B(C₆F₅)₃ adducts of transition metal acyl compounds

Simon A. Llewellyn,* Malcolm L. H. Green and Andrew R. Cowley

Received 20th October 2005, Accepted 15th December 2005 First published as an Advance Article on the web 9th January 2006 DOI: 10.1039/b514889h

The transition metal acyl compounds $[Co(L)(CO)_3(COMe)]$ (L = PMe₃, PPhMe₂, P(4-Me-C₆H₄)₃, PPh₃ and P(4-F-C₆H₄)₃), $[Mn(CO)_5(COMe)]$ and $[Mo(PPh_3)(\eta^5-C_5H_5)(CO)_2(COMe)]$ react with B(C₆F₅)₃ to form the adducts $[Co(L)(CO)_3(C{OB(C_6F_5)_3}Me)]$ (L = PMe₃ **1**, PPhMe₂ **2**, P(4-Me-C₆H₄)₃ **3**, PPh₃ **4**, P(4-F-C₆H₄)₃ **5**), $[Mn(CO)_5(C{OB(C_6F_5)_3}Me)]$ **6** and $[Mo(\eta^5-C_5H_5)(PPh_3)(CO)_2$ - $(C{OB(C_6F_5)_3}Me)]$, **7**. Addition of $B(C_6F_5)_3$ to a cooled solution of $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$, under an atmosphere of CO gave $[Mo(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}Me)]$ **8**. In the presence of adventitious water, the compound $[Co{HOB(C_6F_5)_3}_2{OP(4-F-C_6H_4)_3}_2]$ **9**, was formed from $[Co(P(4-F-C_6H_4)_3) <math>(CO)_3(C{OB(C_6F_5)_3}Me)]$. The compounds **4** and **9** have been structurally characterised. The use of $B(C_6F_5)_3$ as a catalyst for the CO-induced migratory-insertion reaction in the transition metal alkyl compounds $[Co(PPh_3)(CO)_3(Me)]$, $[Mn(CO)_5(Me)]$, $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ and $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ has been investigated.

Introduction

The strong Lewis acid $B(C_6F_5)_3$ has been shown to undergo a diverse range of reactions with transition metal complexes.¹ We have recently shown that compounds of the general formula [Fe(η^5 - C_5H_3)(L)(CO)(COMe)] (L = CO or tertiary phosphine), form adducts of the type [Fe(η^5 - C_3H_3)(CO)(L)(C{OB(C_6F_5)_3}Me)](L = CO or tertiary phosphine), in which $B(C_6F_5)_3$ is bound exclusively to the acyl oxygen atom.² Here we describe the synthesis of a series of $B(C_6F_5)_3$ -bound transition metal acyl compounds, showing that this mode of reactivity is general.

In contrast to the reported reaction between $[Fe(\eta^5-C_5H_5)-$ (L)(CO)(COMe)] (L = CO or tertiary phosphine) and $B(C_6F_5)_3$, the alkyl derivative $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$, has been shown to react with $B(C_6F_5)_3$ to give the unexpected product [Fe{ $C_6F_4C(O)$ -Me-2}(η^5 -C₅H₅)(CO)].³ It was postulated that the mechanism of formation involved the transient 16 electron acyl species $[Fe(\eta^5-C_5H_5)(CO)(C{OB(C_6F_5)_3}Me)]$, suggesting that $B(C_6F_5)_3$ may be a suitable Lewis acid catalyst for migratory-insertion reactions. The use of mild acids/Lewis acids to catalyse migratoryinsertion reactions in transition metal carbonyl complexes has been well documented.⁴⁻⁶ Shriver et al. have shown that BF₃ and AlCl₃ increase the rate of CO-induced carbonylation in [Fe(η^5 - $C_5H_5)(CO)_2(Me)$], [Mn(CO)₅(COMe)] and [Mo(η^5 -C₅H₅)(CO)₃-(Me)] to give the corresponding Lewis acid-coordinated acyl derivatives, $[Fe(\eta^5-C_5H_5)(CO)_2(C{OAlBr_3}Me)]$, $[Mn(CO)_5(C-C_5H_5)(CO)_2(C{OAlBr_3}Me)]$, $[Mn(CO)_5(C-C_5H_5)(CO)_2(C-C_5H_5)(CO)_2(CO)_2(C{OAlBr_3}Me)]$, $[Mn(CO)_5(C-C_5H_5)(CO)_2(C-C_5H_5)(C-C_5H_5)(CO)_2(C-C_5$ $\{OBF_3\}Me\}$, and $[Mo(\eta^5-C_5H_5)(CO)_3(C\{OAlBr_3\}Me)]$ respectively. Similarly Cutler et al. have shown that the catalytic amounts of HBF4 allow carbonylation of [Fe(n⁵-C₅H₅)(PPh₃)-(CO)(Me)] and $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ under very mild conditions.⁶ To establish whether the bulky $B(C_6F_5)_3$ would have a similar catalytic result, the effect of the Lewis acid $B(C_6F_5)_3$ on the ligand-induced migratory-insertion reactions of [Mn(CO)₅-(Me)], $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$, $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$, and [Co(PPh₃)(CO)₃(Me)] has been investigated, as described below.

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

Results and discussion

Syntheses

The cobalt(1) acyl complexes, $[Co(L)(CO)_3(COMe)]$ (L = PMe₃, PPhMe₂, P(4-Me-C₆H₄)₃, PPh₃ and P(4-F-C₆H₄)₃), react with equimolar quantities of B(C₆F₅)₃ at room temperature in CH₂Cl₂ or C₆H₆, to afford a series of compounds in which the Lewis acid coordinates exclusively to the oxygen atom of the acyl carbonyl group (Scheme 1), yielding off-white to orange-brown solids $[Co(L)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$ (L = PMe₃ 1, PPhMe₂ 2, P(4-Me-C₆H₄)₃ 3, PPh₃, 4, P(4-F-C₆H₄)₃ 5). Crystallographic characterisation of the compound 4, confirms the attachment of the B(C₆F₅)₃ to the acyl oxygen atom. Characterising data are summarised in Table 1.



Scheme 1 Synthesis of $B(C_6F_5)_3$ adducts of cobalt(I) acyl compounds.

The analogous reactions of $[Mn(CO)_5(COMe)]$ and $[Mo-(PPh_3)(\eta^5-C_5H_5)(CO)_2(COMe)]$ with $B(C_6F_5)_3$ led to the formation of $[Mn(CO)_5(C\{OB(C_6F_5)_3\}Me)]$, **6** and $[Mo(\eta^5-C_5H_5)-(PPh_3)(CO)_2(C\{OB(C_6F_5)_3\}Me)]$, **7**, respectively. In a related reaction, the addition of $B(C_6F_5)_3$ to a cooled solution of $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$, under an atmosphere of CO gave the compound $[Mo(\eta^5-C_5H_5)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$, **8**. In the presence of adventitious water, the compound $[Co(P(4-F-C_6H_4)_3)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$ decomposed to give $[Co\{HOB-(C_6F_5)_3\}_2\{OP(4-F-C_6H_4)_3\}_2]$, **9**, which has been characterised by X-ray crystallography. Characterising data are summarised in Table 1.

