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FULL PAPER

Organophosphoryl adducts of tris(pentafluorophenyl)borane; crystal and molecular structure of $B(C_6F_5)_3 \cdot Ph_3PO$

Michael A. Beckett,*[a] David S. Brassington,[a] Mark E. Light[b] and Michael B. Hursthouse[b]

[a] *Chemistry Department, University of Wales, Bangor, Gwynedd, UK LL57 2UW*
[b] *Chemistry Department, University of Southampton, Southampton, UK SO17 1BJ*

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A series of 1 : 1 adducts of $B(C_6F_5)_3$ with the organophosphoryl ligands Et_3PO, Ph_3PO, $Pr^n{}_3PO$, $Oct^n{}_3PO$, $(MeO)_3PO$, $(EtO)_3PO$, $(PhO)_3PO$, $(EtO)_2(H)PO$, $(Bu^nO)_2(H)PO$, $(PhO)_2(H)PO$, $(MeO)_2MePO$, $(EtO)_2MePO$, $(EtO)_2PhPO$, and $(EtO)Me_2PO$ have been synthesized and characterised by elemental analysis, mp, and spectroscopic (^1H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR and IR) methods. $B(C_6F_5)_3 \cdot Ph_3PO$ was further characterised in the solid state by a single-crystal X-ray diffraction study. ^{31}P NMR chemical shifts and $\nu(PO)$ IR stretching frequencies are discussed in relation to substituent at phosphorus.

Introduction

The triorganoborane $B(C_6F_5)_3$ has attracted considerable attention recently due to its high thermal and aqueous stability[1,2] and its ability to function as a stoichiometric or catalytic Lewis acid in many useful organic transformations.[3–7] The $B(C_6F_5)_3 \cdot L$ Lewis acid/base adducts are well known with examples reported for $L = NH_3$ and amines,[1,2] nitriles and isocyanides,[8] H_2O,[9,10] *O*-carbonyl donors,[11] PH_3,[12] and organophosphines.[1,2,8,13] We have recently reported[14] in a preliminary communication the synthesis of the first phosphoryl adduct $B(C_6F_5)_3 \cdot Et_3PO$ **1** and used Gutmann's method[15,16] to determine the relative Lewis acidity of $B(C_6F_5)_3$. This report describes the synthesis and characterisation of a series of phosphoryl donor complexes of $B(C_6F_5)_3$, and an investigation into their spectroscopic properties. In particular, changes in the ^{31}P NMR chemical shifts and the phosphoryl stretching frequencies arising from co-ordination of the phosphoryl ligand to $B(C_6F_5)_3$ are described. We also report a single-crystal X-ray structural determination of $B(C_6F_5)_3 \cdot Ph_3PO$ **2** which displays weak intramolecular π-stacking interactions between the eclipsed interlocking C_6F_5 and C_6H_5 rings.

Table 1 Selected spectroscopic data for phosphoryl adducts of $B(C_6F_5)_3$

Compound			
Adduct no.	Ligand	$\Delta\delta$ (^{31}P)[a]	$\Delta\nu(PO)$[b]/cm^{-1}
1	Et_3PO	25.9	−21[c]
2	Ph_3PO	−4.2	−13
3	$Pr^n{}_3PO$	21.6	−26
4	$Oct^n{}_3PO$	22.5	−8[d]
5	$(MeO)_3PO$	−3.9	−56
6	$(EtO)_3PO$	−8.2	−67
7	$(PhO)_3PO$	−9.2	−41
8	$(EtO)_2(H)PO$	−3.0	−78
9	$(BuO)_2(H)PO$	−1.7	−73
10	$(PhO)_2(H)PO$	−1.0	−30
11	$(MeO)_2MePO$	−2.2	−52
12	$(EtO)_2MePO$	0.2	−55
13	$(EtO)_2PhPO$	5.8	−76
14	$(EtO)Me_2PO$	3.8	−23

[a] In $CDCl_3$. $\Delta\delta = \delta_{(adduct)} - \delta_{(free\ base)}$. [b] KBr disk. $\Delta\nu = \nu(PO)_{(adduct)} - \nu(PO)_{(free\ base)}$. [c] Value for free base taken from ref. 29. [d] Thin film.

Results and discussion

The reaction of one equivalent of the phosphoryl compound (L) with one equivalent of $B(C_6F_5)_3$ in pentane solution rapidly afforded the analytically pure adducts, $B(C_6F_5)_3 \cdot L$ **1**–**14**, in moderate to high yields. The phosphoryl compounds used as Lewis bases in this study were the triorganophosphine oxides {Et_3PO, Ph_3PO, $Pr^n{}_3PO$, and $Oct^n{}_3PO$}, and the organoesters of phosphoric acid {$(MeO)_3PO$, $(EtO)_3PO$, and $(PhO)_3PO$}, phosphonic and organophosphonic acids {$(EtO)_2(H)PO$, $(Bu^nO)_2(H)PO$, $(PhO)_2(H)PO$, $(MeO)_2MePO$, $(EtO)_2MePO$, and $(EtO)_2PhPO$}, and a diorganophosphinic acid {$(EtO)Me_2PO$}; compound numbers are given in Table 1. All adducts, except **4**, which was a viscous liquid, were air-stable colourless solids. They were all readily soluble in chlorinated solvents and diethyl ether, but insoluble in toluene and light petroleum. The adducts of the diesters of the phosphonic acids (**8**–**10**) were very deliquescent.

