Synthesis and Molecular Structure of a P_2B_3 Cage Compound: $P_2(BNPr^i_2)_3$

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The reaction of $(Pr^i_2N)B(Cl)P(SiMe_3)_2$ with $(Pr^i_2N)BCl_2$ in a 2 : 1 ratio resulted in the formation of a trigonal bipyramidal cage compound $P_2(BNPr^i_2)_3$ whose structure was determined by *X*-ray diffraction techniques.

Synthetic pathways and structural investigations for main group ring and cluster compounds are attracting renewed interest. Historically, for group 15 elements, syntheses of polyphosphanes and PN, PO, and PS rings and cages have gained special notice while attempts systematically to construct phosphorus ring and cage compounds containing other heteroatoms have lagged behind. The preparation of phosphorus–boron rings has attracted some activity in the past, yet no structurally confirmed examples of molecular BP cage or cluster compounds, with the exception of *exo*-substituted or bridge-substituted boranes or carbaboranes, have been reported. Previous descriptions of the formation and reaction chemistry of a number of monomeric silylphosphane borane compounds by Nöth and co-workers[1] and Fritz and co-workers[2] suggested that reagents of this type might offer a useful starting point for the synthesis of new BP cluster

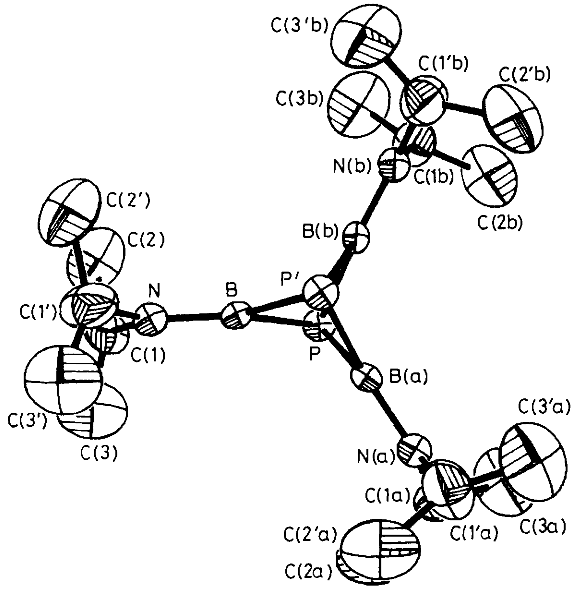

Figure 1. Thermal ellipsoid plot (25% probability ellipsoids) for $P_2(BNPr^i_2)_3$ showing the atom numbering scheme.

compounds. We report here the preparation and molecular structure determination of an unprecedented trigonal bipyramidal cluster, $P_2(BNPr^i_2)_3$ (**1**).

A mixture of $(Pr^i_2N)B(Cl)P(SiMe_3)_2$[3] (10 mmol) with $(Pr^i_2N)BCl_2$ (5 mmol) was heated to 160 °C without solvent in an evacuated Schlenk tube. Over three hours, the colourless mixture became orange and, upon cooling, colourless crystals deposited in an orange oil. A total of 15 mmol of Me_3SiCl was recovered from the reaction flask and (**1**), 1.4 g (71% yield), was isolated by vacuum sublimation [m.p. 124 °C, *m/z* 395 (M^+) ($C_{18}H_{42}B_3N_3P_2$); ^1H n.m.r. (C_6D_6, ref. Me_4Si) δ 3.86 (heptet, J_{HH} 6.7 Hz, Me_2CH) and 1.21 (d, J_{HH} 6.7 Hz, CCH_3); $^{13}C\{^1H\}$ n.m.r. (C_6D_6, ref. Me_4Si) δ 52.5 (t, J_{PC} 5.2 Hz, MeCH), 23.6 (t, J_{PC} 2.3 Hz, CCH_3); $^{31}P\{^1H\}$ n.m.r. (C_6D_6, ref. 85% H_3PO_4) δ −13.0 (s) p.p.m.; $^{11}B\{^1H\}$ n.m.r. (C_6D_6, ref. $Et_2O{\cdot}BF_3$) δ 40.5 (s) p.p.m.; i.r. (hexane)ν_{BN} 1467m, ν_{BN} 1432s, 809w, 796w cm^{-1}.]†

We have recently observed[3] that the reaction of $(Pr^i_2N)B(Cl)P(SiMe_3)_2$ with $LiP(SiMe_3)_2$ results in the formation of a four membered ring compound, $[(Pr^i_2N)BP(SiMe_3)]_2$ (equation 1). No evidence was obtained which suggested the formation of expected diphosphide, $(Pr^i_2N)B[P(SiMe_3)_2]_2$ or a P=B double bonded species. In equation (2), the chemistry resulting from the 2 : 1 combination of $(Pr^i_2N)B(Cl)P(SiMe_3)_2$ and $(Pr^i_2N)BCl_2$ is summarized. At 25 °C there is no apparent reaction between the reagents. However, thermal elimination of Me_3SiCl occurs smoothly at 160 °C, and the novel product, $P_2(BNPr^i_2)_3$, is isolated in high yield.

