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Characterization of Stereoisomers of Spirophosphoranes Bearing an Eight-Membered Ring: Implications on Apicophilicity in Trigonal Bipyramidal Phosphorus

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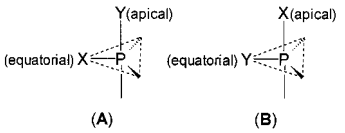
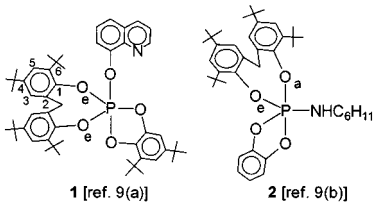
A large number of nucleophilic substitution reactions at tetrahedral phosphorus are assumed to take place through a trigonal bipyramidal (TBP) transition state.[1,2] To rationalize the stereochemistry of the products obtained in these reactions, it is necessary to be able to assess the relative stabilities of various TBPs that can be formed. The energy difference between two isomeric TBPs can be ascertained in terms of the relative preferences for the apical position (apicophilicity) of the attached substituents (cf. **A** and **B**). The apicophilicity of a group is

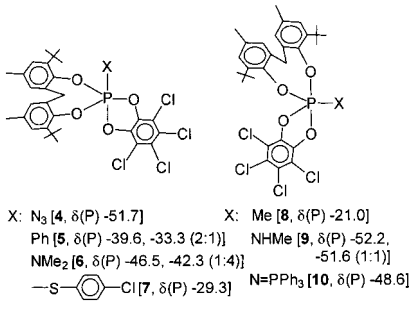


assumed to depend on electronegativity, π-interactions (with phosphorus), and steric factors,[3,4] high apicophilicity being favored by high electronegativity and small size. Most information on relative apicophilicities has been obtained by NMR studies, and on the basis of these Trippett and Corbridge have independently given a relative scale for several substituents.[3, 4]

In cyclic phosphoranes with phosphorus as a part of a 4−7-membered ring, the rings tend to prefer the *a-e* positions in the solid state irrespective of the substituents.[5,6] An interesting case is the isolation of two stereoisomers for the spirophosphorane (o-OC(CF$_3$)$_2$C$_6$H$_4$)$_2$P(n-Bu) by Akiba et al.[7] These isomers differ in the relative orientations of the P−C and P−O bonds of the five-membered rings, although the rings still span the *a-e* sites. The same group has also reported the characterization of configurationally stable enantiomeric and diastereomeric spirophosphoranes containing similar ligands, with the five-membered ring being *a-e* in a TBP environment.[8] A system in which the *a-e* and *e-e* dispositions are equally feasible, depending on the fifth substituent, is the sterically hindered eight-membered ring present in **1** and **2**.[9−11] Hence, we felt that the relative apicophilicities of various groups can be conveniently ascertained using the eight-membered ring. Herein, we demonstrate this utility by determining the relative apicophilicities of several substituents by means of solid-state structures.



The disposition of the substituents in all the seven spirocyclic phosphoranes **4**−**10**[12] is unambiguously proved by X-ray crystallography.[13,14] The essential features are summarized in Figure 1,



which shows the surrounding rings at phosphorus for the P-NMe$_2$ and the P-NHMe compounds **6**·CH$_3$CN and **9**·C$_6$H$_5$CH$_3$ respectively. Compounds **4**, **5**·C$_6$H$_5$CH$_3$, and **7**·$^1/_2$ C$_6$H$_5$CH$_3$ have the ring location and conformation analogous to those in **6**·CH$_3$CN, while compounds **8**·C$_6$H$_5$CH$_3$ and **10** have the ring location and conformation analogous to those in **9**·C$_6$H$_5$CH$_3$. The bond

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(12) **4**: A mixture of CH$_2${4-Me-6-*t*-Bu-C$_6$H$_2$O}$_2$P(N$_3$) (**3**) [mp 138 °C (d), δ(P) 136.7] (0.416 g, 1 mmol) and *o*-chloranil (0.249 g, 1 mmol) was evacuated for 0.5 h. Then dry toluene (5 mL) was added. The red solution became colorless in ca. 10 min. It was concentrated to 1 mL, and heptane (1 mL) was added. Crystals of **4** (0.485 g, 73%) were obtained after 24 h. Mp: 202 °C. ^{1}H NMR (CDCl$_3$): δ 1.22 (s, 18H, *t*-Bu-*H*), 2.33, 2.34 (2 s, 6H, CH_3), 3.74 (br, 1H, CH_AH$_X$), 4.27 (br, 1H, CH$_A$$H_X$), 7.00 (s, 2 H, Ar-*H*), 7.14 (s, 2H, Ar-*H*) ppm. ^{31}P NMR (CDCl$_3$): δ −51.7 ppm. Anal. Calcd for C$_{29}$H$_{30}$Cl$_4$N$_3$O$_4$P: C, 52.99; H, 4.60; N, 6.39. Found: C, 53.12; H, 4.71; N, 6.25. Compounds **5**−**9** [δ(P, CDCl$_3$) given below the structural diagram] were prepared similarly. **10**: To a solution of **4** (0.322 g, 0.49 mmol) in toluene (3 mL) was added Ph$_3$P (0.129 g, 0.49 mmol) at room temperature. The flask was swirled continuously for 0.5 h, during which time Ph$_3$P gradually dissolved with the evolution of nitrogen. The solution was concentrated to 0.2 mL, and heptane (0.5 mL) was added. Crystals of **10** (0.310 g, 71%) were obtained after 2 d. Mp: 190−191 °C (d). ^{1}H NMR (CDCl$_3$): δ 1.28 (br s, 18H, *t*-Bu-*H*), 2.32 (br, 6H, CH_3), 3.28 (d, J = 14.5 Hz, 1H, CH_AH$_X$), 4.61 (d, J = 14.5 Hz, 1H, CH$_A$$H_X$), 6.85−7.48 (m, 19H, Ar-*H*) ppm. ^{31}P NMR (CDCl$_3$): δ −48.6 [s (^2J < 3 Hz), *P*O$_4$N], 13.4 (s, *P*Ph$_3$) ppm. Anal. Calcd for C$_{47}$H$_{45}$Cl$_4$NO$_4$P$_2$: C, 63.31; H, 5.09; N, 1.57. Found: C, 63.25; H, 5.12; N, 1.42.
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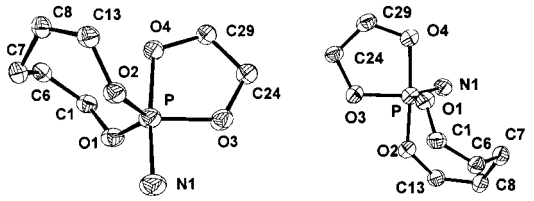