The adducts **1**–**14** were all characterised by satisfactory elemental analysis data, mp, and IR and NMR (^1H, ^{13}C, ^{11}B, ^{19}F, ^{31}P) spectroscopy and full data are given in the Experimental section. The formulation of these products as adducts follows from their ^{11}B NMR chemical shifts (δ −0.2 to −9.3), in the region normally observed for four-co-ordinate tetrahedral boron centres[17] and upfield of the signal for free $B(C_6F_5)_3$ (δ +59[9]), and by confirmatory single-crystal X-ray crystallographic structures of **1**[14] and **2**. The room temperature (20 °C) ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra that we were able to measure were consistent with the proposed structures. ^{19}F spectra were obtained for **1**–**10** and these showed the expected three resonances, of relative intensity 2 : 2 : 1, for *ortho*, *meta*, and *para* aryl substituents at δ *ca.* −164, −135, and −157, respectively.[8] The ^{13}C spectra of adducts showed, in addition to resonances associated with the phosphoryl ligand,[18] doublets {$^1J(CF)$ *ca.* 240 Hz} for the *ortho*, *meta* and *para* resonances of the perfluoroaryl groups of $B(C_6F_5)_3$ at δ *ca.* 148, 137, 140, respectively.[8,18,19] We were unable to observe the *ipso* carbons. ^{31}P NMR data are described in detail below. IR spectra all showed characteristic vibrations associated with $B(C_6F_5)_3$, including a strong band at *ca.* 1100 cm^{-1}, and a strong $\nu(PO)$ at 1130–1260 cm^{-1}. The $\nu(PO)$ vibration is also discussed in detail below.

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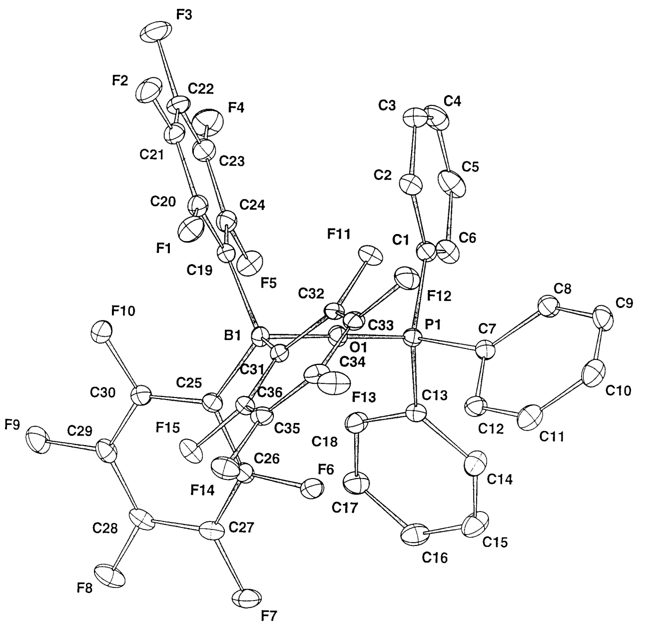

Fig. 1 Molecular structure of $B(C_6F_5)_3 \cdot Ph_3PO$ **2** showing the atomic numbering scheme.

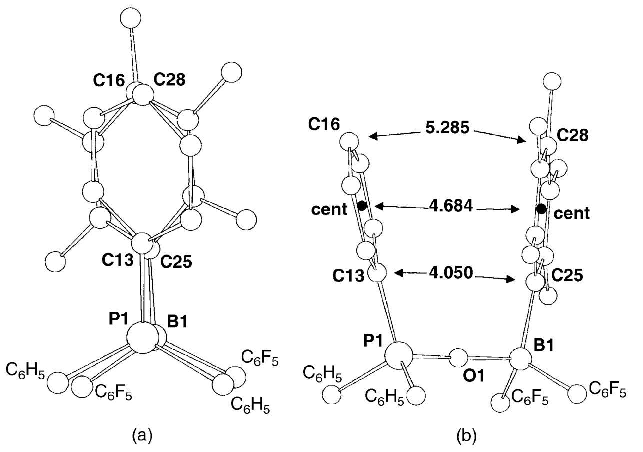

Fig. 2 (a) A view down the P1–O1 bond of **2** showing the eclipsed conformation of the adduct and the π interactions between the phenyl groups of the phosphine oxide and the C_6F_5 groups of the borane. (b) A view of **2** showing the aryl π interactions between a C_6F_5 and a C_6H_5 unit.