Table 1 Characterising data for compounds 1–8

Compound ^a	NMR Data ^b
1 [Co(P(CH ₃) ₃)(CO) ₃ (C{OB(C ₆ F ₅) ₃ }CH ₃)] Orange-brown solid	¹ H: 1.58 [d, ² J _{PH} = 9.8 Hz, 9H, P(CH ₃) ₃], 2.77 [s, 3H, COCH ₃] ¹¹ B{ ¹ H}: -14.71 [s, $B(C_6F_5)_3$]
IK: 1644 m, 1520 m, 1998 s, 2016 s, 2076 w	C_{1}^{H} : 19.06 [d, $J_{PC} = 34.1$ Hz, $P(CH_{3})_{3}$], 49.97 [d, $J_{PC} = 10.4$ Hz, $COCH_{3}$], 117.96 [br s, $B(C_{6}F_{5})_{3}$, C_{ipso}], 135.53 [d, $^{1}J_{FC} = 244.5$ Hz, $B(C_{6}F_{5})_{3}$, C_{meta}], 141.82 [m, $B(C_{6}F_{5})_{3}$, C_{auro}], 146.80 [d, $^{1}J_{FC} = 243.4$ Hz, $B(C_{6}F_{5})_{3}$, C_{auro}], 195.67 [d, $^{2}J_{PC} = 24.2$ Hz, $Co(CO)_{3}$]
	¹⁹ F{ ¹ H}: 136.42 [d, ${}^{3}J_{FF} = 20.2$ Hz, 6F, $o \cdot C_{6}F_{5}$], -161.40 [t, ${}^{3}J_{FF} = 21.1$ Hz, 3F, $p \cdot C_{6}F_{5}$], -168.13 [t, ${}^{3}J_{FF} = 18.8$ Hz, 6F, $m \cdot C_{6}F_{5}$]
2 $[Co(P(C_6H_5)(CH_3)_2)(CO)_3(C{OB(C_6F_5)_3}CH_3)]$ Yellow solid	³¹ P{ ¹ H}: 18.05 [s, $P(CH_3)_3$] ¹ H: 1.90 [br s, 6H, $P(C_6H_5)(CH_3)_2$], 2.76 [br s, 3H, $COCH_3$)], 7.52 [m, 6H, ArH] ¹¹ B{ ¹ H}: -14.74 [s, $B(C_6F_5)_3$]
C 44.5 (44.5), H 1.7 (1.7), N 0 (0)	¹³ C{ ¹ H}: 18.50 [d, ¹ J _{PC} = 32.7 Hz, P(C ₆ H ₅)(CH ₃) ₂], 50.03 [br s, COCH ₃], 119.01 [br s, B(C ₆ F ₅) ₃ , C _{ipso}], 129.71 [m, P(C ₆ H ₅)(CH ₃) ₂], 137.19 [d, ¹ J _{FC} = 232.7 Hz, B(C ₆ F ₅) ₃ , C _{meta}], 142.00 [br s, B(C ₆ F ₅) ₃ , C _{para}], 147.98 [d, ¹ J _{FC} = 243.9 Hz, B(C ₆ F ₅) ₃ , C _{ortho}], 195.08 [br s, C ₁]
IR: 1518 m, 1644 m, 1998 s, 2016 s, 2076 w	$Co(CO)_{3}$] ¹⁹ $F{^{1}H}: -136.42$ [s, 6F, <i>o</i> -C ₆ F_{5}], -161.27 [s, 3F, <i>p</i> -C ₆ F_{5}], -168.06 [s, 6F, <i>m</i> -C ₆ F_{5}] ³¹ $P{^{1}H}: 24.03$ [s, $P(C_{6}H_{3})(CH_{3})_{7}$]
$3 [Co(P(4-CH_3-C_6H_4)_3)(CO)_3(C{OB(C_6F_5)_3}CH_3)]$ Off-white solid	¹ H: 2.37 [s, 9H, 4- CH_3 - C_6H_4], 2.74 [s, 3H, COC H_3], 7.31 [m, 12H, Ar H] ¹¹ B{ ¹ H}: -14.70 [s, $B(C_6F_5)_3$]
C 53.4 (52.7), H 2.3 (2.4), N 0 (0)	¹⁵ C{ ¹ H}: 21.60 [br s, CH ₃ -C ₆ H ₄], 52.14 [br s, COCH ₃], 52.63 [s, CoCOCH ₃], 121.54 [s, B(C ₆ F ₅) ₃ , C _{µvo}], 129.72 [d, $J_{PC} = 14.5$ Hz, ArC], 132.83 [d, $J_{PC} = 12.5$ Hz, P(4-CH ₃ -C ₆ H ₄) ₃], 146.39 [s, P(4-CH ₃ -C ₆ H ₄) ₃], 137.45 [d, ¹ $J_{FC} = 243.8$ Hz, B(C ₆ F ₅) ₃ , C _{meta}], 144.14 [br s, B(C ₆ F ₅) ₃ , C _{µava}], 146.39 [s, P(4-CH ₃ -C ₆ H ₄) ₃], 148.08 [d, ¹ $J_{FC} = 243.8$ Hz, B(C ₆ F ₅) ₃ , C _{meta}], 144.14 [br s, B(C ₆ F ₅) ₃ , C _{µava}], 146.39 [s, P(4-CH ₃ -C ₆ H ₄) ₃], 148.08 [d, ¹ $J_{FC} = 243.8$ Hz, B(C ₆ F ₅) ₃ ,
IR: 1520 m, 1644 m, 1990 s, 2016 s, 2076 w	¹⁹ F{ ¹ H}: -134.82 [br s, 6F, o -C ₆ F ₅], -158.74 [br s 3F, p -C ₆ F ₅], -165.29 [br s, 6F, m -C ₆ F ₅] ³¹ P{ ¹ H}: 48.20 [s, $P(4$ -CH ₁ -C,H ₂),]
4 $[Co(P(C_6H_5)_3)(CO)_3(C{OB(C_6F_5)_3}CH_3)]$ Off-white solid	¹ H: 2.87 [br s, 3H, $COCH_3$], 7.69–7.36 [m, 15H, Ar <i>H</i>] ¹¹ B{ ¹ H}: -14.20 [s, $B(C_6F_5)_3$]
C 51.0 (51.3), H 2.2 (1.9), N 0 (0)	¹⁵ C{ ¹ H}: 49.80 [d, ${}^{7}J_{PC} = 9.4$ Hz, COCH ₃], 117.67 [br s, B(C ₆ F ₅) ₃ , C_{ipuo}], 128.58 [s, P(C ₆ H ₅) ₃], 129.63 [d, ${}^{J}P_{C} = 0.2$ Hz, P(C ₆ H ₅) ₃], 132.20 [s, P(C ₆ H ₅) ₃], 133.17 [d, ${}^{J}P_{C} =$ 10.7 Hz, P(C ₆ H ₅) ₃], 137.16 [d, ${}^{1}J_{FC} = 243.1$ Hz, B(C ₆ F ₅) ₃ , C_{meta}], 140.13 [d, ${}^{1}J_{FC} =$ 246.6 Hz, B(C ₆ F ₅) ₃ , C_{para}], 147.75 [d, ${}^{1}J_{FC} = 240.1$ Hz, B(C ₆ F ₅) ₃ , C_{ortha}], 195.27 [d, ${}^{2}J_{PC} =$ 23.6 Hz, Co(C) ₁
IR: 1520 m, 1646 m, 1994 s, 2024 s, 2082 w	¹⁹ F{ ¹ H}: -134.27 [d, ${}^{3}J_{FF} = 21.4$ Hz, 6F, o -C ₆ F_{s}], -156.42 [t, ${}^{3}J_{FF} = 18.6$ Hz, 3F, p -C ₆ F_{s}], -163.81 [d, ${}^{3}J_{FF} = 20.2$ Hz, 6F, m -C ₆ F_{s}] ³¹ P(¹ H): 50 66 [s, PPb.]
5 $[Co(P(4-F-C_6H_4)_3)(CO)_3(C{OB(C_6F_5)_3}CH_3)]$ Off-white solid	¹ H: 2.87 [s, 3H, COCH ₃], 6.55 [t, ${}^{3}J_{HH} = 8.5$ Hz, 6H, ArH], 6.99 [br s, 6H, ArH] ¹ B{ ¹ H}: -14.09 [br s, $B(C_{6}F_{5})_{3}$]
C 48.5 (48.6), H 1.5 (1.5), N 0 (0)	¹³ C{ ¹ H}: 50.03 [s, COCH ₃], 117.40 [m, P(4-F- C_6H_4) ₃], 126.71 [m, P(4-F- C_6H_4) ₃], 135.77 [s, P(4-F- C_6H_4) ₃], 138.62 [s, B(C_6F_5) ₃ , C_{meta}], 141.89 [s, B(C_6F_5) ₃ , C_{para}], 149.42 [d, ¹ J_{FC} = 236.14 Hz, B(C_6F_5) ₃ , C_{ortho}], 163.20 [s, P(4-F- C_6H_4) ₃], 166.56 [s, P(4-F- C_6H_4) ₃], 195.39 [s, Co(CO) ₃]
IR: 1514 m, 1644 m, 2004 s, 2022 s, 2080 w	$^{19}F_1^{(1H)}: -106.48 \text{ [s, 3F, P(4-F-C_6H_4)_3]}, -134.07 \text{ [s, 6F } o\text{-}C_6F_5], -158.65 \text{ [s, 3F, } p\text{-}C_6F_5], -166.46 \text{ [s, 6F, } m\text{-}C_6F_5]$ $^{31}P_1^{(1H)}: 49.17 \text{ [s, } p(4\text{-}F\text{-}C_6H_4)_3]$
6 [Mn(CO) ₅ (C $\{OB(C_6F_5)_3\}CH_3$)] Off-white solid	¹ H: 2.87 [s, 3H, COC H_3] ¹¹ B{ ¹ H}: 1.48 [br s, B(C ₆ F ₅) ₃]
IR: 1520 m,1646 m, 2004 s, 2086 s, 2116 s	¹³ C{ ¹ H}: 50.91 [s, COCH ₃], 118.96 [br s, B(C ₆ F ₅) ₃ , C_{ipso}], 137.42 [d, ¹ J _{FC} = 229.3 Hz, B(C ₆ F ₅) ₃ , C_{meta}], 140.55 [s, ¹ J _{FC} = 249.3 Hz, B(C ₆ F ₅) ₃ , C_{para}], 147.78 [d, ¹ J _{FC} = 240.2 Hz, B(C ₆ F ₅) ₃ , C_{ortho}], 205.05 [s, Mn(CO) ₅] ¹⁹ F{ ¹ H}: -134.84 [d, ³ J _{FF} = 21.8 Hz, 6F, o-C ₆ F ₅], -157.56 [s, 3F, p-C ₆ F ₅], -164.35 [t,
7 $[Mo(\eta^5-C_5H_5)(P(C_6H_5)_3)(CO)_2(C\{OB(C_6F_5)_3\}CH_3)]$ Yellow solid	${}^{5}J_{FF} = 1/.8 \text{ Hz}, 6F, m-C_{6}F_{5}$ ${}^{1}\text{H}: 2.75 \text{ [s, 3H, COCH_{3}], 5.27 \text{ [s, 5H, }\eta^{5}-C_{5}H_{5}], 7.15-7.50 \text{ [m, 15H, P(C_{6}H_{5})_{3}]}$ ${}^{11}\text{B}\{{}^{1}\text{H}\}: 3.175 \text{ [s, }B(C_{6}F_{5})_{3}]$
C 51.7 (52.2), H 2.4 (2.2), N 0 (0)	¹³ C{ ¹ H}: 50.41 [s, COCH ₃], 97.86 [s, η^5 -C ₅ H ₅], 119.50 [br s, B(C ₆ F ₅) ₃ , C _{ipso}], 129.32 [d, J _{FC} = 10.3 Hz, P(C ₆ H ₅) ₃], 131.68 [m, P(C ₆ H ₅) ₃], 133.15 [m, P(C ₆ H ₅) ₃], 137.22 [d, ¹ J _{FC} = 228.9 Hz, B(C ₆ F ₅) ₃ , C _{meta}], 140.12 [m, B(C ₆ F ₅) ₃ , C _{para}], 147.99 [d, ¹ J _{FC} = 243.0 Hz, B(C, F ₂), C ₂ , 1, 235.3 [d ² -L ₂ = 25.7 Hz, Mo(CO)]
IR: 1520 m, 1644 m, 1898 s, 1970 s	¹⁹ F{ ¹ H}: -134.60 [d, ${}^{3}J_{FF} = 21.4$ Hz, 6F, $o-C_{6}F_{5}$], -159.34 [t, ${}^{3}J_{FF} = 18.6$ Hz, 3F, $p-C_{6}F_{5}$], -165.50 [d, ${}^{3}J_{FF} = 20.2$ Hz, 6F, m-C ₆ F_{5}] ³¹ P(¹ H}: 57.6 [s, $P(C_{1}H_{2})_{1}$]
8 $[Mo(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}CH_3)]$ Orange solid	¹ H: 2.79 [s, 3H, COCH ₃], 5.65 [s, 5H, η^5 -C ₅ H ₅] ¹ B{ ¹ H}: 4.84 [br s, B(C ₆ F ₅) ₅] ¹ B{ ¹ H}: 51 46 [cocH ₃] < 00 [-5 CH ₃] ¹ CH
C 41./ (42.0), H 1.1 (1.0), N 0 (0)	$C_{\{+H\}}$: 51.19 [s, COCH ₃], 96.99 [s, η - $C_{5}H_{5}$], 13/.10 [d, $J_{FC} = 244.5$ Hz, B($C_{6}F_{5}$) ₃ , C_{meta}], 141.79 [s, B($C_{6}F_{5}$) ₃ , C_{para}], 147.58 [d, $^{1}J_{FC} = 244.4$ Hz, B($C_{6}F_{5}$) ₃ , C_{ortho}], 225.97 [s, Mo(CO) ₃]
IR: 1515 m, 1646 m, 1929 s, 2020 s	¹⁹ F (^{1}H) : 135.53 [s, 6F, <i>o</i> -C ₆ <i>F</i> ₅], 156.66 [s, 3F, <i>p</i> -C ₆ <i>F</i> ₅], 163.20 [s, 6F, <i>m</i> -C ₆ <i>F</i> ₅]

