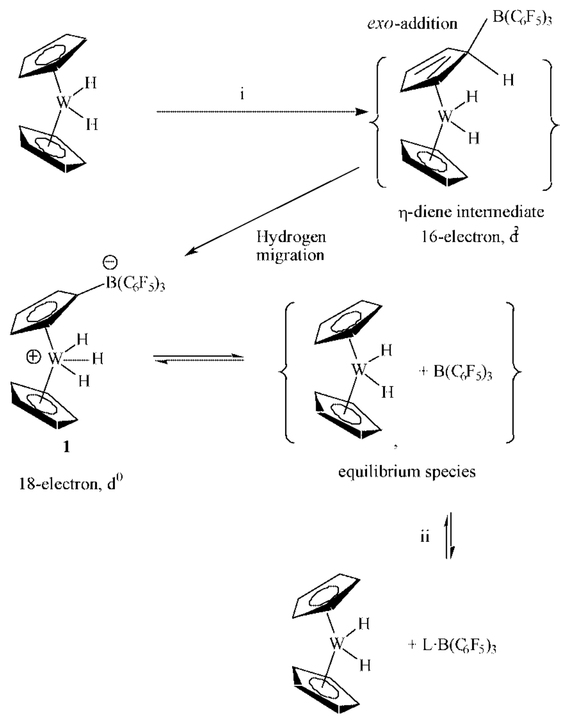
The ^{11}B-{^{1}H} NMR spectrum of **8** showed a single sharp peak at δ −15.8 which remains a singlet in the absence of decoupling, providing further evidence that the borane has not added to a Re–H bond.

The ^{13}C-{^{1}H} NMR spectrum of **8** showed the resonances expected except that of the *ipso*-C_6F_5 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.

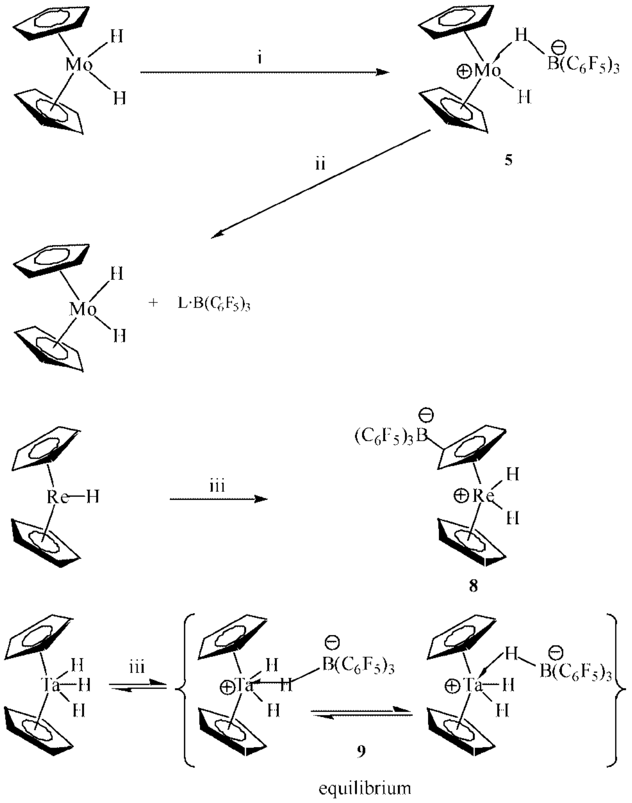
The infrared spectrum of compound **8** showed no bands between 1650 cm^{-1} and 2400 cm^{-1} assignable to Re–H groups. However, the infrared spectrum of the $[Re(\eta\text{-}C_5H_5)_2H_2]^+$ cation showed, at best, only very weak bands around 2000 cm^{-1} for the Re–H stretch[18] and later solution 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 PMe_3 in toluene gave only an extremely small peak at δ −3.9 in the ^{11}B-{^{1}H} NMR spectrum due to $(C_6F_5)_3B{\cdot}PMe_3$ and the resulting ^{1}H NMR spectrum was essentially that of **8**.

The metallocene trihydride $[Ta(\eta\text{-}C_5H_5)_2H_3]$ 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 $[Ta(\eta\text{-}C_5H_5)_2(H)_2(\eta^1\text{-}HB(C_6F_5)_3)]$ **9**. Microanalytical data were correct for a 1 : 1 adduct, but unfortunately NMR spectroscopy failed to confirm unambiguously that adduct formation had occurred. The ^{11}B-{^{1}H} 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 $[Ta(\eta\text{-}C_5H_5)_2H_3]$ 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 ^{1}H 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.