Table 2 Selected bond lengths (Å) and angles (°) for **2**

P1–O1	1.497(2)	B1–O1	1.538(3)
P1–C1	1.791(2)	P1–C7	1.791(2)
P1–C13	1.783(2)	B1–C19	1.632(3)
B1–C25	1.639(3)	B1–C31	1.643(3)
P1–O1–B1	178.7(2)	O1–P1–C1	109.6(1)
O1–P1–C7	109.6(1)	O1–P1–C13	109.9(1)
C1–P1–C7	110.2(1)	C1–P1–C13	108.9(1)
C7–P1–C13	108.7(1)	O1–B1–C19	104.9(2)
O1–B1–C25	105.1(2)	O1–B1–C31	105.1(2)
C19–B1–C25	113.7(2)	C19–B1–C31	112.7(2)
C25–B1–C31	114.2(2)		

The adduct **2** was further characterised in the solid state by a single-crystal X-ray diffraction study. Crystals of **2**, were grown from layered $CHCl_3$–hexane solution, and a drawing of its molecular structure is given in Fig. 1. The molecular structure is essentially as might be expected for the component parts with the acid $B(C_6F_5)_3$ and the base Ph_3PO joined together *via* a O→B co-ordinate bond. The overall structure of **2** is grossly similar to that of **1**[14] but for the angle at O in the B–O–P linkage being almost linear [178.7(2)°] in **2** rather than bent [161.0(2)°] as was found for **1**. These two structures are the only crystallographically characterised structures of phosphoryl adducts of $B(C_6F_5)_3$. The B–C bonds of the borane are almost eclipsed with respect to the P–C bonds of the phosphine oxide, Fig. 2(a). There are weak intramolecular π-stacking interactions between the three Ph groups of the phosphine oxide and the three C_6F_5 groups of the borane, Fig. 2(b). A similar, but stronger, π-stacking interaction has been noted in $B(C_6F_5)_3 \cdot PhC(X)O$ (X = OEt or NPr^i_2)[11] where the bent B–O–C system enables a closer π interaction between the Ph ring of the base and a C_6F_5 ring of the acid. The hydroxy bridged borate anion $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$, with a staggered conformation and a B–O–B angle of 139.6(5)°, has a strong π interaction between two of its C_6F_5 rings.[10] Selected bond length and bond angle parameters for **2** are given in Table 2. Other crystallographically characterised adducts of $B(C_6F_5)_3$ to have been reported include L = PPh_3,[8] RCN {R = Me, 4-MeC_6H_4 or 4-$NO_2C_6H_4$},[8] RNC {R = ^tBu or $CMe_2CH_2{}^tBu$},[8] H_2O,[9] PhC(X)O {X = H or Me},[11] PH_3,[12] and PBu^tH_2.[13] The B and P atoms in **2** are both 4-co-ordinate with angles subtended at these atoms close to those expected for σ-framework sp^3 hybridisation [104.9(2)–114.2(2), av. 109.3°, and 108.7(1)–110.2(1), av. 109.5°, for B and P respectively]. The detailed deviation of angles at B indicates back strain in the acid upon adduct formation with larger C–B1–C angles [112.7(2)–114.2(2), av.113.5°] and smaller O1–B1–C angles [104.9(2)–105.1(2), av. 105.0°]. The deviation from idealised tetrahedral angles at B is less marked than has been observed previously in other adducts.[8,11,13,14] The B1–O1 bond length at 1.538(3) Å is similar to that found for **1** [1.533(3) Å][14] and $BF_3 \cdot Ph_3PO$ [1.516(3) Å)],[20] shorter than that in $BF_3 \cdot PhC(H)O$ [1.591(6) Å][21] and $B(C_6F_5)_3 \cdot H_2O$ [1.597(2) Å],[9] and at the lower end of the range observed [1.52(1)–1.610(8) Å] for $B(C_6F_5)_3 \cdot PhC(X)O$ complexes.[11] Shorter B–O distances have been reported in metal–oxo adducts of $B(C_6F_5)_3$, *e.g.* $[WO\{OB(C_6F_5)_3\}_3]^{2-}$ [1.491(3)–1.508(3) Å][22] and $[Zr(Cp^*)_2\{OB(C_6F_5)_3\}]$ [1.460(6) Å].[23] As noted above, the two-co-ordinate O atom bridges the P and B atoms with a P1–O1–B1 angle of 178.7(2)°. P–O–M angles in Ph_3PO complexes are variable and range from 123.0(4) (in $SeOCl_2 \cdot Ph_3PO$[24]) to 180° (in $AlCl_3 \cdot Ph_3PO$[18]) and a possible explanation for this has been offered in terms of the relative π-acceptor properties of the acid.[25] However, in view of the large difference in this angle for **1** and **2** it is clear that other factors also need to be considered. The angle at O when bound to main group atoms (X) from the 2nd short period is renowned for its flexibility and intermolecular crystal packing forces are sufficient to cause a remarkable difference in B–O–X angles.[26] The intramolecular π-stacking interactions noted above for **2** are maximised with a linear B–O–P linkage and we suggest that this must be a dominant factor in the energetics of this system. The P–O bond length at 1.497(2) Å is, within error as found for **1**,[14] similar to that found for $BF_3 \cdot Ph_3PO$ [1.523(3) Å)],[20] and slightly longer than that found for Ph_3PO (1.483(2) Å)[27] indicating a slight reduction of bond order upon adduct formation.