^{*a*} Analytical data are given as found (calculated) in %. Selected IR data (cm⁻¹) were recorded as either Nujol mulls between KBr plates, **1–5**, or as CH₂Cl₂ solutions, **6–8**. ^{*b*} NMR data given as chemical shift ($\delta = 0$ ppm) [multiplicity, relative intensity, J in Hz, assignment] and were obtained in C₆D₆/CD₂Cl₂.

The reaction of cooled solutions $(-78 \ ^{\circ}C)$ of the transition metal alkyl compounds, [Co(PPh₃)(CO)₃(Me)], [Mn(CO)₅(Me)], $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ and $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ with $B(C_6F_5)_3$ and CO gave the $B(C_6F_5)_3$ -coordinated acyl adducts: $[Co(PPh_3)(CO)_3(C{OB(C_6F_5)_3}Me)], [Mn(CO)_5(C{OB(C_6F_5)_3}-$ Me)], $[Mo(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}Me)]$ and $[Fe(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}Me)]$ $C_5H_5)(CO)_2(C\{OB(C_6F_5)_3\}Me)]$, in yields of 40–99%. By contrast, under the same pressures of CO, but in the absence of $B(C_6F_5)_3$, $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ and $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ were inactive towards carbonylation. However, the compounds [Co(PPh₃)(CO)₃(Me)] and [Mn(CO)₅(Me)] underwent carbonylation even in the absence of $B(C_6F_5)_3$ to give the acyl derivatives in yields of 70–99%. The effect of $B(C_6F_5)_3$ on the migratoryinsertion may be rationalised in terms of the formation of an intermediate acyl species, $[M(C{OB(C_6F_5)_3}Me)]$, on reacting with the metal alkyl compound, [M(CO)(Me)]. The vacant site formed during this migration, possibly stabilised by a M-F interaction, would then be filled by CO, to give the observed Lewis acid bound acyl derivatives (Scheme 2). Such M-F interactions have recently been reported by Roesky et al. in the compound $[LAlB(C_6F_5)_3](L = HC(CMeNAr)_2; Ar = 2,6-iPr_2C_6H_3]^7$



 $X = C_6 F_5$, L = CO

Scheme 2 Proposed pathway in $B(C_6F_5)_3$ catalysed migratory-insertion.

