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Axial Preference of a Phenyl Group in a Trigonal Bipyramidal Tetraoxyphosphorane. A Unique Five-Coordinated Geometry[1]

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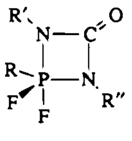
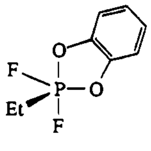
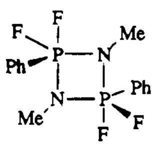
Normally axial positions in trigonal bipyramidal geometries of main group elements are occupied by the most electronegative elements that are present.[2] The most prevalent exception arises when four- or five-membered rings comprise part of the ligand framework. For example, this is found for the cyclic phosphoranes **1**−**3**.[3−8]



1[3-5]



2[6]

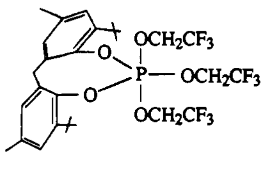


3[7]

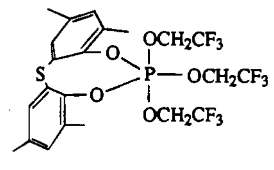
Here, ring strain relief prevails as the dominant factor when the ring occupies axial−equatorial sites of a trigonal bipyramid rather than diequatorial sites. As a consequence, the most electronegative element is displaced to an equatorial position.

In our work with larger cyclic systems, we have found that eight-membered rings can assume diequatorial positions, *e.g.*, **4**−**6**,[9−11] as well as axial−equatorial positions of a trigonal bipyramid, *e.g.*, **7**.[10] However, in phosphoranes **4**−**6**, the axial sites are occupied by the most electronegative ligand, the trifluoroethoxy group. For the less substituted eight-membered ring in **7**, although the ring takes preference in occupying the axial site, the electronegativity of the trifluoroethoxy group relative to the ring O−aromatic component is not expected to be too different.

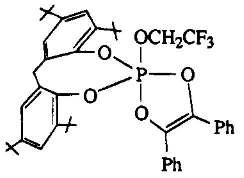
We now report the synthesis[12] and structure[13] of a unique geometry in a five-coordinated tetraoxyphosphorane (**8**) having the same eight-membered-ring system as in the bicyclic pentaoxyphosphorane **6**.[11] This provides the first example of a phenyl group occupying an axial position of a TBP in preference to a more electronegative group. The electronegativity of the phenyl group on the Pauling scale is 2.6,[14] considerably less than that of oxygen, 3.4.[15] The bicyclic phosphorane **8** retains its pentacoordinated state in solution as evidenced by a comparison of its ^{31}P NMR chemical shift of −40.77 ppm[16] obtained in $CDCl_3$ solution with its solid state value of −40.20 ppm. An earlier example of a phenyl group occupying an axial position of a TBP is provided by an X-ray structure of PPh_5.[17]



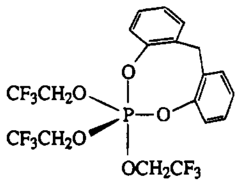
4[9,10]



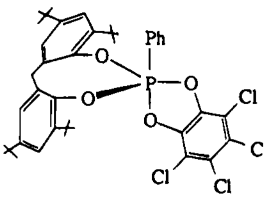
5[10]



6[11]



7[10]



8

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(12) Synthesis was achieved by oxidative addition of a quinone to a tricoordinated phosphite. A mixture of [2,2′-methylenebis((4,6-di-*tert*-butylphenyl)oxy)]phenylphosphine, $[CH_2(t\text{-}Bu)_4C_{12}H_4O_2]PPh$ (0.500 g, 0.942 mmol), and tetrachloro-1,2-benzoquinone (0.232 g, 0.942 mmol) was prepared in toluene (15 mL). The mixture was heated gradually until the oil bath reached a temperature of 150 °C. It was stirred at this temperature for 75 min. The color of the solution changed from red to almost colorless. Solvent was removed completely under vacuum, and the resulting solid was extracted with a mixture of CH_2Cl_2 and *n*-hexane (100 mL/50 mL). Needlelike crystals of **8** were formed upon passing a slow stream of dry nitrogen over the solution; mp 248 °C dec (yield 0.72 g, 99%). ^1H NMR ($CDCl_3$, ppm): 1.09 (s, 18 H, $C(CH_3)_3$), 1.29 (s, 18 H, $C(CH_3)_3$), 3.65 (d, $^2J_{HH} = 14.23$ Hz, 1 H, CH_2), 4.50 (d, $^2J_{HH} = 14.23$ Hz, 1 H, CH_2), 7.08−8.20 (m, 9 H, H(Ar)). ^{31}P NMR ($CDCl_3$, ppm): −40.77 (s). ^{31}P NMR (solid state, ppm): −40.20. Anal. Calcd for $C_{41}H_{47}O_4Cl_4P$: C, 63.3; H, 6.1. Found: C, 63.3; H, 6.2. [2,2′−Methylenebis((4,6-di--*tert*-butylphenyl)oxy)]phenylphosphine was prepared as described previously.[20]

(13) X-ray study: $C_{41}H_{47}O_4Cl_4P$, fw = 776.56, orthorhombic space group *Fdd*2 (No. 43), $a = 44.787(5)$ Å, $b = 34.648(8)$ Å, $c = 10.3709(9)$ Å, $V = 16093(4)$ Å^3, $Z = 16$, $D_{calc} = 1.282$ g/cm^3, $\mu_{Mo\,K\alpha} = 3.73$ cm^{-1}. A total of 2460 independent reflections were measured (Enraf-Nonius CAD4 diffractometer, 23 ± 2 °C, graphite-monochromated Mo radiation, $\lambda(K(\alpha) = 0.710\,73$ Å, $2\theta_{max} = 43°$). Anisotropic refinement of non-hydrogen atoms, with hydrogen atoms riding in ideal positions with fixed isotropic thermal parameters, gave $R(F) = 0.0395$ and $R_w\ (F^2) = 0.0773$ for the 1578 reflections with $I > 2\sigma_I$.