Phosphorus-31 NMR data for all the adducts are given in the Experimental section and Δδ values ($\delta_{\text{adduct}} - \delta_{\text{free base}}$), which ranged from from −9.2 to 25.9, are given in Table 1. Rather than reflecting change of electron density at P, these shifts are a consequence of the Lewis acid perturbing the ^{31}P chemical shift tensors, which have a component along the PO axis of the phosphoryl ligand.[28] Owing to variations in molecular symmetry, these ^{31}P chemical shift tensors will differ for each class of phosphoryl derivative, with the effect that Δδ values are unlikely to be uniform. The P atoms in the phosphoryl compounds with alkyl substituents were deshielded upon co-ordination to $B(C_6F_5)_3$, whilst in phosphoryl compounds with alkoxy or aryloxy groups the P atoms were slightly shielded upon co-ordination. This substituent effect appears additive with Δδ values broadly following the order phosphates

(≈ -5) < alkylphosphonates (≈ -1) < dialkylphosphinates ($\approx +4$) < trialkylphosphine oxides ($\approx +24$). Burford and co-workers[18,20] observed deshielding of the phosphorus centre in adducts of Ph_3PO with BF_3, BCl_3, $AlCl_3$, $AlBr_3$ and $GaCl_3$, and slight shielding at phosphorus in $(PhO)_3PO\cdot AlCl_3$. The $\Delta\delta$ values obtained for the $B(C_6F_5)_3$ adducts of phosphonic acid esters (≈ -2) were similar to those for alkylphosphonate esters indicating that the effect of H was comparable to that of an alkyl group. The phosphoryl derivatives that showed the largest $\Delta\delta(^{31}P)$ values were the trialkylphosphine oxides, with the $\Delta\delta$ value for Et_3PO being marginally greater than those of $Pr^n{}_3PO$ and $Oct^n{}_3PO$.

Symons and Eaton[29] have noted that the phosphoryl stretch of Et_3PO was solvent dependent and have correlated $\Delta\nu$(PO) with Gutmann's[15,16] acceptor number (AN) solvent scale. We were interested to see if there were any noteworthy changes associated with $\Delta\nu$(PO) for the phosphoryl adducts **1**–**14** of the relatively strong Lewis acid, $B(C_6F_5)_3$. Related to this, Lappert[30,31] used $\Delta\nu$(CO) of ethyl acetate upon adduct formation as a measure of Lewis acidity, and we have recently prepared $B(C_6F_5)_3\cdot MeC(OEt)O$ and examined its IR spectrum.[14] The ν(PO) stretching data for adducts **1**–**14** are given in the Experimental section and $\Delta\nu$(PO) values are reported in Table 1; the negative $\Delta\nu$(PO) values indicate that ν(PO) is shifted to lower wavenumber upon co-ordination to $B(C_6F_5)_3$. The $\Delta\nu$(PO) values ranged from -8 to -78 cm^{-1}. Detailed examination of the data revealed that the magnitude of $\Delta\nu$(PO) was lowest for triorganophosphine oxides and greatest for species with OR or OAr groups at P. The $\Delta\nu$(PO) ranges associated with the various classes of compounds, arranged in decreasing order of P–C bonds, were -8 to -26 (phosphine oxides), -23 (phosphinate esters), -52 to -78 (phosphonate esters), and -41 to -67 (phosphate esters). The adducts of phosphonate esters had similar $\Delta\nu$(PO) ranges irrespective of whether H or alkyl was bound to P, although a smaller shift was observed for **10**. A theoretical study[8] has demonstrated that $B(C_6F_5)_3$ is a hard acid and that its bonding to Lewis bases is dominated by electrostatic effects. The phosphoryl bond may be drawn as a resonance hybrid of two limiting canonical forms $R_3P^+–O^-$ and $R_3P^-{\equiv}O^+$, with the former having a heavier weighting. An electrostatic interaction with $B(C_6F_5)_3$ would further favour the former and effectively reduce the PO bond order, and hence ν(PO). The absolute value of ν(PO) for phosphoryl derivatives may accurately be calculated[32] using an empirical relationship involving additive electronegativities (inductive effects) of substituents at P. The $\Delta\nu$(PO) values upon adduct formation are greatest where π resonance from a substituent is possible indicating that structures such as $(PhO)_2(PhO^+{=})P–O^-$ may be important in lowering the PO bond order upon adduct formation.

Conclusion

A linear co-ordination mode for the phosphoryl group has been observed in the solid state of the adduct $B(C_6F_5)\cdot Ph_3PO$ and this has been attributed to intramolecular π-stacking interaction between aryl rings, rather than electronic effects or destabilising steric interactions associated with the acceptor or the phosphoryl group. Variations in $\Delta\delta(^{31}P)$ and $\Delta\nu$(PO) data for the series of phosphoryl adducts of $B(C_6F_5)_3$ have been accounted for in terms of substituent effects at phosphorus.

Experimental

(a) General

Reactions were carried out under N_2 in dried solvents. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer as KBr discs or as thin films between NaCl plates, ^1H, ^{13}C, ^{11}B and ^{31}P NMR on a Bruker AC250 CP/MAS NMR spectrometer operating at 250, 62.8, 80.2 and 101.25 MHz respectively and ^{19}F NMR spectra on a Bruker 350 at 338.0 MHz. Chemical shifts are given in ppm with positive values towards high frequency (downfield) of $SiMe_4$ (^1H, ^{13}C), $BF_3\cdot OEt_2$ (^{11}B), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). Elemental analysis (C,H,N) were obtained on a Carlo-Erba MOD-1106 instrument using helium as a carrier gas. The phosphoryl free bases, with the exception of $Me_2(EtO)PO$ which was prepared by a standard method,[33] were obtained commercially and used as supplied. $B(C_6F_5)_3$ and $B(C_6F_5)_3\cdot Et_3PO$ **1** were prepared by literature methods.[14,34]

(b) Synthesis

The adducts **2**–**14** were all prepared in an analogous manner to **1** as described in ref. 14. Selected spectroscopic data are given in Table 1 and full characterisation data are given below. Crystals of **2** suitable for a single-crystal X-ray diffraction analysis were grown by diffusion of a hexane into a $CHCl_3$ solution of **2**.

