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Inorganic Triphenylphosphine

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Abstract: A completely inorganic version of one of the most famous organophosphorus compounds, triphenylphosphine, has been prepared. A comparison of the crystal structures of inorganic triphenylphosphine, PBaz₃ (where Baz = B₃H₂N₃H₃) and PPh₃ shows that they have superficial similarities and furthermore, the Lewis basicities of the two compounds are remarkably similar. However, their oxygenation and hydrolysis reactions are starkly different. PBaz₃ reacts quantitatively with water to give PH₃ and with the oxidizing agent ONMe₃ to give the triply-O-inserted product P(OBaz)₃, an inorganic version of triphenylphosphite; a corresponding transformation with PPh₃ is inconceivable. Thermodynamically, what drives these striking differences in the chemistry of PBaz₃ and PPh₃ is the great strength of the B–O bond.

The diatomic fragments BN and CC are isoelectronic and the chemical consequences of this simple relationship have been appreciated ever since the 1926 discovery of borazine which is isoelectronic to benzene and dubbed "inorganic benzene" (Figure 1).^[1] The substitution of a BN unit for a CC in an organic molecule has a transformative effect on the properties of the compound as illustrated by the three comparisons given in Figure 1 from the fields of photochemistry,^[2–7] medicinal chemistry^[8–13] and hydrogen storage.^[14–18]

Since BN and CC are considered to be isosteres, the explanation for the sharply different properties of BN / CC analogues most likely lies in differences in the bonding and electronegativity. The energies and sizes of the atomic orbitals formally combining to form the molecular orbitals of a CC bond are self-evidently matched whereas the mismatched energies and sizes of the atomic orbitals combining in the BN bond make the σ -bonding dipolar and the π -bonding weaker due to less efficient overlap.^[19–22] The result is that BN compounds are generally kinetically and thermodynamically more reactive than their CC analogues. Thus, borazine has superficial similarities with benzene (e.g. both are colourless liquids under ambient conditions) but the aromaticity of borazine, as determined computationally and experimentally, is significantly lower than the aromaticity of benzene (e.g. NICS values for benzene and borazine are -11.5 and -2.1 respectively),^[23–25] and the dominant mechanisms by which they undergo substitution are fundamentally different: electrophilic aromatic substitution for benzene, addition-elimination for borazine.^[26,27]

B-trisubstituted borazines (Figure 2) are readily prepared and their chemistry has been well studied^[28–33] but the chemistry of the less accessible B-monosubstituted borazines (XBaz, Figure 2) has been little developed;^[34–36] for example, 2-hydroxyborazine (HOBaz), the borazine analogue of phenol, has

only been partially characterised *in situ* as part of a mixture of products formed in the photochemical oxidation of borazine.^[37] In addition, no borazines that contain P–B bonds have been reported which may be due to the anticipated high reactivity of the P–B bond.^[38]

Figure 1. Examples of isoelectronic compounds featuring BN for CC substitution.

Figure 2. Examples of substituted borazines.

There are thousands of academic articles and patents featuring PPh₃ and globally it is produced on a multi-kiloton scale per annum because of its multitude of applications.^[39,40] We were intrigued to know whether it would be possible to make "inorganic" triphenylphosphine (Figure 2, tris(2-boraziny)phosphine; PBaz₃) and if so, how its properties would compare with "conventional" triphenylphosphine (PPh₃). Here we report the successful synthesis of PBaz₃ and show that it has

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Lewis basicity similar to that of PPh_3 but the high reactivity of the P–B bond leads to oxygenation chemistry that is unprecedented with conventional phosphines.

Synthesis and characterization of PBaz₃. We have previously shown that P–B bonds can be readily formed by a chlorosilane elimination reaction between a chloroborane and a silylphosphine.^[41] Pleasingly, the reaction between chloroborazine and $\text{P}(\text{SiMe}_3)_3$ produced PBaz₃ quantitatively (Scheme 1) according to multinuclear NMR spectroscopy (see Supporting Information for details). The reaction was monitored by ^{31}P NMR spectroscopy which showed that the conversion of $\text{P}(\text{SiMe}_3)_3$ to PBaz₃ proceeded smoothly over 5 h via two intermediates which are assigned to the monoborazinyl $(\text{Me}_3\text{Si})_2\text{PBaz}$ and diborazinyl $\text{Me}_3\text{SiPBaz}_2$.

