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The "Anomalous" Basicity of $P(NHCH_2CH_2)_3N$ Relative to $P(NMeCH_2CH_2)_3N$ and $P(NBzCH_2CH_2)_3N$: A Chemical Consequence of Orbital Charge Balance?

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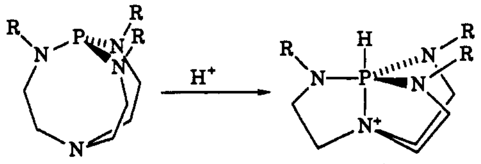
The prophosphatrane **1** was recently shown to be ca. 10^7 times more basic in solution toward H^+ than any known phosphine derivative, giving the unusually robust phosphatrane cation **4**.[1]

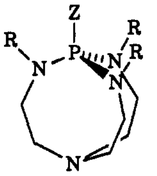


(1)

1 R = Me
2 R = H
3 R = CH_2Ph

4(Cl)
5(Cl)
6(Cl)

Here we report that although analogue **3** is less basic than **1** as expected on inductive grounds, such reasoning fails to explain our observation that the parent analogue **2** is more basic than either **1** or **3**. As in the synthesis of **1**, for which **4(Cl)** is the precursor,[1] **5(Cl)** and **6(Cl)** are the sources of **2** and **3**, respectively, and they are made in an analogous manner. Although, like **1**, **3** can be isolated and purified, prophosphatrane **2** has resisted isolation owing to facile polymerization. However, the previously characterized prophosphatrane derivative **7**[2] and the analogously synthesized **8** and **9**[3] reported here are sufficiently stable in solution for spectroscopic measurements. Moreover, **10**,[2] **11**,[2] and **12**[4] have been isolated and characterized, and **11** has been structured by X-ray means.[2]



7 R = Me, Z = Se
8 R = H, Z = Se
9 R = CH_2Ph, Z = Se
10 R = Me, Z = O
11 R = Me, Z = S
12 R = H, Z = O

From ^{31}P NMR peak integrations of separate DMSO solutions of **4** and **5** and of **4** and **6** treated with a stoichiometric deficit of KO-*t*-Bu, it was demonstrated that **6** is more acidic than **4** and that **4** is more acidic than **5**, which provides the basicity order **3** < **1** < **2** for the corresponding conjugate bases. Assuming a pK_a of 28.6 for HO-*t*-Bu in DMSO,[5] a pK_a of 29.6 is calculated for **5** and an upper limit of 26.8 is estimated for **4** and **6** in DMSO.[6] There is ample evidence in the literature that, for bases of similar structure, rising solution- and gas-phase basicity for similar phosphorus-containing bases can be linearly correlated with decreasing $^1J(^{31}P-^{77}Se)$ values of their selenium adducts[7,8] and with decreasing $^1J(^{31}P-^1H)$ couplings of their protonated forms.[8,9] Such coupling trends are also found for the selenium adducts of prophosphatranes **3**, **1**, and **2** [**9** (774 Hz), **7** (754 Hz), and **8** (590 Hz), respectively] and for their corresponding protonated forms [**6** (506 Hz), **4** (491 Hz) and **5** (453 Hz)].

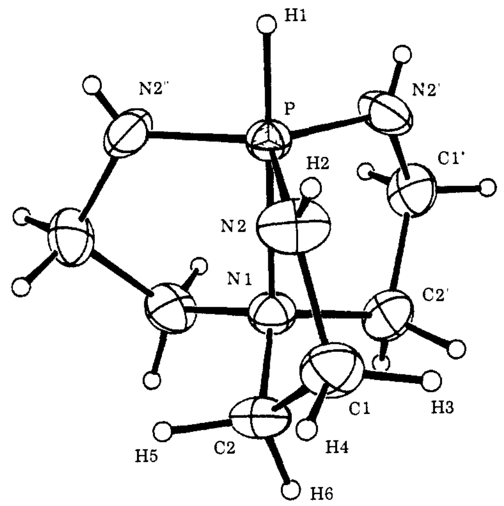


Figure 1. ORTEP drawing of cation **5**, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are drawn as arbitrarily sized spheres for clarity.

A comparison of the crystallographic parameters for cation **4**[1] with those of **5**[10] (see Figure 1) does not provide a satisfactory rationale for the basicity order **1** < **2**. In fact, the $P-N_{ax}$ bond in **4** is unexpectedly slightly shorter [1.976 (8) Å] than in **5** [2.0778 (4) Å], and the $N_{eq}-P-N_{ax}$ angle in **4** [85.9 (4)°, 86.5 (2)°] is larger than in **5** [84.01 (3)°], giving rise to a slightly more distorted TBP for **5**. The other metrics are all within experimental error for the two structures. While steric effects of the carbon substituents in **4** and **6** might be expected to enhance their acidity relative to **5**, it is puzzling that the trigonal-bipyramidal geometry of **5** is more axially distorted than that of **4** with an accompanying longer $P-N_{ax}$ bond. Van der Waals contacts between the exocyclic substituents of the planar equatorial nitrogens and the hydrogen or selenium substituents on phosphorus also do not offer a rationale for the trends in the $^1J(PH)$ and $^1J(PSe)$ values, assuming that the solid-state structures of **4** and **5** reflect their solution structures.