$B(C_6F_5)_3\cdot Ph_3PO$ 2. Yield 37%. mp 278–280 °C. Calc. for $C_{36}H_{15}BF_{15}OP$: C, 54.7; H, 1.9. Found: C, 54.7; H, 1.8%. NMR ($CDCl_3$/RT): ^1H (δ), 7.6 (m); ^{13}C-{^1H} (δ), 128.8 (d) J(CP) 2.8, 129.0 (d) J(CP) 2.7, 131.8 (d) J(CP) 10.5, 136.7 (d) ^1J(CF) 237, 139.2 (d) ^1J(CF) 254, 147.8 (d) ^1J(CF) 241 Hz; ^{11}B-{^1H} (δ), -9.2; ^{19}F (δ), -134.9 , -158.7, -164.9; ^{31}P-{^1H} (δ), +24.3. IR (KBr disk/cm^{-1}): 3010, 1684, 1646, 1517, 1464, 1376, 1285, 1177 (P=O), 1126, 1102, 978, 848, 793, 773, 750, 684, 616, 575, 532.

$B(C_6F_5)_3\cdot Pr^n{}_3PO$ 3. Yield 54%. mp 140–141 °C. Calc. for $C_{27}H_{21}BF_{15}OP$: C, 47.1; H, 3.0. Found: C, 47.1; H 2.8%. NMR ($CDCl_3$/RT): ^1H (δ), 1.0 (dt, 3H) ^3J(HH) 7.0, ^4J(PH) 1.5, 1.5 (m, 2H), 1.83 (m, 2H); ^{13}C-{^1H} (δ), 14.9 (d) ^3J(PC) 4, 15.5 (d) ^2J(PC) 17.0, 27.1 (d) ^1J(PC) 65.0, 137 (d) ^1J(CF) 252, 140.0 (d) ^1J(CF) 255, 147.7 (d) ^1J(CF) 238 Hz; ^{11}B-{^1H} (δ), -2.6; ^{19}F (δ), -134.5, -158.4, -164.6; ^{31}P-{^1H} (δ), +69.3. IR (KBr disk/cm^{-1}): 3000, 1519, 1461, 1373, 1284, 1132 (P=O), 1102, 979, 861, 797, 767, 738, 679, 615, 579.

$B(C_6F_5)_3\cdot Oct^n{}_3PO$ 4. Yield 51%. Oily liquid. Calc. for $C_{42}H_{51}BF_{15}OP$: C, 56.1; H, 5.7. Found: C, 56.1; H 5.5%. NMR ($CDCl_3$/RT): ^1H (δ), 0.9 (t, 3H) ^3J(HH) 6.4, 1.25 (m, 12H), 1.85 (m, 2H); ^{13}C-{^1H} (δ), 13.9, 21.05 (d) J(CP) 3.8, 22.5, 25.3 (d) ^1J(CP) 65.8, 28.7, 28.8, 30.57, 30.7 (d) ^2J(PC) 15.7, 31.6, 137.1 (d) ^1J(CF) 238, 139.6 (d) ^1J(CF) 258, 147.8 (d) ^1J(CF) 240 Hz; ^{11}B-{^1H} (δ), -3.8; ^{19}F (δ), -134.5, -158.7, -164.6; ^{31}P-{^1H} (δ), +70.6. IR (thin film/cm^{-1}): 2929, 1644, 1517, 1467, 1376, 1284, 1143 (P=O), 1100, 981, 912, 742, 650.

$B(C_6F_5)_3\cdot (MeO)_3PO$ 5. Yield 48%. mp 210–212 °C. Calc. for $C_{21}H_9BF_{15}O_4P$: C, 38.7; H, 1.4. Found: C, 38.7; H 1.4%. NMR ($CDCl_3$/RT): ^1H (δ) 3.68 (d) ^3J(PH) 10.7 Hz; ^{13}C-{^1H} (δ), 56.0 (d) ^2J(CP) 132, 136.9 (d) ^1J(CF) 254, 139.8 (d) ^1J(CF) 245, 147.8 (d) ^1J(CF) 241 Hz; ^{11}B-{^1H} (δ), -1.7; ^{19}F (δ), -135.1, -157.8, -164.6; ^{31}P-{^1H} (δ), -2.55. IR (KBr disk/cm^{-1}): 2995, 1648, 1510, 1470, 1378, 1284, 1226 (P=O), 1104, 1075, 984, 865, 775, 738, 678, 618, 576, 512.