Figure 1. Molecular structures of (a) **6**·CH_3CN and (b) **9**·$C_6H_5CH_3$ showing only selected atoms around phosphorus. Selected bond distances and angles: (a) **6**·CH_3CN, P−O(1) 1.601(3), P−O(2) 1.598(3), P−O(3) 1.657(3), P−O(4) 1.764(3), and P−N(1) 1.682(3) Å, and O(4)−P−N(1) 174.92(16)°; (b) **9**·$C_6H_5CH_3$, P−O(1) 1.600(3), P−O(2) 1.641(3), P−O(3) 1.646(3), P−O(4) 1.756(4), and P−N(1) 1.611(5) Å, and O(4)−P−O(2) 175.65(17)°.

parameters clearly show the trigonal bipyramidal geometry around phosphorus. Important points to be noted here are the following.

(i) A secondary amino group (−NMe_2) is more apicophilic than a primary amino group (−NHMe). This is rather surprising because the −NMe_2 group is certainly bulkier than the −NHMe group. Even from the point of view of (group) electronegativity, we expect the −NMe_2 group to have lower electronegativity [Mulliken electronegativities: −NHMe, 8.5; −N(Me)Et, 8.4[15]] and hence lower apicophilicity than −NHMe. However, what is observed is the opposite of this.

(ii) The phenyl group is definitely more apicophilic than the methyl group. Although this is consistent with Trippett's observation,[3] it contradicts that of Corbridge.[4]

(iii) A structural proof for the high apicophilicity of an *S*-aryl group (compound **7**) is provided convincingly.

(iv) Although the dicoordinated nitrogen in **10** should be more electronegative than the tricoordinated nitrogen in **6**, it is less apicophilic clearly because of steric factors. However, the dicoordinated nitrogen connected to P in the azidophosphorane **4** is apical, because of lower steric constraints and higher group electronegativity.[15] The role of the eight-membered ring in placing the azido group apical is also important; it is worth noting that in the previously reported phosphorane [MeNC(O)NMe]$_2$P(N_3) the azido group is placed equatorially.[5a]

The dimethylamino compound (**6**) shows three peaks in the ^{31}P NMR spectrum (toluene-d_8) at 233K (δ −42.2, −43.1, −47.1). As the temperature is raised, the two downfield signals merge, whereas the upfield signal broadens and starts diminishing in intensity. At higher temperatures only one signal (δ −42.8), nearly at the center of the downfield signals, is observed. A similar behavior is noticed in the ^{1}H NMR also. The ^{31}P NMR spectrum (toluene-d_8) of the methyl compound (**8**) shows two major peaks at δ −15.8 and −21.0 and a small peak at δ −27.2 at 233 K; the peaks at δ −15.8 and −27.2 broaden and disappear at higher temperatures. These results suggest the preference for one of the stereoisomers in each case at higher temperatures. Holmes and co-workers have observed two ^{31}P NMR signals for some phosphoranes containing eight-membered rings; however, in their case the isomer ratio remained unchanged throughout the temperature range studied.[16]

In conclusion, we have devised a way to ascertain unequivocally the relative apicophilicities of several functional groups. Distinction between the more apicophilic substituents, such as −OR, −SR, etc., may perhaps be made by modifying the eight-membered ring in spirocyclic phosphoranes, for instance, by changing the *t*-Bu group at the 6-position to *i*-Pr.[17]

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Supporting Information Available: X-ray structure determination and crystal data for **4**−**10** including the full ORTEP diagrams; variable-temperature NMR spectra for **6**, **8**, and **9**; and characterization data for **5**−**9** (PDF). X-ray crystallographic data, in CIF format, are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For the unsubstituted eight-membered ring, an *a-e* disposition in a TBP environment is strongly favored; using the same eight-membered ring as in **1** or **2**, earlier investigations could not distinguish between the apicophilicities of −Ph and −Et groups.[10]