Scheme 1. Synthesis of tris(2-borazinyl)phosphine (PBaz₃).

The white, malodorous, solid PBaz₃ was isolated in yields of up to 97% simply by removal of the volatiles. The ^{31}P NMR spectrum of solutions of PBaz₃ in THF under argon at ambient temperatures is unchanged over a period of one month. The ^{31}P NMR signal at -205 ppm for PBaz₃ is very broad ($w_{1/2} = 340$ Hz)

and remains broad at high (+80 °C) temperatures, consistent with short quadrupolar relaxation times and unresolved coupling to the nine $^{11}\text{B}/^{10}\text{B}$ nuclei. The δ_{P} of PBaz₃ is 200 ppm to high field of PPh_3 ($\delta_{\text{P}} = -5.0$ ppm), and much closer to that of $\text{P}(\text{SiMe}_3)_3$ ($\delta_{\text{P}} = -251$ ppm) and PH_3 ($\delta_{\text{P}} = -241$ ppm) reflecting the very different magnetic environments of the P atom in PBaz₃ and PPh_3 . The ^{11}B and ^1H NMR spectra of PBaz₃ show the expected signals.

Crystals of PBaz₃ suitable for X-ray crystallography were obtained from its saturated solution in CH_2Cl_2 stored at -20 °C and its crystal structure is shown in Figure 3 alongside the structure of PPh_3 .^[42] The molecular structure of PBaz₃ shows a propeller-like orientation of the planar borazinyl substituents with near C_3 symmetry and a pyramidal geometry at phosphorus. Ostensibly the structures of PBaz₃ and PPh_3 are similar but they differ significantly in the details: (1) The P–B bond lengths in PBaz₃ are ca. 0.1 Å longer than the P–C bond lengths in PPh_3 paralleling the difference in the covalent radii ($r_{\text{C}} = 0.73(2)$ Å, $r_{\text{B}} = 0.84(3)$ Å). (2) The geometry at P in PBaz₃ is considerably flattened, in accord with Bent's Rule^[43] which predicts that the p-character of P–X π -bonds (e.g. in PX_3 where X = F, OR, NR_2 , CR_3 , BR_2) should decrease with decreasing electronegativity of X; the flattening at P is also consistent with some π -character in the P–B bonds (see below). (3) The orientation of the rings in PBaz₃ is less propeller-like than in PPh_3 as is clear by comparison of the side-on views in Figure 3 which show that the acute angle (56°) between the planes of the rings in PBaz₃ contrasts with the approximately orthogonal (82°) rings in PPh_3 . (4) The long P–B bonds make the P atom less crowded in PBaz₃ than in PPh_3 as shown by the calculated crystallographic cone angles^[44] of 137° (PBaz₃) and 154° (PPh_3).

Figure 3. Molecular structures of PBaz₃ and PPh_3 .^[42] Two views of the structures are given: (a) along the C_3 axis and (b) perpendicular to the C_3 axis, to facilitate the comparison. (c) Plots of the HOMOs of PBaz₃ and PPh_3 (isovalues 0.05). Selected bond lengths (Å) and angles: P1–B1 1.923(2), P1–B4 1.9230(19), P1–B7 1.9255(18), B1–P1–B4 106.34(8), B4–P1–B7 107.78(8), B1–P1–B7 107.44(8), B1–P1–B7–N9 52.94(11), B7–P1–B4–N6 55.98(10), B4–P1–B1–N3 57.74(10).