Reaction conditions and yields obtained for the COinduced migratory-insertions are summarised in Table 2. The lower yields observed for the carbonylation of $[Fe(\eta^5-C_3H_3)(CO)_2(Me)]$ may be attributed to a higher reactivity of the compound $[Fe(\eta^5-C_3H_5)(CO)_2(Me)]$ with $B(C_6F_5)_3$ (with regards to C–F activation) when compared with that of $[Mn(CO)_5(Me)]$ and $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$. The formation of $[Mo(\eta^5-C_3H_3)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$ represents a stabilisation of the otherwise thermodynamically unstable $[Mo(\eta^5 C_3H_3)(CO)_3(COMe)]$ system. Shriver *et al.* have noted a similar effect in the compound $[Mo(\eta^5-C_3H_3)(CO)_3(C\{OAlBr_3\}Me)]$.⁵ The products of all carbonylation reactions were unambiguously identified by comparison of the NMR and IR spectroscopic data with reference samples of the compounds in question.

X-Ray crystallography

The molecular structure of the compound **4** is given in Fig. 1. Selected bond lengths (\AA) and angles $(^{\circ})$ are summarised in Table 3



Fig. 1 The molecular structure of $[Co(PPh_3)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$ 4, thermal ellipsoids are drawn at 40% probability.

and molecular parameters are presented in Table 7. The cobalt centre has a trigonal bipyramidal geometry, typical of cobalt acyl complexes of this type,8 with a bis-axial arrangement of the acyl and phosphine groups. The X-ray structure confirms the connection of the $B(C_6F_5)_3$ to the O atom of the acyl group with a B-O bond length of 1.561(3) Å, and shows a distorted tetrahedral coordination about the boron centre. The Co-C_{acvl} length of 1.931(3) Å is 0.057 Å shorter than is found in the parent acyl compound [Co(PPh₃)(CO)₃(COMe)]⁹ (see Table 4), and is approaching the 1.912 Å Co-C distance found in the Fischercarbene complexes [(Ph₃Ge)(CO)₃Co(=C(OEt)Et)].¹⁰ This is consistent with a strengthening of the Co-Cacyl upon coordination of the Lewis acid. Thus the Co–C_{acyl} bond length may be described as intermediate between the single Co-C and the double Co=C bond lengths. The coordination of $B(C_6F_5)_3$ to the O acyl atom in the compound [Co(PPh₃)(CO)₃(COMe)] leads to an increase in C=O_{acyl} bond length from 1.195 Å, in the parent acyl compound,

 Table 2
 Results for the carbonylation of transition metal alkyl compounds

Starting material	Conditions	Product	Yield (%)
$[Co(PPh_3)(CO)_3(Me)]$	СО	[Co(PPh ₃)(CO) ₃ (COMe)]	99
	CO, $B(C_6F_5)_3$	$[Co(PPh_3)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$	99
$[Fe(\eta^3-C_5H_5)(CO)_2(Me)]$	CO B(C E)	$[Fe(\eta^3-C_5H_5)(CO)_2(COMe)]$ $[Fe(\eta^5-C_5H_5)(CO)_2(C_5OB(C_5E_5))]Me)]$	0
[Mn(CO)₅(Me)]	$CO, D(C_6\Gamma_5)_3$ CO	$[Mn(CO)_{5}(COMe)]$	72
L ())(-)]	CO, $B(C_6F_5)_3$	$[Mn(CO)_5(C{OB(C_6F_5)_3}Me)]$	99
$[Mo(\eta^{5}-C_{5}H_{5})(CO)_{3}(Me)]$	CO	$[Mo(\eta^{5}-C_{5}H_{5})(CO)_{3}(COMe)]$	0
	CO, $B(C_6F_5)_3$	$[Mo(\eta^{2}-C_{5}H_{5})(CO)_{3}(C\{OB(C_{6}F_{5})_{3}\}Me)]$	99

		,	
4			
Co(1)–C(22)	1.931(3)	O(4)-B(1)-C(24)	111.17(19)
Co(1) - P(1)	2.2640(7)	C(2)-Co(1)-C(3)	114.57(13)
C(22)–C(23)	1.497(4)	Co(1)-C(22)-C(23)	121.69(17)
O(4) - B(1)	1.561(3)		
C(22)–O(4)	1.268 (3)		
CO terminal ^a	1.136 (3)		
9			
Co(1)–O(1)	1.920(2)	O(1)–Co(1)–O(2)	100.9(1)
Co(1)–O(3)	1.933(2)	O(1)-Co(1)-O(3)	118.8(1)
O(1) - P(1)	1.499(2)	O(2)–Co(1)–O(3)	118.5(1)
O(3) - B(1)	1.484(4)	O(3)–Co(1)–O(4)	102.7(8)
Co(1)–O(2)	1.941(2)	Co(1)–O(1)–P(1)	169.4(16)
Co(1)–O(4)	2.022(19)	O(3)–B(1)–C(37)	103.3(2)
O(2)–P(2)	1.493(2)	O(3)-B(1)-C(43)	112.4(2)
O(4) - B(2)	1.532(3)	Co(1)–O(3)–H(1)	103.5(2)
O(4) - H(2)	0.72(8)	Co(1)–O(4)–H(2)	100(7)
^{<i>a</i>} Average of 3 box	nd lengths.		

Table 3 Selected bond lengths (Å) and angles (°) for compounds 4 and 9

to 1.268(3) Å in **4**. This is longer than has been observed for any other reported cobalt(1) acyl compound (Table 4).

The 1.561(3) Å O–B bond length observed for the compound **4** is comparable with those seen for the related compounds $[Fe(\eta^5-C_3H_5)(CO)_2(C\{OB(C_6F_5)_3\}Me)]$, and $[Fe(\eta^5-C_5H_5)(PMe_3)(CO)(C\{OB(C_6F_5)_3\}Me)]$,² in which O–B bond lengths are 1.570(3) Å, and 1.559(3) Å respectively. The O–B bond length observed for the compound **4** is shorter than those seen in organic analogues of general formula $[PhC\{OB(C_6F_5)_3\}R]$: see Table 4, in which the average O–B bond length is 1.593(6) Å. The average C_{co} –Co– C_{acyl} bond angle observed for the compound **4** is 88.82°.

The reaction of B(C₆F₅) with water has been well documented,¹⁴ and the presence of adventitious water has given rise to some unusual complexes.² During the attempted crystal growth of the compound **5**, crystals of $[Co{HOB(C_6F_5)_3}_2{OP(4-F-C_6H_4)_3}_2]$ that were suitable for structural characterisation were formed. The molecular structure of compound **9** is shown in Fig. 2. Selected bond lengths (Å) and angles (°) are given in Table 3 and molecular parameters are presented in Table 7. Bond lengths of similar compounds are given in Table 5, for comparison. The cobalt centre shows a distorted tetrahedral geometry, with Co–O bond lengths of between 1.920(2) Å and 2.022(19) Å. These values are similar to those reported for $[Co_4(PO_4)_4]$ -containing complexes.¹⁵



Fig. 2 The molecular structure of $[Co{HOB(C_6F_5)_3}_2{OP(4-F-C_6H_4)_3}_2]$ **9**, thermal ellipsoids are drawn at 40% probability.

The O–B bond lengths in compound **9** are 1.484(4) Å and 1.532(3) Å. The second of these values is similar to those reported for the related compounds $[Fe(\eta^5-C_3H_3)(PPh_3)(CO){HOB-(C_6F_5)_3}]$, 1.508(2) Å, $[Ti(\eta^5-C_3H_5)_2][HOB(C_6F_5)_3]$,¹⁸ 1.519(3) Å, $[InMe{HOB(C_6F_5)_3}{1,2-(NiPr)_2C_8H_5}]$,¹⁷ 1.528(3) Å, and $[Pt{HOB(C_6F_5)_3}(bu_2bpy)Me]^{16}$ (bu_2bpy = 4,4-di-*tert*-butyl-2,2-bipyridine), 1.526(3) Å. The O–B bond length in all of these compounds is longer than the 1.487(3) Å O–B bond length that has been reported for the anion $[HOB(C_6F_5)_3]^{-16}$ However, the shorter O–B bond in **7**, at 1.484(4) Å, is similar.