$B(C_6F_5)_3\cdot (EtO)_3PO$ 6. Yield 47%. mp 150–151 °C. Calc. for $C_{24}H_{15}BF_{15}O_4P$: C, 41.5; H, 2.2. Found: C, 41.3; H 2.1%. NMR ($CDCl_3$/RT): ^1H (δ), 1.3 (t, 3H) ^3J(HH) 7.3, 3.9 (quint, 2H) ^3J(HH) 7.3, ^3J(PH) 7.3; ^{13}C-{^1H} (δ), 15.8 (d) ^3J(PC) 6.7, 63.7 (d) ^2J(PC) 5.7, 136.5 (d) ^1J(CF) 240, 139.3 (d) ^1J(CF) 269, 148.1 (d) ^1J(CF) 231 Hz; ^{11}B-{^1H} (δ), -3.7; ^{19}F (δ), -135.6, -157.7, -164.9; ^{31}P-{^1H} (δ), -10.1. IR (KBr disk/cm^{-1}): 2995, 1647, 1521, 1472, 1378, 1287, 1208 (P=O), 1106, 1049, 981, 774, 739, 677, 617.

$B(C_6F_5)_3\cdot (PhO)_3PO$ 7. Yield 35%. mp 185–186 °C. Calc. for $C_{36}H_{15}BF_{15}O_4P$: C, 51.6; H, 1.8. Found: C, 51.3; H 1.5%. NMR

(CDCl$_3$/RT): ^{1}H (δ), 7.3 (m); ^{13}C-{^{1}H} (δ), 119.8 (d) ^3J(CP) 4.7 *ortho*, 126.1 *para*, 129.9 *meta*, 136.7 (d) ^1J(CF) 244, 141.4 (d) ^1J(CF) 251, 147.9 (d) ^1J(CF) 255 Hz; ^{11}B-{^{1}H} (δ), −1.2; ^{19}F (δ), −135.4, −157.1, −164.1; ^{31}P-{^{1}H} (δ), −27.5. IR (KBr disk/cm^{-1}): 3050, 1646, 1590, 1525, 1464, 1376, 1287, 1255 (P=O), 1158, 1106, 1040, 982, 911, 764, 736, 686, 675, 616.

B(C$_6$F$_5$)$_3$·(EtO)$_2$(H)PO 8. Yield 48%. mp 120–122 °C. Calc. for C$_{22}$H$_{11}$BF$_{15}$O$_3$P: C, 40.7; H, 1.7. Found: C, 40.5; H 1.7%. NMR (CDCl$_3$/RT): ^{1}H (δ), 1.33 (6H), 4.04 (4H), 6.5 (d, 1H) ^1J(PH) 700; ^{13}C-{^{1}H} (δ), 15.8 (d) ^3J(CP) 6.7, 63.6 (d) ^2J(PC) 6.8, 137.0 (d) ^1J(CF) 253, 140.9 (d) ^1J(CF) 264, 147.9 (d) ^1J(CF) 247 Hz; ^{11}B-{^{1}H} (δ), −2.1; ^{19}F (δ), −135.5, −157.5, −164.3; ^{31}P-{^{1}H} (δ), +3.4 ^1J(PH) 700 Hz. IR (KBr disk/cm^{-1}): 2997, 1647, 1521, 1472, 1380, 1288, 1180 (P=O), 1107, 1043, 970, 772, 682, 551.

B(C$_6$F$_5$)$_3$·(Bu^{n}O)$_2$(H)PO 9. Yield 37%. mp 44–46 °C. Calc. for C$_{24}$H$_{15}$BF$_{15}$O$_3$P: C, 44.2; H, 2.7. Found: C, 43.9; H 2.7%. NMR (CDCl$_3$/RT): ^{1}H (δ), 0.9 (q, 6H) ^3J(HH) 6.7, 1.3 (m, 4H), 1.6 (m, 4H), 4.1 (m, 4H), 6.9 (d, 1H) ^1J(PH) 750; ^{13}C-{^{1}H} (δ), 15.3, 15.4, 15.5, 15.6, 64.8, 64.9, 67.5, 67.6, 137.0 (d) ^1J(CF) 245, 140.0 (d) ^1J(CF) 245, 147.8 (d) ^1J(CF) 239 Hz; ^{11}B-{^{1}H} (δ), −2.2; ^{19}F (δ), −135.4, −157.3, −164.3; ^{31}P-{^{1}H} (δ), +5.2 ^1J(PH) 750 Hz. IR (KBr disk/cm^{-1}): 3000, 1692, 1646, 1598, 1518, 1469, 1379, 1289, 1188 (P=O), 1104, 976, 907, 734, 650.

B(C$_6$F$_5$)$_3$·(PhO)$_2$(H)PO 10. Yield 55%. mp 130–132 °C. Calc. for C$_{30}$H$_{11}$BF$_{15}$O$_3$P: C, 48.2; H, 1.5. Found: C, 47.9; H 1.4%. NMR (CDCl$_3$/RT): ^{1}H (δ), 7.2 (d, 1H) ^1J(PH) 740, 7.2 (m, 10H); ^{13}C-{^{1}H} (δ), 120.1 (d) J(PC) 4.8 Hz, 126.4, 130.2, 137.1 (d) ^1J(CF) 238, 139.9 (d) ^1J(CF) 149, 147.8 (d) ^1J(CF) 238; ^{11}B-{^{1}H} (δ), −0.2; ^{19}F (δ), −135.5, −156.7, −163.7; ^{31}P-{^{1}H} (δ), −1.2 ^1J(PH) 739 Hz. IR (KBr disk/cm^{-1}): 3000, 1649, 1596, 1519, 1472, 1373, 1290, 1250 (P=O), 1190, 1102, 1025, 961, 861, 761, 685.