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, PMe_3 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.

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.* $(\eta\text{-}C_5H_5\{BR_3\})$, 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 $(\eta\text{-}C_5H_5\{BR_3\})$ 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 $[Mo(\eta\text{-}C_5H_5)_2H_2]$ adds $B(C_6F_5)_3$ to the Mo–H bond whilst for $[W(\eta\text{-}C_5H_5)_2H_2]$ the reaction with $B(C_6F_5)_3$ proceeds *via* addition to the η-cyclopentadienyl ring may be associated with the greater ease of oxidation of 6d transition metals compared with that for the corresponding 5d metals. The tantalum trihydride is a d^0 compound so further oxidation is not possible; thus addition to the Ta–H bonds is the only option. For the d^4 compound $[Re(\eta\text{-}C_5H_5)_2H]$ the observation that the product is formed by *exo*-addition to the η-cyclopentadienyl ring followed by proton

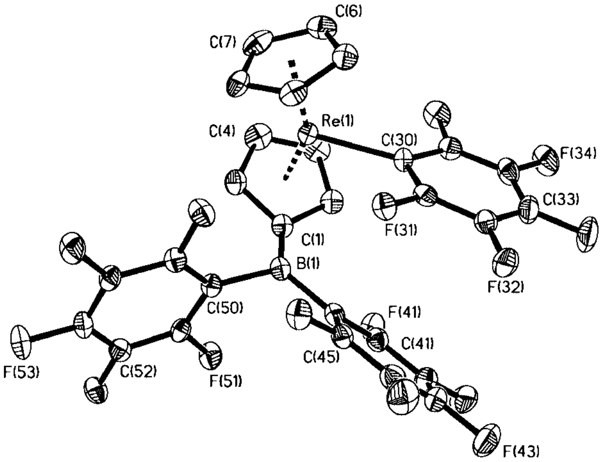


Fig. 2 Molecular structure of compound [Re(η-C_5H_5)(η-C_5H_4-{$B(C_6F_5)_2$})(C_6F_5)] **10**.

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

The reaction between [Re(η-$C_5H_5)_2CH_3$] 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 CH_3-moiety (at δ 0.30). We note that the compound [Re-(η-$C_5H_5)_2CH_3$] in CD_2Cl_2 has two peaks, at δ 4.27 (η-C_5H_5) and 0.39 (CH_3). The ^{11}B-{^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(η-$C_5H_5)_2(CH_3)$] + $B(C_6F_5)_3$ and the adduct [Re(η-$C_5H_5)_2(CH_3{\cdot}B(C_6F_5)_3)$]. Unfortunately the ^{19}F NMR spectra were broad and complex, possibly due to hindered rotation and the sample was too dilute to give meaningful ^{13}C-{^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-{^1H} NMR spectrum.

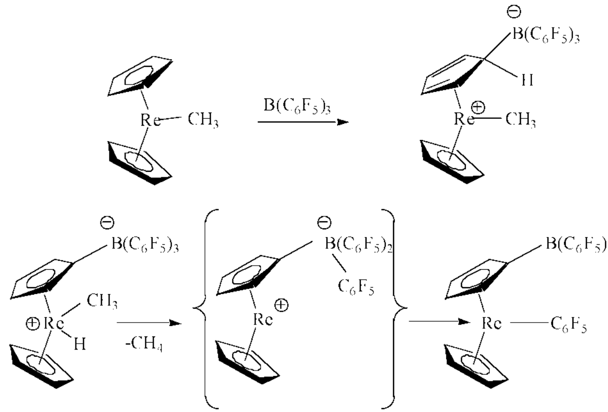
As the sample was warmed from −10 to +25 °C, the reaction mixture changed steadily from yellow *via* orange to bright red and gas evolution was observed. At the same time the ^1H NMR spectra developed two weak Re–hydride resonances, at δ −12.32 and −11.83, whilst the C_5H_5 region showed 6 clear peaks. 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 ^{13}C-{^1H} NMR at δ −2. These latter bands can be assigned unambiguously to CH_4. After room temperature was reached these bands assigned to CH_4 had reduced in intensity due to the diminished solubility of CH_4 in CD_2Cl_2 with the increase of temperature. This was confirmed by recooling the sample, which restored the original intensity of the CH_4 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)	2.174(3)	C(1)–B(1)	1.526(3)
Re(1)–Cp_{cent}	1.90	B(1)–C(40)	1.581(3)
Re(1)–Cp'_{cent}	1.88	B(1)–C(50)	1.602(3)
C(1)–B(1)–C(40)	126.7(2)	C(40)–B(1)–C(50)	115.70(18)
C(1)–B(1)–C(50)	115.2(2)		