In each of the two $[HOB(C_6F_5)_3]$ moieties, short $O \cdots F$ bond distances between one of the *ortho*-fluorine atoms and the appropriate OB oxygen atom (2.686 Å and 2.739 Å) are observed. These values are significantly smaller than the sum of the van der Waals radii (O 1.52 Å and F 1.47 Å), and suggest an interaction between the *ortho*-fluorine atom of the C_6F_5 group and the oxygen atom of the B–O–Co bond. In each case, the C–F bond of the *ortho*-fluorine was observed to be the longest of the five C–F bonds in the C_6F_5 group (by *ca*. 0.05 Å). Similar interactions have been

	Co–C	C–O _{acyl}	C–O _{terminal} ^a	O–B
$\begin{array}{l} [Co(PPh_{3})(CO)_{3}(C\{OB(C_{6}F_{5})_{3}\}Me)]\\ [Co(PPh_{3})(CO)_{3}(COMe)]^{9}\\ [Co(PPh_{3})(CO)_{3}(C(O)OMe)]^{11}\\ [Co(PPh_{3})(CO)_{3}(C(O)CH_{2}Cl)]^{8} \end{array}$	$ \begin{array}{r} 1.931(3) \\ 1.988(6) \\ 1.976^{b} \\ 1.999(5) \end{array} $	1.268(3) 1.195(7) 1.196 ^b 1.180 ^b	$ \begin{array}{r} 1.136(3) \\ 1.145^{b} \\ 1.138^{b} \\ 1.142(3) \end{array} $	1.561(3) — —
$\label{eq:constraint} \begin{split} & [\text{Co}(\text{PPh}_3)(\text{CO})_3(\text{C}(\text{O})\text{O}^n\text{Bu})]^{12} \\ & [(\text{Ph}_3\text{Ge})(\text{CO})_3\text{Co}(=\text{C}(\text{OEt})\text{Et})]^{10} \\ & [\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_2(\text{C}\{\text{OB}(\text{C}_6\text{F}_5)_3\}\text{Me})]^2 \\ & [\text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\text{PMe}_3)(\text{CO})(\text{C}\{\text{OB}(\text{C}_6\text{F}_5)_3\}\text{Me})]^2 \\ & \text{PhC}\{\text{OB}(\text{C}_6\text{F}_5)_3\}\text{H}^{13} \\ & \text{PhC}\{\text{OB}(\text{C}_6\text{F}_5)_3\}\text{CH}_3^{13} \\ & \text{PhC}\{\text{OB}(\text{C}_6\text{F}_5)_3\}\text{OEt}^{13} \end{split}$	1.967(2) 1.912 [*] 1.919(2) 1.904(2) — —	120.1(2) 	1.141(2) 1.13 1.141(3) — — —	

Table 4 Selected bond lengths (Å)

^a Average for 3 terminal CO groups. ^b esd not given.

Table 5	Selected bond lengths (Å)	from compounds	containing [HOB(C ₆ F ₅) ₃] ⁻
---------	---------------------------	----------------	---

Compound	Со–О	O–B	O–P
$[Co{HOB(C_6F_5)_3}_2{OP(4-F-C_6H_4)_3}_2]$	1.920(2), 2.022(19)	1.484(4), 1.532(3)	1.499(2), 1.493(2)
$[Fe(\eta^5-C_5H_5)(PPh_3)(CO){HOB(C_6F_5)_3}]^2$		1.508(2)	
$[Pt{HOB(C_6F_5)_3}(bu_2bpy)Me]^{a_{16}}$		1.526(3)	
$[InMe{HOB(C_6F_5)_3}]{1,2-(NiPr)_2C_8H_5}]^{17}$		1.528(3)	
$[Ti(\eta^5 - C_5 H_5)_2][HOB(C_6 F_5)_3]^{18}$		1.519(3)	
$[NEt_3H][HOB(C_6F_5)_3]^{16}$		1.487(3)	
$[H_2 O \cdot B(C_6 F_5)_3]^{19}$		1.597 (2)	

noted in the compounds $[Fe(\eta^5-C_5H_5)(PPh_3)(CO){HOB(C_6F_5)_3}]^2$ and $[Ti(\eta^5-C_5H_5)_2][HOB(C_6F_5)_3]$.¹⁸ Two short $Co \cdots F$ (from C_6F_5) bond distances of 2.752 Å and 2.750 Å were also observed.

NMR Spectroscopy

The ¹H NMR spectra for the $B(C_6F_5)_3$ adducts 1–5 show a downfield shift of the singlet resonance, assigned to the acyl methyl protons, when compared with their parent acyl compounds. This is consistent with a reduction in the electron density at the methyl group, caused by coordination of the Lewis acid. For the compounds 1-5 these methyl resonances are broad (ca. 30-200 Hz). The corresponding resonances in the parent acyl compounds are much sharper (ca. 10 Hz).²⁰ Addition of 1 equivalent of $B(C_6F_5)_3$ to solutions of compounds 1-5, led to a sharpening of the ¹H and ³¹P{¹H} NMR resonances in all instances, suggesting an equilibrium between the $B(C_6F_5)_3$ coordinated and free acyl compounds. Similar equilibria have been suggested to exist between benzaldehyde/acetophenone and $B(C_6F_5)_3$ ²¹ The exchange equilibria between the Lewis acid adducts 1-5 and the non-coordinated parent acyl compounds were explored further by a series of variable temperature (VT) NMR studies. Typically, as the temperature was reduced from $25 \degree C$ to $-60 \degree C$, the resonance assigned to the methyl acyl group sharpened, indicating that as the temperature decreased, both the relative amount of B(C₆F₅)₃-coordinated adduct increases, and the rate of exchange decreases, leading to sharper resonances. By contrast, the compounds 6-8, showed sharp methyl resonances.

The ${}^{19}F{}^{1}H$ NMR chemical shifts of the $B(C_6F_5)_3$ moiety in the compounds **1–8** (Table 1) show a characteristic up-field shift of the *ortho, meta* and *para* resonances, when compared with those

of free B(C₆F₅)₃, that is most emphasised for the *para* resonances. Typically, these *para* resonances show an up-field shift of *ca*. 15 ppm. Table 6 lists ¹⁹F{¹H} NMR data for B(C₆F₅)₃ containing compounds in which a 4-coordinate boron centre is present (data for B(C₆F₅)₃ is also included). Comparison of the ¹⁹F{¹H} data for the compounds **1–8** with these data, suggests a 4-coordinate boron centre is present in these compounds. The ¹¹B{¹H} NMR spectra for the compounds **1–5** show broad resonances (Table 1) that are typically 70 ppm up-field from the un-coordinated B(C₆F₅)₃. These resonances fall into the typical range δ + 5 to δ – 25 seen for organometallic compounds containing coordinated B(C₆F₅)₃.

The ¹³C{¹H} NMR spectra of the compounds **1–5** show a characteristic change of the carbonyl resonances on coordination of $B(C_6F_5)_3$. In the parent acyl compounds, the terminal carbonyl resonances are observed as broad singlets at *ca*. δ 200, and the acyl carbonyl resonance occurs at *ca*. δ 240. This later resonance shows coupling of the ¹³C{¹H} nucleus to the ³¹P{¹H} nucleus of the tertiary phosphine ligand. In the corresponding adducts, the compounds **1–5**, the terminal carbonyl resonances are also observed at *ca*. δ 200. On coordination to $B(C_6F_5)_3$, the carbonyl resonances of the [COMe] moiety were no longer detectable. This may be due to exchange between $B(C_6F_5)_3$ and the oxygen atom of the acyl group. Similarly, the ¹³C{¹H} spectra of the compounds **6–8** show only carbonyl resonances assignable to terminal carbonyl groups.