$$2(Pr^i_2N)B(Cl)P(SiMe_3)_2 + 2\,LiP(SiMe_3)_2 \rightarrow 2\,LiCl + 2\,P(SiMe_3)_3 + [(Pr^i_2N)BP(SiMe_3)]_2 \quad (1)$$

$$2(Pr^i_2N)B(Cl)P(SiMe_3)_2 + (Pr^i_2N)BCl_2 \xrightarrow{160\,^\circ C} Me_3SiCl + P_2(BNPr^i_2)_3 \quad (2)$$

The $^{31}P\{^1H\}$ n.m.r. spectrum of (**1**) displays a single resonance at δ −13.0 p.p.m., and the $^{11}B\{^1H\}$ n.m.r. spectrum shows one broad resonance centred at δ 40.5 p.p.m. consistent with a single environment for both the phosphorus and boron atoms. The ^{31}P shift for (**1**) is upfield of the shifts found for many tri-co-ordinate phosphanes yet downfield of the shifts reported for $[(Pr^i_2N)BP(SiMe_3)]_2$ (−133.6 p.p.m.),[3] $[(Me_2N)BP(SiMe_3)]_2$ (−153, p.p.m.),[2] and $P[B(NMe_2)_2]_3$ (−200 p.p.m.).[2] The intermediate value for δ ^{31}P probably results from a balance of heteroatom substituent group electronic effects and geometric factors (small B–P–B bond angles, *vide infra*) at the phosphorus atoms. The boron shift is slightly upfield of the resonance in $[(Pr^i_2N)BP(SiMe_3)]_2$ (50.6 p.p.m.) and comparable with the shift in $(Pr^i_2N)B(Cl)P(SiMe_3)_2$ (40.6 p.p.m.).[3] Factors which affect the magnitude of B–P coupling constants are also not well understood;[4,5] however, the lack of resolvable B–P coupling in (**1**) appears to be consistent with the small B–P–B bond angles which in turn suggest large p and small s orbital contributions in the B–P bonds.

The molecular stoicheiometry and structure of (**1**) are confirmed by *X*-ray crystallographic methods, and a view of the molecule is shown in Figure 1. The molecule has a trigonal bipyramidal structure with the two phosphorus atoms in apical positions and the three boron atoms occupying the trigonal vertices. The P–B bond distance, 1.969(8) Å, is identical within experimental error to the average P–B bond distance in the four membered ring compound[3] $[(Pr^i_2N)BP(SiMe_3)]_2$, 1.951(5) Å. Both distances are longer than the average P–B distances in the four membered ring compound[6] $[Me_2C(CH_2)_3CMe_2NBP(CEt_3)]_2$, 1.924(2) Å, and the three membered ring compound[7] $(Et_2N)B(PBu^t)_2$, 1.893(2) Å. The B–N bond length, 1.34(2) Å, is slightly shorter than those in $[(Pr^i_2N)BP(SiMe_3)]_2$, 1.384(5) Å, and $(Et_2N)B(PBu^t)_2$, 1.382(3) Å, and significantly shorter than the B–N distance in $[Me_2C(CH_2)_3CMe_2NBP(CEt_3)]_2$, 1.431(2) Å, suggesting that there is a degree of B–N π overlap[8] in (**1**). Consistent with this suggestion, the sums of the bond angles about the B and N atoms are 360.0 and 359.9°, respectively. The B–P–B angle, 68.9(2)°, suggests that the phosphorus centres may be considered to be highly compressed phosphanes, and the P–B–P angle, 98.5(5)°, is a little larger than the related angles in the four membered ring compounds.

Anisotropic least-squares refinements reveal orientational disorder in the Pr^i carbon atoms which is responsible for the large *R* value. In addition, this results in an unrealistic structural artifact: a planar geometry for the central Pr^i carbon atom, C(1). Attempts to resolve this disorder problem employing different disorder models result in more unrealistic C–C and C–N bond distances and C–C–C and N–C–C angles. Resolution of this problem will require chemical modifications of the R group on nitrogen or co-ordination of the phosphorus atom.

The synthesis of (**1**) suggests that this molecule represents only one member of a family of boron–phosphorus ring and cluster compounds which should be accessible by modifica-

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† *Crystal data* for (**1**): $C_{18}H_{42}B_3N_3P_2$, M = 395.0, hexagonal, space group $P6_3/m$, $a = b$ = 10.474(2), c = 13.889(4) Å, U = 1319.5(7) Å^3, Z = 2, μ(Mo-K_α) = 1.67 cm^{-1}, D_c = 0.99 g cm^{-3}. Intensity data were collected at −40 °C on a Syntex P3/F automated diffractometer operating in the ω scan mode and using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). A total of 611 unique, space group allowed reflections were collected with 604 reflections observed at the F >3.0 $\sigma(F)$ level. The structure was solved by direct methods and refined by the block diagonal least-squares method to give R = 12.6%. A test of the space group selection was made by attempted solution in the space group $P6_3$; however, this refinement led to unrealistic thermal parameters for several atoms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

tions of the preparative scheme outlined here. Furthermore, it is anticipated that the co-ordination chemistry of (**1**) should prove to be interesting.

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