DFT calculations have been carried out (PBE0-D3BJ/cc-pVTZ) in order to compare the electronic structures of PBaz₃ with PPh₃. Both calculated structures closely matched the structures obtained by X-ray crystallography (see SI). The surface contour maps of the canonical HOMOs for PBaz₃ and PPh₃ are clearly identifiable as the lone pairs on the P atoms (Figure 3c) and the calculated energies of these orbitals are very similar: -6.165 eV (PPh₃) and -6.321 eV (PBaz₃). NBO calculations show that the HOMO of PBaz₃ has 64% p-character which is significantly more than the 54% for PPh₃; the greater p-character is also apparent from the shapes of the HOMO orbitals (Figure 3c). The calculated bond indices for P–B in PBaz₃ (1.07) and P–C in PPh₃ (0.92) support the idea that there is a small amount of P–B π -bonding present in PBaz₃.^[45]

Reaction of PBaz₃ with BH₃. Addition of H₃B·THF to PBaz₃ generated a product that has been characterised in solution by ³¹P and ¹¹B NMR spectroscopy and assigned the structure Baz₃P·BH₃ (Scheme 2); the analogous Ph₃P·BH₃ is formed similarly from H₃B·THF and PPh₃.^[46] The ³¹P and ¹¹B NMR signals for the Baz₃P·BH₃ are at δ_P = -171 and δ_B = -42 ppm which correspond to coordination chemical shifts of $\Delta\delta_P$ = +34 and $\Delta\delta_B$ = -41 ppm; these values are similar to those for Ph₃P·BH₃ ($\Delta\delta_P$ = +26 and $\Delta\delta_B$ = -38 ppm).

In order to determine the relative Lewis base strengths of PBaz₃ and PPh₃, the position of the equilibrium shown in Scheme 2 has been investigated by ³¹P NMR spectroscopy. When Ph₃P·BH₃ and PBaz₃ or Baz₃P·BH₃ and PPh₃ were mixed in THF, an equilibrium was slowly established over several hours in favour of Ph₃P·BH₃ and integration of the ³¹P NMR signals for the constituents led to an estimate of the equilibrium constant *K* to be ~140. Since this equates to a ΔG ~ 3 kcal mol⁻¹, it is concluded that the Lewis basicity of PPh₃ is similar but slightly greater than PBaz₃. Our calculations (DLPNO-CCSD(T)/def2-TZPP//PBE0-D3BJ/def2-SVP) show that the borane binding enthalpy (calculated *in vacuo* and neglecting entropic corrections) of PPh₃ (34 kcal mol⁻¹) is greater than that of PBaz₃ (26 kcal mol⁻¹) in line with the experimental observation favoring PPh₃·BH₃.

Scheme 2. Reactions of PBaz₃ with BH₃, H₂O and ONMe₃.

Hydrolysis and oxygenation of PBaz₃. The reactivity of the P–B bond in PBaz₃ towards water and oxidizing agents is very different from the P–C bond in PPh₃. For example, while PPh₃ is completely inert to water, PBaz₃ is extremely moisture sensitive. PBaz₃ reacts rapidly and quantitatively with water to give PH₃ (δ_P = -241 ppm, quartet, J_{PH} = 187 Hz) and a species tentatively

assigned to 2-hydroxyborazine (HOBaz, Scheme 2) on the basis of the ¹¹B NMR spectrum which showed a doublet at +30 ppm ($^1J_{BH}$ = 139 Hz) and a singlet at +24 ppm in a 2:1 intensity ratio.

When a sub-stoichiometric amount of H₂O was added to PBaz₃, the ³¹P NMR spectrum of the resulting solution contained two species in addition to PBaz₃ and PH₃ and these are assigned, on the basis of their ³¹P parameters, to the intermediate secondary phosphine Baz₂PH (δ_P = -203 ppm, doublet, J_{PH} = 200 Hz) and primary phosphine BazPH₂ (δ_P = -228 ppm, triplet, J_{PH} = 203 Hz) (see Supporting Information); the J_{PH} values for Ph₂PH (216 Hz) and PhPH₂ (199 Hz) are very similar to the borazinyolphosphine analogues. The hydrolysis of PBaz₃ is reminiscent of the hydrolysis of P(SiMe₃)₃ under the same conditions to give H_nP(SiMe₃)_{3-n} (*n* = 1–3; see Supporting Information for details); this is an illustration of the similar reactivity of P–B and P–Si bonds which can be viewed as a manifestation of the B/Si diagonal relationship.