Conclusion

The reaction between $B(C_6F_5)_3$ and the compounds $[Co(L)-(CO)_3(COMe)]$ (L = PMe₃, PPhMe₂, P(4-Me-C₆H₄)₃, PPh₃ and P(4-F-C₆H₄)₃), [Mn(CO)₅(COMe)] and [Mo(PPh₃)(η⁵-C₅H₅)(CO)₂-(COMe)] gave the adducts $[Co(L)(CO)_3(C{OB(C_6F_5)_3}Me)]$

Table 6 Comparison of $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR resonances

		$^{19}\mathrm{F}\{^{1}\mathrm{H}\}(\delta)$		
Compound	$^{11}\mathrm{B}\{^{1}\mathrm{H}\}(\delta)$	ortho	para	meta
$B(C_6F_5)_3$	65.47	-128.6	-144.3	-164.6
$[Fe{(\mu-CN)B(C_6F_5)_3}(\eta^5-C_5H_5)(CO)_2]^{22}$	-22.4 (br)	-134.0	-158.6	-164.7
$[Fe(\eta^{5}-C_{5}H_{5})(PMe_{3})(CO)(C\{OB(C_{6}F_{5})_{3}\}Me)]^{2}$	-14.1 (br)	-133.5	-156.8	-163.8
$[Mo[NB(C_6F_5)_3(SCNMe_2)_3]^{23}$	-6.5 (br)	-134.2	-163.9	-169.0
$[MoO{OB(C_6F_5)_3}(\eta^2-ONEt_2)_2]^{24}$	2.4 (br)			
$[Mo{OB(C_6F_5)_3}{HB(dmpz)_3}(S_2CNMe_2)]^{a}$ ²⁵	2.5 (br)			
$[Re{OB(C_6F_5)_3}]{HB(pz)_3}(OCH_2CH_2O)]^{b^{-25}}$	4.6 (br)			
$[W(\eta^5 - C_5 H_5)_2 \{OB(C_6 F_5)_3\}]^{26}$	1.6 (s)			
$[Mo(C_5H_4Me)_2 {OB(C_6F_5)_3}]^{26}$	2.3 (s)			

Published on 09 January 2006. Downloaded by Brown University on 26/10/2014 08:18:30.

(L = PMe₃ 1, PPhMe₂ 2, P(4-Me-C₆H₄)₃ 3, PPh₃ 4, P(4-F-C₆H₄)₃ 5), [Mn(CO)₅(C{OB(C₆F₅)₃}Me)] 6 and [Mo(η^5 -C₅H₅)(CO)₂(C{OB(C₆F₅)₃}Me)] 7. Addition of B(C₆F₅)₃ to a cooled solution of [Mo(η^5 -C₅H₅)(CO)₃(Me)], under an atmosphere of CO gave [Mo(η^5 -C₅H₅)(CO)₃(C{OB(C₆F₅)₃}Me)], 8. The use of B(C₆F₅)₃ as a catalyst for the CO-induced migratory-insertion has been demonstrated.

Experimental

All manipulations of air- and/or moisture-sensitive compounds were carried out under an inert atmosphere of dinitrogen, in either an inert-atmosphere box or using standard Schlenk line techniques. Solvents used in the preparation of air- and/or moisture-sensitive compounds were dried by passage through an alumina column under a positive pressure of dinitrogen. Dinitrogen was passed through the dried solvents for twenty minutes before use. Deuterated solvents were degassed using three freeze-pump-thaw cycles and were vacuum distilled from potassium or sodium (d₆-benzene, d₈-toluene) or CaH₂ (CD_2Cl_2) . Solution NMR spectra were recorded with either a Varian UNITY plus (1H: 500.0 MHz, 13C: 125.7 MHz, 31P: 202.4 MHz, ¹⁹F: 470.4, ¹¹B: 160.4 MHz) or a Varian Mercury 300 (1H: 300.2 MHz, 13C: 75.5 MHz, 31P: 121.5 MHz, 19F 282.3 MHz,) spectrometer. The spectra were either internally referenced relative to the residual protio-solvent (1H) and solvent (¹³C) resonances relative to trimethylsilane (¹H, ¹³C, $\delta = 0$ ppm), or were referenced externally, relative to H_3PO_4 (³¹P, $\delta = 0$ ppm), CFCl₃ (¹⁹F, $\delta = 0$ ppm), or BF₃.Et₂O (¹¹B, $\delta =$ 0 ppm). Infrared spectra were recorded on either a Perkin-Elmer 1710 FTIR spectrometer or a Perkin-Elmer 1600 FTIR instrument in the range 4000-400 cm⁻¹. Samples were prepared either as Nujol mulls between KBr plates, or as solutions in CH_2Cl_2 . Data are quoted in wavenumbers (cm⁻¹). The following compounds were synthesised according to literature methods: [Co(PPh₃)(CO)₃(Me)],²⁸ $B(C_6F_5)_{3}^{27}$ $[Co(L)(CO)_3(COMe)]$ $(L = PMe_3, PPhMe_2, P(4-Me-C_6H_4)_3, and P(4-F-C_6H_4)_3)^{20}$ $[Co(PPh_3)(CO)_3(COMe)]^{29}$ $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]^{30}$ $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]^{30}$ $C_5H_5)(PPh_3)(CO)(COMe)]^{31}$ [Mn(CO)₅(COMe)]³² [Mo(η⁵- $C_5H_5)(PPh_3)(CO)_2(COMe)]$,³³ [Mo(η^5 -C₅H₅)(CO)₃(Me)].³⁰

Preparation of [Co(PMe₃)(CO)₃(C{OB(C₆F₅)₃}Me)] 1

A solution of $B(C_6F_5)_3$ (580 mg, 1.14 mmol) in dichloromethane (10 ml) was added slowly to a yellow solution of $[Co(PMe_3)(CO)_3(COMe)]$ (300 mg, 1.14 mmol) in dichloromethane (20 ml). The resulting solution was left stirring at room temperature for 2 h, giving a pale yellow solution. Solvents were removed under reduced pressure, to yield 1 as a sticky yellow solid, which was then dried under vacuum. Yield of 1 = quantitative.

Preparation of $[Co(PPhMe_2)(CO)_3(C{OB(C_6F_5)_3}Me)] 2$

A solution of $B(C_6F_5)_3$ (47 mg, 0.09 mmol) in dichloromethane (20 ml) was added slowly to a yellow solution of $[Co(PPhMe_2)-(CO)_3(COMe)]$ (30 mg, 0.09 mmol) in dichloromethane (20 ml). The resulting solution was left stirring at room temperature for 2 h to give a pale yellow solution. Solvents were removed under reduced pressure, to yield 2 as a sticky orange solid, which was then dried under vacuum. Yield of 2 = quantitative.

Preparation of $[Co(P(4-Me-C_6H_4)_3(CO)_3(C{OB(C_6F_5)_3}Me)]$ 3

A solution of $B(C_6F_5)_3$ (187 mg, 0.366 mmol) in benzene (20 ml) was added dropwise to a yellow solution of $[Co(P(4-Me-C_6H_4)_3)(CO)_3(COMe)]$ (180 mg, 0.366 mmol) in benzene (20 ml). The resulting solution was left stirring at room temperature for 48 h, forming an orange solution. Solvents were removed under reduced pressure leaving **3** as an off-white solid, which was then dried under vacuum. Yield of **3** = quantitative.

Preparation of [Co(PPh₃)(CO)₃(C{OB(C₆F₅)₃}Me)] 4

A solution of $B(C_6F_5)_3$ (285 mg, 0.557 mmol) in benzene (20 ml) was added dropwise to a yellow solution of $[Co(PPh_3)(CO)_3-(COMe)]$ (250 mg, 0.557 mmol) in benzene (20 ml). The resulting solution was left stirring at room temperature for 2 h to give a pale yellow/green solution. Solvents were removed under reduced pressure and the resulting solid was dried under vacuum to yield **4** as an off white solid. Crystals suitable for structural characterisation were grown by slow diffusion of pentane into a saturated benzene solution. Yield of **4** = quantitative.