10

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 inert-atmosphere 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, ^{11}B and ^{13}C 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 (^{13}C) resonances and measured relative to tetramethylsilane ($\delta = 0$); or referenced externally to $BF_3{\cdot}Et_2O$ (^{11}B, $\delta = 0$). 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 spectea 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 NEt_3 (99%) were purchased from Aldrich and pre-dried before use over activated 4 Å molecular sieves. [W(η-$C_5H_5)_2$-H_2],[15] PMe_3,[21] [Mo(η-$C_5H_5)_2H_2$],[14] [Mo(η-$C_5H_4Me)_2H_2$],[14] [Mo-(η-$C_5H_4Pr^i)_2H_2$],[15] [Mo(η-$C_5H_4Bu^n)_2H_2$],[15] [Re(η-$C_5H_5)_2H$],[22] [Ta(η-$C_5H_5)_2H_3$],[23] $B(C_6F_5)_3$,[5,7] $PhB(C_6F_5)_2$,[24] $ClB(C_6F_5)_2$[25] and $HB(C_6F_5)_2$[13] were prepared by literature methods.

Preparations

[W(η-C_5H_5)(η-C_5H_4{$B(C_6F_5)_3$})H_3] 1. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm^3) a solution of $B(C_6F_5)_3$ (0.530 g, 1.04 mmol) in petroleum ether (bp 100–120 °C) (10 cm^3) 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 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.750 g (91%).

$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2(C_6H_5)\})H_3]$ 2. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (30 cm^3) was added dropwise a solution of $B(C_6F_5)_2(C_6H_5)$ (0.430 g, 1.02 mmol) in petroleum ether (bp 100–120 °C) (15 cm^3). 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 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.550 g (75%).

$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2H\})H_3]$ 3. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm^3) was added dropwise a solution of $HB(C_6F_5)_2$ (0.355 g, 1.03 mmol) in petroleum ether (bp 100–120 °C) (20 cm^3). 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 cm^3) then petroleum ether (bp 40–60 °C) (2 × 30 cm^3) and dried *in vacuo* overnight. It was shown to be pure by microanalysis. Yield: 0.470 g (72%).

$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2Cl\})H_3]$ 4. To a stirred solution of $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.316 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (20 cm^3) was added dropwise a solution of $ClB(C_6F_5)_2$ (0.400 g, 1.05 mmol) in petroleum ether (bp 100–120 °C) (10 cm^3). Immediate precipitation of a flocculent grey-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 100–120 °C) (3 × 10 cm^3) 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 cm^3) under a flow of dinitrogen. Yield: 0.450 g (65%).

$[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ 5. To a cold (−78 °C) solution of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (0.550 g, 2.41 mmol) in toluene (30 cm^3) was added dropwise $B(C_6F_5)_3$ (1.240 g, 2.42 mmol) in toluene (30 cm^3). 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 cm^3) to yield the product as a blue powder which was dried overnight *in vacuo*. Yield: 1.1 g (62%).

$[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}H_2B(C_6F_5)_2)]$ 6. To a cold (−78 °C) solution of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (0.228 g, 1.00 mmol) in toluene (25 cm^3) a solution of $HB(C_6F_5)_2$ (0.346 g, 1.00 mmol) in toluene (30 cm^3) 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 cm^3). The product was crystallised from toluene (−80 °C) as blue needles. Yield: 0.2 g (35%).

$[Mo(\eta\text{-}C_5H_4Me)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ 7. To a cold (−78 °C) solution of $[Mo(\eta\text{-}C_5H_4Me)_2H_2]$ (0.310 g, 1.21 mmol) in toluene (20 cm^3) was added a solution of $B(C_6F_5)_3$ (0.620 g, 1.21 mmol) in toluene (20 cm^3) 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 cm^3). The product purity was confirmed by microanalysis. Yield 0.5 g (54%).

$[Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_3\})H_2]$ 8. To a stirred solution of $[Re(\eta\text{-}C_5H_5)_2H]$ (0.317 g, 1.00 mmol) in petroleum ether (bp 100–120 °C) (40 cm^3) was slowly added a solution of $B(C_6F_5)_3$ (0.530 g, 1.04 mmol) in petroleum ether (bp 100–120 °C) (10 cm^3). 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 cm^3) and recrystallised from toluene as a brown microcrystalline solid at −80 °C. Purity as **8**$\cdot 0.5C_6H_5Me$ was confirmed by microanalysis and NMR spectroscopy. Yield: 0.53 g (65%).