The Gibbs free energy change (ΔG) for the observed PBaz₃ hydrolysis to PH₃ was calculated to be -73 kcal mol⁻¹ (using our standard DLPNO-CCSD(T) approach) which is a strong thermodynamic driving force and almost 100 kcal mol⁻¹ more favourable than the ΔG calculated for the analogous hypothetical PPh₃ hydrolysis (+26 kcal mol⁻¹, Scheme 3). This contrasting outcome is attributed to B–O bonds (~130 kcal mol⁻¹) being much stronger than C–O bonds (~85 kcal mol⁻¹).

Scheme 3. Thermodynamics of hydrolysis and oxygenation of PPh₃ and PBaz₃. Values of ΔG in kcal mol⁻¹; the red reaction arrows indicate the experimentally observed reactions.

We have previously shown that O atoms can be inserted into the P–B bonds of borylphosphines by treatment with ONMe₃; this occurred even when the P lone pair of the borylphosphine was coordinated to Rh.^[47] It was therefore of interest to investigate whether inorganic triphenylphosphine, PBaz₃ could be converted directly to inorganic triphenylphosphite, P(OBaz)₃ (Scheme 2). The *in situ* ³¹P{¹H} NMR spectrum of the PBaz₃/ONMe₃ reaction mixture showed, after 5 min, a sharp singlet at δ_P +119 ppm (*cf.* for P(OPh)₃, δ_P 129 ppm) as the only P-containing product; this is a change in ³¹P NMR shift of over +300 ppm from the signal of PBaz₃. Consistent with the structure of P(OBaz)₃, the ¹¹B NMR spectrum displayed two broad signals at +31 ppm ($^1J_{BH}$ ~ 125 Hz) and +23 ppm in a 2:1 ratio.

Treatment of PPh₃ with ONMe₃ gives O=PPh₃ whereas no similar reaction occurred to give O=PBaz₃ and the only observed product was the phosphite P(OBaz)₃. In order to probe the source of this sharp difference in chemistry, calculations were carried out on two alternative monooxygenation reactions (with O₂) that produce phosphine oxide or phosphinite (Scheme 3).

These calculations predict that there would be a strong thermodynamic preference for phosphinite formation with PBaz₃ but phosphine oxide formation with PPh₃. Calculated bond dissociation energies indicate that the P–B in PBaz₃ (90 kcal mol^{−1}) is stronger than the P–C in PPh₃ (81 kcal mol^{−1}) and therefore the unconventional oxidation chemistry of PBaz₃ is driven by the high B–O bond strength.

The chemistry of borazine has intrigued chemists for over 90 years. The synthesis of triborazinylphosphine (PBaz₃), an inorganic analogue of triphenylphosphine (PPh₃), is a notable achievement because it is the most elaborate molecular borazine so far reported and the first borazine to contain a B–P bond. The structures and Lewis basicity of PBaz₃ and PPh₃ are similar but their oxygenation and hydrolysis chemistry could hardly be more different. For example, PBaz₃ catches fire in air (presumably due to the formation of PH₃) while PPh₃ is indefinitely air-stable even in solution. Controlled oxidation transforms PBaz₃ into "inorganic triphenyl phosphite", P(OBaz)₃ by three O insertions into the P–B bonds while PPh₃ produces simply triphenylphosphine oxide. These striking differences in chemistry are thermodynamically driven by the very high B–O bond strength. The extreme sensitivity of PBaz₃ to air and moisture producing PH₃, precludes many applications for PBaz₃ in catalysis but its synthesis opens up the possibility of developing more stable ligands containing a single boraziny substituent and the prospect of producing uncharted borazines that contain B bonded to other 2nd row elements such as Si and S.

Keywords: Main Group Elements • Phosphorus • Boron • Inorganic Chemistry • Structure Elucidation

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Inorganic versus organic: the molecular structures and Lewis basicities of triphenylphosphine and tris(2-borazanyl)phosphine appear similar but their hydrolysis and oxygenation chemistry could hardly be more contrasting.

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