Preparation of $[Co(P(4-F-C_6H_4)_3)(CO)_3(C{OB(C_6F_5)_3}Me)] 5$

A solution of $B(C_6F_5)_3$ (181 mg, 0.352 mmol) in benzene (20 ml) was added slowly to a yellow solution of $[Co(P(4-F-C_6H_4)_3)(CO)_3(COMe)]$ (180 mg, 0.352 mmol) in benzene (20 ml). The resulting solution was left stirring at room temperature overnight, forming an orange solution. Solvents were removed under reduced pressure to yield **5** as an off-white solid that was dried under vacuum. Yield of **5** = quantitative.

Preparation of [Mn(CO)₅(C{OB(C₆F₅)₃}Me)] 6

A sample of $[Mn(CO)_5(COMe)]$, (100 mg, 0.420 mmol) was dissolved in toluene (20 ml) and was cooled to -78 °C. A solution of $B(C_6F_5)_3$, (215 mg, 0.420 mmol) in toluene (20 ml) was then added. The resulting solution was allowed to warm to room temperature under stirring for 1 h. During this time the solution changed colour from pale yellow to colourless. Removal of solvents under reduced pressure left **6** as an off-white solid, which was dried under vacuum. Yield of **6** = quantitative.

Preparation of $[Mo(\eta^5-C_5H_5)(PPh_3)(CO)_2(C{OB(C_6F_5)_3}Me)]$ 7

 $[Mo(\eta^5-C_5H_5)(PPh_3)(CO)_2(COMe)]$ (200 mg, 0.381 mmol) was dissolved in dichloromethane (20 ml). A solution of $B(C_6F_5)$, (195 mg, 0.381 mmol) in dichloromethane (20 ml) was then added dropwise and the solution stirred at room temperature for 2 h. Removal of solvents under reduced pressure gave 7 as a yellow solid, which was dried under vacuum. Yield of 7 = quantitative.

Preparation of $[Mo(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}Me)] 8$

 $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ (250 mg, 0.961 mmol) was dissolved in dichloromethane (20 ml) and cooled to -78 °C. A solution of $B(C_6F_5)_3$ (291 mg, 0.961 mmol) in dichloromethane (20 ml) was

then added dropwise. The cooled Schlenk was then quickly pumpfilled 5 times with 0.5 bar CO. This was then stirred under a 0.5 bar CO atmosphere at -78 °C for 1 h, and at room temperature for 17 h. During this time the solution darkened from yellow to orange. Removal of volatiles yielded a pale orange solid. This was washed with pentane (3 × 20 ml) to give **8** as a pale orange solid that was dried under vacuum. Yield of **8** = 472 mg (61.4%).

Preparation of $[Co{HOB(C_6F_5)_3}_2{OP(4-F-C_6H_4)_3}_2]$ 9

A 50 mg sample of $[Co(P(4-F-C_6H_4)_3)(CO)_3(C\{OB(C_6F_5)_3\}Me)]$ was dissolved in benzene (10 ml) and was introduced into one half of a crystallisation bridge. The other half was filled with pentane (10 ml). After 3 weeks blue crystals of **9** suitable for structural characterisation were isolated.

Reaction of $[Co(PPh_3)(CO)_3(Me)]$ with $B(C_6F_5)_3$ under a CO atmosphere

The compound $[Co(PPh_3)(CO)_3(Me)]$ (100 mg, 0.238 mmol) was dissolved in dichloromethane (10 ml) and cooled to -78 °C. A solution of $B(C_6F_5)_3$ (121 mg, 0.238 mmol) in dichloromethane (10 ml) was then added. A 1 atm pressure of CO was then introduced, and the resulting mixture stirred for 1 h. Solvents were removed under reduced pressure to leave a yellow powder. ¹H, ³¹P{¹H}, ¹⁹F{¹H} NMR and IR spectroscopies indicated the quantitative formation of $[Co(PPh_3)(CO)_3(C{OB(C_6F_5)_3}Me)]$.

Reaction of [Co(PPh_3)(CO)_3(Me)] under a CO atmosphere in the absence of $B(C_6F_5)_3$

The compound $[Co(PPh_3)(CO)_3(Me)]$ (100 mg, 0.238 mmol) was dissolved in dichloromethane (10 ml) and cooled to -78 °C. A 1 atm pressure of CO was then introduced. and the resulting mixture stirred for 1 h. Solvents were removed under reduced pressure to leave a yellow powder. ¹H, ³¹P{¹H}, ¹⁹F{¹H} NMR and IR spectroscopies indicated the quantitative formation of $[Co(PPh_3)(CO)_3(COMe)]$.

Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ with $B(C_6F_5)_3$ under a CO atmosphere

A solution of $[Fe(\eta^5-C_5H_3)(CO)_2(Me)]$ (25 mg, 0.13 mmol) in toluene (10 ml) was cooled to -78 °C. A solution of $B(C_6F_5)_3$ (66 mg, 0.13 mmol) in toluene (10 ml) was then added, and the reaction vessel purged with CO. A 0.5 atm pressure of CO was then introduced, and the solution stirred at -78 °C for 1 h. The cardice/acetone bath was then removed and the solution stirred for a further 24 h. Removal of solvents under reduced pressure left an orange solid. ¹H, ¹⁹F{¹H}, ¹¹B{¹H} NMR and IR spectroscopies indicated that the solid contained 40% [Fe(η^5 -C₅H₅)(CO)₂(C{OB(C₆F₅)₃}Me)], as judged by integration of the (η^5 -C₅H₅) environments from the ¹H NMR spectrum.

Reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(Me)]$ under a CO atmosphere in the absence of $B(C_6F_5)_3$

A solution of $[Fe(\eta^5-C_5H_5)(CO)_2(Me)]$ (25 mg, 0.13 mmol) in toluene (10 ml) was cooled to -78 °C, and the reaction vessel purged with CO. A 0.5 atm pressure of CO was then introduced, and the solution stirred at -78 °C for 1 h. The cardice/acetone

bath was then removed and the solution stirred for a further 24 h. Removal of solvents under reduced pressure left an orange solid. ¹H NMR and IR spectroscopies indicated that only unreacted [Fe(η^{5} -C₅H₅)(CO)₂(Me)] was present.

Reaction of [Mn(CO)₅(Me)] with B(C₆F₅)₃ under a CO atmosphere

A solution of $[Mn(CO)_5(Me)]$ (100 mg, 0.476 mmol) in dry dichloromethane (10 ml) was cooled to -78 °C. A solution of $B(C_6F_5)_3$ (195 mg, 0.476 mmol) in dichloromethane (10 ml) was then added, and the reaction vessel purged with CO. A 0.5 atm pressure of CO was then introduced, and the solution allowed to warm to room temperature under stirring. Stirring was continued at room temperature for 1 h. Removal of solvents under reduced pressure yielded a white solid. ¹H, ¹³C{¹H} NMR and IR data indicated the quantitative formation of [Mn(CO)₅(C{OB(C₆F₅)₃}Me)].