The greater stability and hence weaker acidity of cation **5** compared with **4** and **6** may stem from a dominant electronic stabilization effect associated with greater delocalization and hence greater charge balance in the phosphorus orbitals involved in the three-center four-electron $H-P-N_{ax}$ bond, for which a rationale is tentatively proposed. It is reasonable to assume that the contributions of the excitation energy and of the orbital radial extensions to the dominating Ramsey paramagnetic shielding term

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(3) Compound **8** was generated from **5(OTf)** (0.30 g, 0.92 mmol in 2.5 mL of ice-cooled THF) by adding *n*-BuLi (0.95 mL, 0.98 M in hexanes, 0.92 mmol) and, after stirring for 10 min, adding 0.073 g (1.0 mmol) of red selenium. After an additional 10 min of stirring, the mixture was used for spectroscopic measurement. Because **5(Cl)** is insoluble in THF, **5(OTf)** was prepared from a 10-mL CH_2Cl_2 solution of $HOSO_2CF_3$ (3.88 g, 15.5 mmol) which was added to an ice-cooled 35-mL CH_2Cl_2 solution of $(HMeNCH_2CH_2)_3N$[1] (2.26 g, 15.5 mmol) and 2.52 g (15.5 mmol) of $P(NMe_2)_3$. After the reaction mixture was allowed to warm to room temperature and stirred for 15 min, the solvent was removed under vacuum and the residue washed with hexanes, giving spectroscopically pure **5(OTf)**. Adduct **9** was synthesized from 0.31 g (0.70 mmol) of **3** in 3 mL of toluene and 0.054 g (0.69 mmol) of red selenium. The precipitated selenide was dissolved in THF for spectroscopic measurements.

(4) Compound **12** was prepared from a solution of **2** in MeCN made by adding **5(OTf)** (0.303 g, 0.934 mmol in 10 mL of MeCN) to a 15-mL suspension of KO-*t*-Bu (0.105 g, 0.937 mmol in 15 mL of MeCN) followed by bubbling in O_2 for 4 h. Volatilization in vacuo followed by extraction with MeCN (25 mL) gave upon evaporation of the solvent a nearly quantitative yield of **12**.

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(6) Cations **4** and **6** by ^{31}P NMR spectroscopy appear to be completely deprotonated by KO-*t*-Bu in DMSO. In the pK_a calculations it was assumed that **4** and **6** could be present up to 5% concentration without detection by ^{31}P NMR spectroscopy.

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(10) Crystal data: cubic space group $P2_13$ (No. 198), $a = 9.9443$ (2) Å, $V = 983.39$ (2) $Å^3$, $Z = 4$, $d_{calcd} = 1.423$ g/cm^3, μ(Mo Kα) = 5.034 cm^{-1}; 705 unique reflections for $4° < 2\theta < 50°$; 616 observed $[F_o^2 > 3\sigma(F_o^2)]$ at −25 °C. Refinement of 56 parameters converged with agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0204$ and $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o^2)]^{1/2} = 0.0254$. The refinement was carried out on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs. Details of the crystallographic procedures appear in the supplementary material.

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of a large atom such as phosphorus are relatively constant among the analogous cations **4**–**6**. Since the anomalously high ^{31}P NMR shielding value in **5** (−42.9 ppm) compared with **6** (−11.0 ppm) and **4** (−10.1 ppm) obviously cannot be rationalized upon inductive grounds, the only major factors remaining in the model are the orbital charge imbalance terms in the paramagnetic shielding equation which then must be small for **5** compared with **4** and **6**, thus leading to pronounced ^{31}P shielding associated with greater orbital charge balance[11] in **5**. Decreased orbital charge imbalance signaling a greater basicity of **2** can also account for the upfield shift of **2** (89.3 ppm) relative to the shifts of **1** and **3** (120.8[1] and 128.3 ppm, respectively).

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Supplementary Material Available: ^{1}H, ^{13}C, and ^{31}P NMR and high-resolution mass spectral data and tables of X-ray crystallographic data, positional parameters, bond distances and angles, and general displacement parameters for **5(Cl)** (7 pages); listing of observed and calculated structure factors for **5(Cl)** (4 pages). Ordering information is given on any current masthead page.