B(C$_6$F$_5$)$_3$·(MeO)$_2$MePO 11. Yield 42%. mp 226–228 °C. Calc. for C$_{21}$H$_9$BF$_{15}$O$_3$P: C, 39.7; H, 1.4. Found: C, 39.4; H 1.4%. NMR (CDCl$_3$/RT): ^{1}H (δ), 1.3 (d) ^2J(PH) 17.7; 3.6 (d) ^3J(PH) 11.6 Hz; ^{13}C-{^{1}H} (δ), 8.7 (d) ^1J(CP) 146, 52.9 (d) ^2J(CP) 6.7, 136.9 (d) ^1J(CF) 258, 139.2 (d) ^1J(CF) 259, 147.9 (d) ^1J(CF) 240.0 Hz; ^{11}B-{^{1}H} (δ), −1.2; ^{19}F (δ), −135.5, −157.2, −164.1; ^{31}P-{^{1}H} (δ), +29.9. IR (KBr disk/cm^{-1}): 2997, 1642, 1554, 1519, 1472, 1373, 1313, 1278, 1190 (P=O), 1103, 982, 855, 797, 774, 738, 678, 618.

B(C$_6$F$_5$)$_3$·(EtO)$_2$MePO 12. Yield 47%. mp 145–147 °C. Calc. for C$_{23}$H$_{13}$BF$_{15}$O$_3$P: C, 41.6; H, 1.9. Found: C, 41.6; H 1.7%. NMR (CDCl$_3$/RT): ^{1}H (δ), 1.20 (t, 6H) ^3J(HH) 7.0, 1.60 (d, 3H) ^2J(HP) 18, 4.1 (m, 4H); ^{13}C-{^{1}H} (δ), 9.8 (d) ^1J(CP) 162, 15.6 (d) ^2J(CP) 6.7, 65.7 (d) ^3J(CP) 6.8, 137.2 (d) ^1J(CF) 246.0, 139.7 (d) ^1J(CF) 244, 147.7 (d) ^1J(CF) 245.0 Hz; ^{11}B-{^{1}H} (δ), −2.5; ^{31}P-{^{1}H} (δ), +27.8. IR (KBr disk/cm^{-1}): 3002, 1647, 1518, 1462, 1397, 1376, 1321, 1285, 1190 (P=O), 1107, 1031, 968, 905, 851, 824, 792, 774, 740, 674.

B(C$_6$F$_5$)$_3$·(EtO)$_2$PhPO 13. Yield 49%. mp 170–172 °C. Calc. for C$_{28}$H$_{15}$BF$_{15}$O$_3$P: C, 47.4; H, 2.1. Found: C, 47.3; H 1.8%. NMR (CDCl$_3$/RT): ^{1}H (δ), 1.2 (t, 6H) ^3J(HH) 6.5, 3.91 (t, 4H) ^3J(HH) 7.3, 7.44 (m, 5H); ^{13}C-{^{1}H} (δ), 15.9, 63.5, 128.9 (d) J(CP) 12.5, 131.2 (d) J(CP) 10.1, 133.6 (d) J(CP) 4.8, 137.0 (d) ^1J(CF) 252.0, 139.9 (d) ^1J(CF) 258, 147.4 (d) ^1J(CF) 273.0 Hz; ^{11}B-{^{1}H} (δ), −1.6; ^{31}P-{^{1}H} (δ), +16.55. IR (KBr disk/cm^{-1}): 3001, 2995, 1734, 1684, 1654, 1560, 1522, 1456, 1291, 1174 (P=O), 1096, 1027, 976, 804, 749, 694, 560, 534.

B(C$_6$F$_5$)$_3$·(EtO)Me$_2$PO 14. Yield 42%. mp 168–170 °C. Calc. for C$_{22}$H$_{11}$BF$_{15}$O$_2$P: C, 41.7; H, 1.8. Found: C, 41.6; H 1.7%. NMR (CDCl$_3$/RT): ^{1}H (δ), 1.27 (q, 3H) ^3J(HH) 7.0, 1.70 (d, 6H) ^2J(PH) 14.0, 4.1 (m, 2H); ^{13}C-{^{1}H} (δ), 13.4 (d) ^1J(CP) 99, 15.6 (d) ^3J(PC) 7.6, 64.4 (d) ^2J(CP) 7.6, 137.1 (d) ^1J(CF) 254, 139.7 (d) ^1J(CF) 251, 147.8 (d) ^1J(CF) 236 Hz; ^{11}B-{^{1}H} (δ), −9.3; ^{31}P-{^{1}H} (δ), +54.5. IR (KBr disk/cm^{-1}): 3002, 1648, 1559, 1521, 1458, 1399, 1375, 1319, 1284, 1187 (P=O), 1102, 1042, 971, 890, 853, 797, 772, 743, 682, 617.