$[Ta(\eta\text{-}C_5H_5)_2(H)_2(\eta^1\text{-}HB(C_6F_5)_3)]$ 9. To a stirred solution of $[Ta(\eta\text{-}C_5H_5)_2H_3]$ (0.314 g, 1.00 mmol) in toluene (20 cm^3) was added a solution of $B(C_6F_5)_3$ (0.512 g, 1.00 mmol) in toluene (15 cm^3). 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 cm^3) 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.

$[Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_2\})(C_6F_5)]$ 10. In an NMR tube, a mixture of $[Re(\eta\text{-}C_5H_5)_2CH_3]$ (0.016 g, 48 mmol) and $B(C_6F_5)_3$ (0.025 g, 49 mmol) was quickly cooled to liquid nitrogen temperature. CD_2Cl_2 (0.8 cm^3) 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 CH_2Cl_2 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 $[Re(\eta\text{-}C_5H_5)_2CH_3]$ (0.050 g, 0.15 mmol) in CH_2Cl_2 (0.8 cm^3) with neat CH_2Cl_2 (2.0 cm^3) followed by careful addition of a solution of $B(C_6F_5)_3$ (0.075 g, 0.15 mmol) in CH_2Cl_2 (0.5 cm^3) 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 $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_3\})H_3]$ 1 and L [where L = THF, NEt_3 or PMe_3]. To a solution of $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4B(C_6F_5)_3)H_3]$ **1** (20 mg, 0.024 mmol) in toluene (10 cm^3) was added an excess of the Lewis base L; either THF (3 drops), NEt_3 (3 drops) or PMe_3 (1 cm^3 of a 0.105 M solution in petroleum ether (bp 40–60 °C)). The solutions rapidly became

Table 4 Crystal structure data

	4	**10**
Molecular formula	$WClF_{10}C_{22}H_{12}B$	$ReC_{28}H_9F_{15}B$
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)
α/°	80.26(3)	90.00
β/°	74.88(3)	90.00
γ/°	67.53(2)	90.00
V/Å^3	1020.4	4789.4
Space group	$P\bar{1}$	$Pbca$
Z	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 ^{1}H and ^{11}B-{^{1}H} NMR spectroscopy and showed that all three experiments gave virtually quantitative formation of $[W(\eta\text{-}C_5H_5)_2H_2]$ and $(C_6F_5)_3B{\cdot}L$ [L = THF, NEt_3 or PMe_3]. In the case where L = THF, a small amount (*ca.* 10%) of $[W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4B(C_6F_5)_3)H_3]$ remained. Where L = PMe_3, some of the residue proved to be insoluble in C_6D_6 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 $(C_6F_5)_3B{\cdot}NEt_3$ (C_6D_6, 298 K): ^{1}H, δ 0.51 (m, 9H, NCH_2CH_3), 1.62 (m, 6H, NCH_2CH_3); ^{11}B-{^{1}H}, δ −3.9 (s).

NMR data for $(C_6F_5)_3B{\cdot}THF$ (C_6D_6, 298 K): ^{1}H, δ 1.42 (m, 4H, C_4H_8O), 3.55 (m, 4H, C_4H_8O); ^{11}B-{^{1}H}, δ −3.7 (s).

Between $[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ 5 and 4-methylpyridine. To a suspension of $[Mo(\eta\text{-}C_5H_5)_2(H)(\eta^1\text{-}HB(C_6F_5)_3)]$ **5** (45 mg, 0.061 mmol) in toluene (5 cm^3), 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 C_6D_6 was undertaken. This allowed the products to be identified as $[Mo(\eta\text{-}C_5H_5)_2H_2]$ and $(C_6F_5)_3B{\cdot}$4-methylpyridine (which has been independently synthesised).

NMR data for $(C_6F_5)_3B{\cdot}NC_5H_4(CH_3)$ (C_6D_6, 298 K): ^{1}H, δ 1.39 (s, 3H, $NC_5H_4CH_3$), 6.14 (d, 2H, $^3J_{HH}$ = 6.5, $NC_5H_4CH_3$, H$_m$), 7.89 (d, 2H, $^3J_{HH}$ = 6.5, $NC_5H_4CH_3$, H$_o$); ^{11}B-{^{1}H}, δ −4.0.

Between $[Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\{B(C_6F_5)_3\})H_2]$ 8 and PMe_3. The compound $[Re(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4B(C_6F_5)_3)H_2]$ **8** (20 mg, 0.024 mmol) was dissolved in toluene (10 cm^3) and PMe_3 (1 cm^3 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 CRYSTALS[28] 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.

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