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Putting "Bottoms on Baskets". The First Main-Group-Element Single-Atom Bridge of a Calixarene

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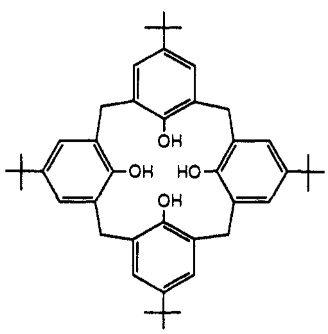
Calixarenes are unique macromolecules that have been shown to be important as complexing agents, biomimics, physiological compounds, and catalysts.[1] We have been interested in putting a "bottom on the basket" of *p-tert*-butylcalix[4]arene (**1**) by connecting the oxygens with a single "hypervalent" main-group atom. A recent report in which a metal atom is used to tie the oxygens together[2] prompts us to communicate our efforts. We herein report the reaction of **1** with tris(dimethylamino)phosphine, which links all four oxygens to the phosphorus in an unexpected coordination mode.



(1)

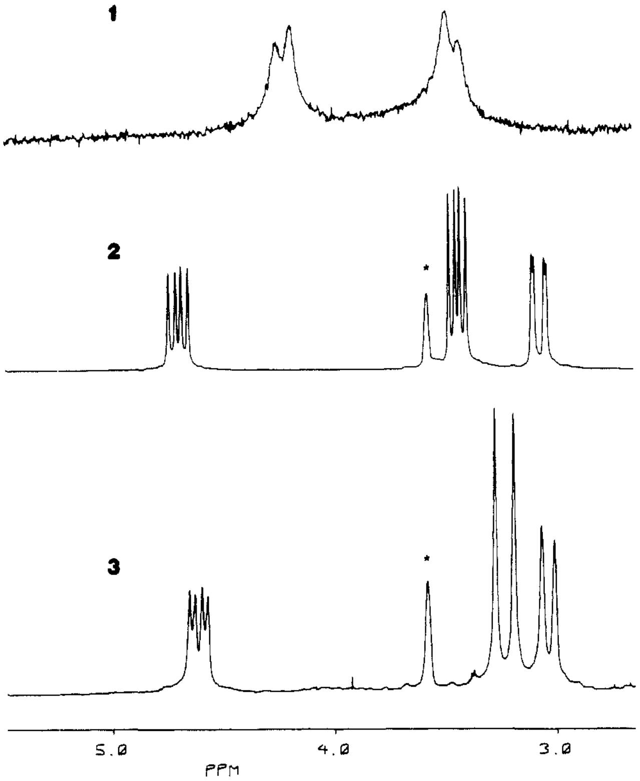
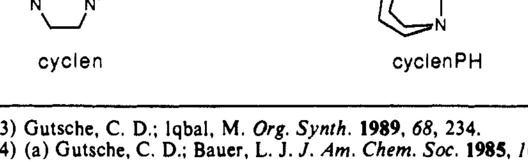


Figure 1. Portion of the ^{1}H NMR spectra of **1** in $CDCl_3$, **2** in THF-d_8, and **3** in THF-d_8. Peaks marked with an asterisk are due to THF-d_8. Coupling constant data for **2**: δ 3.07 ($^5J_{PH}$ = 2.0 Hz), 4.69 ($^5J_{PH}$ = 6.4 Hz, $^2J_{HH}$ = 11.2 Hz), 3.44 ($^3J_{PH}$ = 9.7 Hz, $^3J_{HH}$ = 5.6 Hz). For **3**: δ 3.04 ($^5J_{PH}$ not observed), 4.61 ($^5J_{PH}$ = 4.9 Hz, $^2J_{HH}$ = 11.3 Hz), 3.44 ($^3J_{PH}$ = 16.9 Hz).

Treatment of **1**[3] with $P(NMe_2)_3$ in benzene yields a precipitate (**2**) which, when dissolved in THF-d_8, shows a peak in the ^{31}P NMR spectrum at δ −120 with a large phosphorus–proton coupling constant of 733 Hz. The upfield position of the ^{31}P chemical shift indicates a high coordinate phosphorus, and the large coupling constant suggests a direct P–H bond. The OH resonance at δ 10.33 in the ^{1}H NMR spectrum of **1** is absent in **2**. The *tert*-butyl and aromatic protons appear as singlets at δ 1.20 and 7.01, respectively, while the P–H resonance is centered at δ 4.45. The methylene resonances at δ 3.07 and 4.69 are doublets of doublets and are shown in Figure 1 (the second doublet at δ 3.07 is barely discernible). One doublet of each resonance is due to phosphorus coupling (confirmed by ^{1}H{^{31}P} NMR spectroscopy) while the other is due to geminal proton coupling. These peaks can be compared to the starting material in Figure 1 (the broadness of the peaks in **1** and their assignments have been discussed elsewhere).[1,4] Doublets for these methylene resonances (in systems with no phosphorus coupling) have been taken to indicate the cone conformation for calix[4]arenes.[1] If these were the only peaks present, it would suggest that the reaction proceeded analogously to that for the synthesis of cyclenphosphorane (cyclenPH),[5] where



(1)

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