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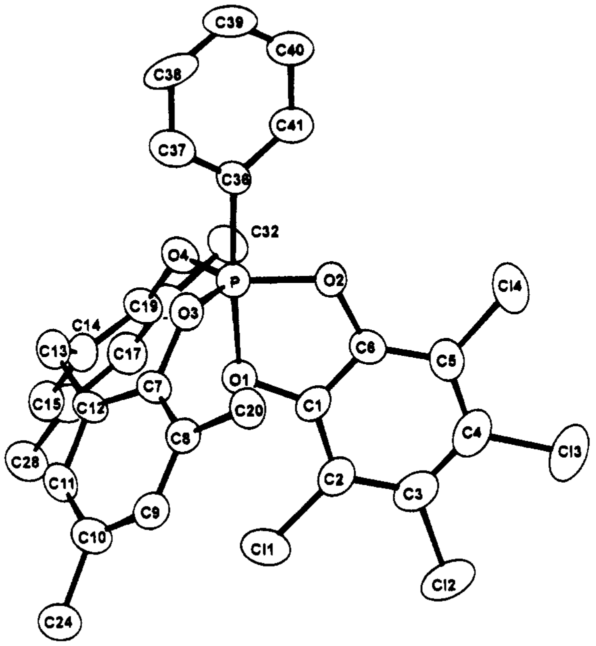
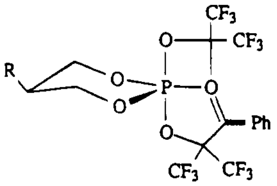


Figure 1. ORTEP plot of **8**. The pendant carbon atoms of the *t*-Bu groups and all hydrogen atoms are omitted for clarity. Bond lengths (Å): P–C36 = 1.838(8), P–O1 = 1.760(6), P–O2 = 1.662(5), P–O3 = 1.602(6), P–O4 = 1.610(6). Bond angles (deg): O1–P–C36 = 176.1(3), O3–P–O4 = 116.1(3), O3–P–O2 = 120.1(3), O4–P–O2 = 123.8(3), O3–P–C36 = 92.3(3), O4–P–C36 = 91.6(3), O2–P–C36 = 89.3(3), O3–P–O1 = 90.5(3), O4–P–O1 = 89.6(3), O2–P–O1 = 86.9(3), P–O3–C7 = 126.8(5), P–O4–C19 = 127.8(5).

Here the P–C_{ax} bonds have lengths of 1.989(7) and 1.986(6) Å while the P–C_{eq} bond lengths are shorter, as expected, 1.830(7), 1.865(6), and 1.855(6) Å. In the present phosphorane structure, the P–C axial bond length in **8** is 1.838(8) Å, considerably shorter than the axial P–C lengths in PPh_5 due to the presence of the more electronegative oxygen ligands.

As demonstrated earlier from X-ray studies,[9–11] a diequatorial orientation in a TBP geometry for a ring of a cyclic pentaoxyphosphorane has been found only when an eight-membered ring is employed.[18] With the use of seven-[19–22] and six-membered[19,23–25] rings like that observed earlier for five-membered rings, the site occupancy in a TBP is invariably axial–equatorial as shown by X-ray studies. In the case of the tetraoxyphosphoranes **9**[26] and **10**,[27] however, Bentrude and co-workers found a diequatorial orientation for the six-membered ring in a TBP with the use of an additional constrained cyclic system.



9 [26] R = H

10 [27] R = *t*-Bu

We have commented[20,22] on the greater flexibility of the eight-membered ring present in derivatives **4–7** compared to six- and seven-membered rings in oxyphosphoranes. The present work supports this assertion in that there exists only a small energy difference for this type of ring[11] in its occupancy of the two sets of positions of a TBP geometry and thus allows the phenyl group access to its normally unfavored location in an axial site. We speculate that the reason this has occurred in the present instance for **8** is associated with the presence of the *tert*–butyl substituents on the eight-membered ring. A steric effect is suspected involving the *tert*–butyl groups *ortho* to the ring oxygen atoms which would be greater if the ring occupied axial–equatorial sites. This feature appears probable from an examination of the structures of **4–7**[9–11] where **7**,[10] containing an unsubstituted cyclic system, is the only one with an axial–equatorial ring orientation.

The eight-membered ring conformation in **8**, like that in **4–6**, is in a symmetrical chair arrangement. This contrasts with the ring in **7**,[10] which is described as a twisted boat or tub with the phosphorus atom and the opposite methylene group *syn* to each other. Further, the bicyclic derivative **8**, like **6**,[11] is unique in having both kinds of the TBP positions occupied by the cyclic components.

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Supporting Information Available: An ORTEP plot of **8** (Figure S1), an ORTEP plot showing the conformation of the eight-membered ring for **8** (Figure S2), crystal data and structure refinement for compound **8** (Table 1), and atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom parameters for **8** (Tables 2–5) (9 pages). Ordering information is given on any current masthead page.

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(18) From NMR studies, Denney and co-workers concluded that, for a pentaoxyphosphorane composition similar to **4**, the eight-membered ring was located in diequatorial sites. The same conclusion was made by these authors for a similar tris(trifluoroethoxy)phosphorane having a seven-membered ring: Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus, Sulfur Relat. Elem.* **1985**, *22*, 99. However, we were not able to verify this from X-ray studies of related phosphoranes with seven-membered rings.[19–22]

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