Reaction of $[Mn(CO)_5(Me)]$ under a CO atmosphere in the absence of $B(C_6F_5)_3$

A solution of $[Mn(CO)_5(Me)]$ (100 mg, 0.476 mmol) in dry dichloromethane (10 ml) was cooled to -78 °C. The reaction vessel was then purged with CO. A 0.5 atm pressure of CO was then introduced, and the solution allowed to warm to room temperature under stirring. Stirring was continued at room temperature for 17 h. Removal of solvents under reduced pressure yielded a white solid. The ¹H and ¹³C{¹H} NMR and IR data of this solid indicated the formation of $[Mn(CO)_5(COMe)]$ in a yield of 72% as judged by integration of CH₃ resonances.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(Me)]$ with $B(C_6F_5)_3$ under a CO atmosphere

The compound $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ (100 mg, 0.385 mmol) was dissolved in dichloromethane (10 ml) and the resulting solution cooled to -78 °C. A solution of $B(C_6F_5)_3$ (195 mg, 0.385 mmol) in dichloromethane (10 ml) was then added. The reaction vessel was then purged with CO. A 0.5 atm pressure of CO was then introduced and the solution stirred for 1 h, then allowed to warm to room temperature under stirring. The solution was then stirred at room temperature for a further 1 h. Removal of solvents under reduced pressure yielded a yellow solid. The ¹H, $^{13}C{H}$ NMR and IR spectra indicated the quantitative formation of $[Mo(\eta^5-C_5H_5)(CO)_3(C{OB(C_6F_5)_3}Me)]$

Reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(Me)]$ under a CO atmosphere in the absence of $B(C_6F_5)_3$

The compound $[Mo(\eta^5-C_5H_5)(CO)_3(Me)]$ (100 mg, 0.385 mmol) was dissolved in dichloromethane (10 ml) and was cooled to -78 °C. The reaction vessel was then purged with CO. A 0.5 atm pressure of CO was then introduced and the solution allowed to warm to room temperature under stirring. The solution was then stirred at room temperature for 1 h. Removal of solvents under reduced pressure yielded a yellow solid. The ¹H NMR and IR spectra of this residue indicated that only unreacted starting materials were present

	4	9
Chemical formula	$C_{41}H_{18}BCoF_{15}O_4P$	$C_{72}H_{26}B_2CoF_{36}O_4P_2$
Formula weight	960.28	1781.43
Crystal system	Monoclinic	Monoclinic
Space group	$P 2_1/c$	$P 2_1/c$
a/Å	12.5164(3)	20.2640(2)
b/Å	17.0794(5)	13.0854(2)
c/Å	18.0656(4)	25.3366(2)
γ/°	90	90
β/°	99.4628(11)	93.9521(5)
T/K	150	150
$V/Å^3$	3809.4	6702.3
Ζ	4	4
μ/mm^{-1}	0.610	0.458
Reflections measured	37239	87004
Unique reflections	8941	15818
R_{int}	0.073	0.042
Observed reflections	5530	10011
Parameters refined	568	1062
R	0.0390	0.0504
wR	0.0480	0.0599

Crystallography

Data collections were performed by Dr A. R. Cowley, using an Enraf-Nonius KappaCCD diffractometer (graphitemonochromated MoK_a radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package.³⁴ The crystal structures were solved using direct-methods program SIR92,³⁵ which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS³⁶ program suite. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Crystal structure diagrams were produced using the CRYSTALS³⁶ program suite. Molecular parameters are presented in Table 7.

CCDC reference numbers 287089 and 287090.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514889h

Acknowledgements

We thank the EPSRC for a grant (S.A.L).

References

- 1 W. E. Piers, Adv. Organomet. Chem., 2005, 52, 1-76.
- 2 G. D. W. Anderson, O. J. Boys, A. R. Cowley, J. C. Green, M. L. H. Green, S. A. Llewellyn, C. M. von Beckh, S. I. Pascu and I. C. Vei, *J. Organomet. Chem.*, 2004, **689**, 4407–4419.

- 3 M. L. H. Green, J. Haggitt and C. P. Mehnert, J. Chem. Soc., Chem. Commun., 1995, 1853–1854.
- 4 S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson and D. F. Shriver, *J. Am. Chem. Soc.*, 1979, **101**, 5864–5866.
- 5 S. B. Butts, S. H. Strauss, E. M. Holt, R. E. Stimson, N. W. Alcock and D. F. Shriver, J. Am. Chem. Soc., 1980, **102**, 5093–5100.
- 6 T. C. Forschner and A. R. Cutler, Organometallics, 1985, 4, 1247-1257.
- 7 Z. Yang, X. Ma, R. B. Oswald, H. W. Roesky, H. Zhu, C. Schulzke, K. Starke, M. Baldus, H.-G. Schmidt and M. Noltemeyer, *Angew. Chem.*, *Int. Ed.*, 2005, 44, 7072–7074.
- 8 V. Galamb, G. Palyi, R. Boese and G. Schmid, *Organometallics*, 1987, 6, 861–867.
- 9 D. J. Darensbourg, A. L. Phelps, N. Le Gall and L. Jia, J. Am. Chem. Soc., 2004, 126, 13808–13815.
- 10 F. Carre, G. Cerveau, E. Colomer, R. J. P. Corriu, J. C. Young, L. Ricard and R. Weiss, J. Organomet. Chem., 1979, 179, 215–226.
- 11 D. Milstein and J. L. Huckaby, J. Am. Chem. Soc., 1982, 104, 6150-6152.
- 12 T. Bartik, T. Kruemmling, C. Krueger, L. Marko, R. Boese, G. Schmid, P. Vivarelli and G. Palyi, J. Organomet. Chem., 1991, 421, 323–333.
- 13 D. J. Parks, W. E. Piers, M. Parvez, R. Atencio and M. J. Zaworotko, Organometallics, 1998, 17, 1369–1377.
- 14 A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, L. H. Doerrer, S. Cafferkey and M. B. Hursthouse, *Chem. Commun.*, 1998, 2529–2530.
- 15 S. Natarajan, S. Neeraj, A. Choudhury and C. N. R. Rao, *Inorg. Chem.*, 2000, **39**, 1426–1433.
- 16 G. S. Hill, L. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, Organometallics, 1997, 16, 525–530.
- 17 I. A. Guzei, F. Delpech and R. F. Jordan, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2000, 56, E327–E328.
- 18 R. Choukroun, C. Lorber and L. Vendier, *Eur. J. Inorg. Chem.*, 2004, 317–321.
- 19 L. H. Doerrer and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1999, 4325–4329.
- 20 S. A. Llewellyn, M. L. H. Green and A. R. Cowley, J. Organomet. Chem., 2005, 690, 2358–2364.
- 21 D. J. Parks, J. M. Blackwell and W. E. Piers, J. Org. Chem., 2000, 65, 3090–3098.
- 22 I. C. Vei, S. I. Pascu, M. L.H. Green, J. C. Green, R. E. Schilling, G. D. W. Anderson and L. H. Rees, *Dalton Trans.*, 2003, 2550–2557.
- 23 L. H. Doerrer, A. J. Graham and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1998, 3941–3946.
- 24 L. H. Doerrer, J. R. Galsworthy, M. L. H. Green, M. A. Leech and M. Muller, J. Chem. Soc., Dalton Trans., 1998, 3191–3194.
- 25 L. H. Doerrer, J. R. Galsworthy, M. L. H. Green and M. A. Leech, J. Chem. Soc., Dalton Trans., 1998, 2483–2488.
- 26 J. R. Galsworthy, J. C. Green, M. L. H. Green and M. Muller, J. Chem. Soc., Dalton Trans., 1998, 15–20.
- 27 J. L. W. Pohlmann and F. E. Brinckman, Z. Naturforsch., B: Anorg. Chem. Org. Chem. Biochem. Biophys. Biol., 1965, 20, 5–11.
- 28 C. C. Tso and A. R. Cutler, Polyhedron, 1993, 12, 149-158.
- 29 R. F. Heck and D. S. Breslow, J. Am. Chem. Soc., 1962, 84, 2499-2502.
- 30 T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 1956, 3, 104-124.
- 31 M. Green and D. J. Westlake, J. Chem. Soc. A, 1971, 367-371.
- 32 R. J. McKinney and S. S. Crawford, Inorg. Synth., 1989, 26, 155-161.
- 33 O. G. Adeyemi and N. J. Coville, Organometallics, 2003, 22, 2284-2290.
- 34 Z. Otwinowski and W. Minor, Methods Enzymol., 1997, 276, 307-326.
- A. Altomare, G. Carascano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, 26, 343.
 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I.
- 36 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS*, Chemical Crystallography Laboratory, Oxford, UK, 2001.