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The Preparation of 1 : 1 Phosphine : Triarylboron Complexes. The X-ray Crystal Structure of $(C_6F_5)_3B{\cdot}PH_3$

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The tris(fluoroaryl) boron compounds $B(C_6F_5)_3$ and $B(C_6H_3F_2\text{-}2,6)_3$ undergo reversible 1 : 1 adduct formation with phosphine (PH_3); the X-ray crystal structure of $(C_6F_5l_3B{\cdot}PH_3)$ **1** has been determined.

The toxic nature of PH_3 has inhibited its study and consequently very few complexes of PH_3 have been reported. The only structurally characterized phosphine complexes have all involved bonding to transition metals,[1] although the parent $BH_3 : PH_3$ complex has been investigated, and parameters determined, *via* high level (6-31G**) *ab initio* geometry optimisation.[2]

The rapidly increasing use of PH_3 in the deposition of InP and other III–V semiconductors has stimulated interest in its chemistry. We have found that phosphine coordinates to some fluorine substituted trisarylboranes $B(C_6H_xF_{5-x})_3$ to form 1 : 1 complexes. The most stable complex isolated to date is $(C_6F_5)_3\,B{\cdot}PH_3$ **1** obtained by absorbing PH_3 into a frozen (78 K) toluene solution of $(C_6F_5)B$.[3] After warming to room temperature and removal of the excess of PH_3 by evaporation and the solvent *in vacuo*, compound **1** was obtained as a white solid.

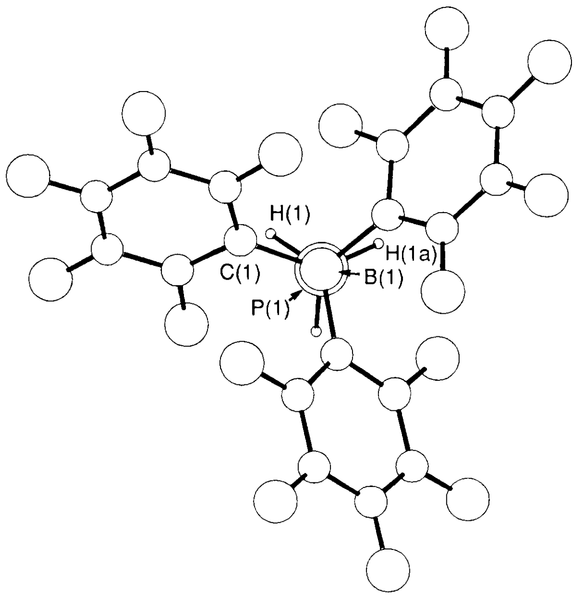

Fig. 1 The structure of one of the three independent molecules of $[(C_6F_5)_3B{\cdot}PH_3]$ **1**; selected bond lengths (Å) and angles (°): B(1)–P(1) 2.044(8), B(2)–P(2) 2.046(8), B(3)–P(3) 2.048(8), H(1)–P(1) 1.242(28), H(2)–P(2) 1.328(27), H(3)–P(3) 1.358(26), C(1)–B(1)–P(1) 104.1(3), C(2)–B(2)–P(2) 104.8(3), C(3)–B(3)–P(3) 104.2(3); H(1)–P(1)–B(1) 116.4(14), H(2)–P(2)–B(2) 121.7(13), H(3)–P(3)–B(3) 117.5(12), H(1)–P(1)–H(1a) 101.8(17), H(2)–P(2)–H(2a) 94.9(17), H(3)–P(3)–H(3a) 100.4 (15)

The ^1H NMR spectrum (C_7D_8, 250 MHz) at 283 K showed a broad doublet at δ 3.34 (J_{HP} 410.2 Hz) (*cf.* PH_3 gives δ, 1.56; J_{HP} 186 Hz) which was resolved at 263 K to a doublet of septets ($^5J_{HF}$ 5.2 Hz) showing coupling presumably to the six equivalent fluorines in the 2,6-positions of the phenyl groups. The IR spectrum (Nujol mull) showed that the ν_{P-H} stretching vibration had shifted from 2327 in PH_3 to 2405 cm^{-1} in **1**. A single crystal of **1** grown from dichloromethane solution was used to determine its X-ray crystal structure,† which confirmed the expected molecular structure (Fig. 1) involving approximately tetrahedral boron (average CBF = 104.4 ± 0.3°). The unit cell contains six molecules with extensive P–H · · · F intermolecular hydrogen bonding with consequent wide variations in P–H bond lengths (1.24–1.36 Å) and HPH bond angles (94.9–101.8°), but it is clear that the bonds are significantly shorter and the angles wider than in gaseous PH_3 (P–H = 1.42 Å; HPH = 94°). The long P–B bond length (average 2.046 ± 0.002 Å compared with the sum of the covalent radii 1.90 Å) suggests a weak P→B coordinate bond and accordingly the complex releases gaseous phosphine when heated (*ca.* 50 °C) *in vacuo*. A value of 2.022 Å was obtained for B–P *via* the *ab initio* calculation.[2] Preliminary static vapour pressure measurements suggest an enthalpy of dissociation of *ca.* 80 kJ mol^{-1}.

The electron-attracting ability of the boron is clearly important in stabilising the phosphine adduct since BPh_3 does not form a complex whereas $B\,(C_6H_3F_2\text{-}2,6)_3$ forms a weaker complex than **1**.

The reversible formation and dissociation of **1** suggests that

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† *Crystal data* for **1**: $C_{18}H_3BF_{15}\,P$, M = 546.0, trigonal, space group $P\bar{3}$, $a = b$ = 15.065(6), c = 14.614 (4) Å. U = 2872.35 Å^3, Z = 6, D_c = 1.89 g cm^{-3}, μ (Mo-$K\alpha$) = 2.83 cm^{-1}. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-$K\alpha$ radiation. The data were corrected for Lorentz polarization and absorption effects. Full-matrix least-squares refinement of 329 parameters gave R = 0.0436, R_w = 0.0370 for 2718 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

it may be a useful, safe storage material for the purification and generation of PH_3 under controlled conditions.[4]

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