(c) Crystal structure of 2

Cell dimensions and intensity data for **2** were recorded at 150 K, using a Nonius KappaCCD area detector diffractometer mounted at the window of a molybdenum rotating anode (50 kV, 90 mA, λ = 0.71073 Å). The crystal-to-detector distance was 30 mm and ϕ and Ω scans (2° increments, 10 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs COLLECT,[35] DENZO[36] and maXus[37] and an empirical absorption correction was applied using SORTAV.[38,39] The structure was solved *via* direct methods[40] and refined by full matrix least squares[40] on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference map and fully refined. Crystal data: C$_{36}$H$_{15}$BF$_{15}$OP, M_r = 790.26, T = 150(2) K, monoclinic, space group $C2/c$, a = 31.0247(4), b = 9.4124(2), c = 22.5961(3) Å, β = 105.9570(13)°, V = 6344.19(18) Å^3, μ = 0.207 mm^{-1}, Z = 8, reflections collected 31694, independent reflections 5572 (R_{int} = 0.069), final R indices [$I > 2\sigma I$] $R1$ = 0.0395, $wR2$ = 0.0934, R (all data) $R1$ = 0.0620, $wR2$ = 0.1031.

CCDC reference number 155795.

See http://www.rsc.org/suppdata/dt/b1/b100981h/ for crystallographic data in CIF or other electronic format.

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References

1 A. G. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 212.

2 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245.

3 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 3623.

4 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015.

5 K. Ishihara, N. Hanaki, M. Funahashi, M. Miyata and H. Yamamoto, *Bull Chem. Soc. Jpn.*, 1995, **68**, 1721.

6 D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440.

7 W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345.

8 H. Jacobsen, H. Berke, S. Doring, G. Kehr, G. Erker, R. Frohlich and O. Meyer, *Organometallics*, 1999, **18**, 1724.

9 L. H. Doerrer and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1999, 4325.

10 A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer and M. B. Hursthouse, *Chem. Commun.*, 1998, 2529.

11 D. J. Parks, W. E. Piers, M. Parvez, R. Atencio and M. J. Zaworotko, *Organometallics*, 1998, **17**, 1369.

12 D. C. Bradley, M. B. Hursthouse, M. Motevalli and Z. Dao-Hong, *J. Chem. Soc., Chem. Commun.*, 1991, 7.

13 D. C. Bradley, I. S. Harding, A. D. Keefe, M. Motevalli and D.-H. Zheng, *J. Chem. Soc., Dalton Trans.*, 1996, 3931.

14 M. A. Beckett, D. S. Brassington, S. J. Coles and M. B. Hursthouse, *Inorg. Chem. Commun.*, 2000, **3**, 530.

15 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235.

16 V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225.

17 H. Noeth and B. Wrackmeyer, in *NMR Basic Principles and Progress*, Springer Verlag, Berlin, 1978, vol. 14.

18 N. Burford, B. W. Royan, R. E. v H. Spence, T. S. Cameron, A. Linden and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 1521.

19 S. Doring, G. Erker, R. Frohlich, O. Meyer and K. Bergander, *Organometallics*, 1998, **17**, 2183.
20 N. Burford, R. E. v H. Spence, A. Linden and T. S. Cameron, *Acta Crystallogr., Sect. C*, 1990, **46**, 92.
21 M. T. Reetz, M. Hullmann, W. Massa, S. Berger, P. Rademacher and P. Heymanns, *J. Am. Chem. Soc.*, 1986, **108**, 2405.
22 G. Barrado, L. Doerrer, M. L. H. Green and M. A. Leech, *J. Chem. Soc., Dalton Trans.*, 1999, 1061.
23 A. R. Siedle, R. A. Newmark, W. M. Lamanna and J. C. Huffman, *Organometallics*, 1993, **12**, 1491.
24 Y. Hermodsson, *Ark. Kemi*, 1969, **30**, 15.
25 N. Burford, B. W. Royan, R. E. v H. Spence and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 2111.
26 D. Murphy, J. P. Sheehan, T. R. Spalding, G. Ferguson, A. J. Lough and J. F. Gallagher, *J. Mater. Chem.*, 1993, **3**, 1275.
27 G. Ruban and V. Zabel, *Cryst. Struct. Commun.*, 1976, **5**, 671.
28 S. Un and M. P. Klein, *J. Am. Chem. Soc.*, 1989, **111**, 5119.
29 M. C. R. Symons and G. Eaton, *J. Chem. Soc., Faraday Trans. 1*, 1982, 3033.
30 M. F. Lappert, *J. Chem. Soc.*, 1961, 817.
31 M. F. Lappert, *J. Chem. Soc.*, 1962, 542.
32 J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *J. Am. Chem. Soc.*, 1954, **76**, 5185.
33 G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, 1951, **73**, 5466.
34 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.
35 Collect, data collection software, Nonius B. V., Delft, 1998.
36 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
37 S. Mackay, C. J. Gilmore, C. Edwards, M. Tremayne, N. Stuart and K. Shankland, maXus: a computer program for the solution and refinement of crystal structures from diffraction data, University of Glasgow, Nonius BV, Delft, and MacScience Co. Ltd., Yokohama, 1998.
38 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
39 R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.
40 SHELX 97, Programs for Crystal Structure Analysis (Release 97-2), G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Göttingen, 1998.