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Does a Sterically Bulky Group Occupy the Equatorial Site in Trigonal Bipyramidal Phosphorus?

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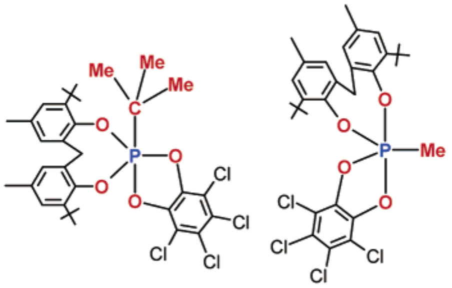
ABSTRACT



The sterically bulky *tert*-butyl group occupies an apical position in trigonal bipyramidal phosphorus in the compound {CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$}P(*t*-Bu)(1,2-$O_2C_6Cl_4$) in contrast to the occupation of an equatorial position by the small methyl group in {CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$}-P(Me)(1,2-$O_2C_6Cl_4$); this observation contradicts the familiar "apicophilicity rules" for trigonal bipyramidal phosphorus. Low-temperature solution ^{31}P NMR spectra of {CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$}P(R)(1,2-$O_2C_6Cl_4$) (R = Me, Et, and *n*-Bu) show the presence of more than two isomers.

In numerous nucleophilic substitution reactions at a tetrahedral P(V) center, an unstable intermediate (or a transition state species) involving pentacoordinate phosphorus is often assumed.[1,2] Stereochemistry of the products formed would depend on the disposition of the substituents in the transition state species just before its breakup, and hence several investigations have been directed at finding the relative tendency of a group to occupy the apical site (apicophilicity) in the commonly assumed trigonal bipyramidal geometry (**I**).[1b,2] Even in neutral molecules the question of apical/equatorial preferences is a topic of interest.[1a] It is said that large and bulky groups will tend to occupy equatorial positions because the latter involve the least interaction with the remaining substituents on the trigonal bipyramid.[1b] On this basis, one would assume that a *tert*-butyl group would prefer an equatorial site relative to a methyl group. In this Letter, we provide an example for the reverse phenomenon, thus violating the commonly held tenet.[3] We believe that this result has ramifications for our basic understanding of the pentacoordinated state itself.[4] We also show that the solid-

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(1) (a) Holmes, R. R. *Pentacoordinated Phosphorus, Vol. II, Reaction Mechanisms*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980. (b) Corbridge, D. E. C. *Phosphorus−An Outline of Its Chemistry, Biochemistry and Technology*; Elsevier: Amsterdam, 1990; pp 997−999. (c) Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869. (d) Uchimaru, T.; Uebayashi, M.; Hirose, T.; Tsuzuki, S.; Yliniemela, A.; Tanabe, K.; Taira, K. *J. Org. Chem.* **1996**, *61*, 1599. (e) Yang, Y.-C. *Acc. Chem. Res.* **1999**, *32*, 109. (f) Vayron, P.; Renard, P.-Yves.; Valleix, A.; Mioskowski, C. *Chem. Eur. J.* **2000**, *6*, 1050.

(2) (a) Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89. (b) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, V. D., Eds.; Sutherland, I. O., Vol. Ed.; Pergamon: Exeter, U.K., 1979; Vol. 2, pp 1233−1256. (c) Nakamoto, M.; Kojima, S.; Matsukawa, S.; Yamamoto, Y.; Akiba, K.-y. *J. Organomet. Chem.* **2002**, *643−644*, 441.

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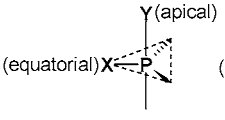
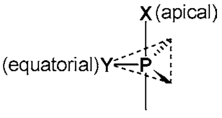
and solution-state structures of the methyl compound differ; theoretical calculations, however, suggest the apical site to be favored in the case of the *tert*-butyl compound.



I(a)



I(b)

Reaction of the P(III) precursors $\{CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2\}PR$ [R = Et, *n*-Bu, *t*-Bu] with tetrachloro-1,2-benzoquinone readily affords the pentacoordinate derivatives $\{CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2\}P(R)(1,2\text{-}O_2C_6Cl_4)$ [R = Et (**1**), *n*-Bu (**2**), *t*-Bu (**3**)];[5,6] the methyl analogue $\{CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2\}P(Me)(1,2\text{-}O_2C_6Cl_4)$ (**4**) was prepared as before.[7] Here the five-membered ring is always apical-equatorial; the eight-membered ring is either diequatorial or apical-equatorial, thus allowing us to find out the relative apicophilicities of the different (fifth) substituents. An X-ray structure of **3** (Figure 1) clearly shows that the bulky *t*-Bu group is at the apical position of a trigonal bipyramid;[8,9] this can be contrasted with the equatorial disposition of the methyl group in **4**.[7] The P−C bond distance in **3** [1.879(2) Å; carbon apical] is significantly longer than that in **4** [1.792(3) Å, carbon equatorial[7]], in line with the general trend. However, as mentioned above, the *tert*-butyl group was expected to go equatorial and the methyl group apical,[1(b)] and hence we made an attempt to study the ^{31}P NMR of these compounds in solid as well as in solution state. Compound **3** showed a single peak in both the solution [δ(P) −22.6; temperature range 233−300 K] and solid state [δ(P) −23.5]. The δ[P(solid, 298 K)] value for the *n*-butyl compound **2** is close to the upfield peak seen at low temperatures in solution [Figure 2, Table 1]. The ethyl compound **1** (ethyl group is apical in the solid state as shown by the X-ray structure; see Supporting Information for

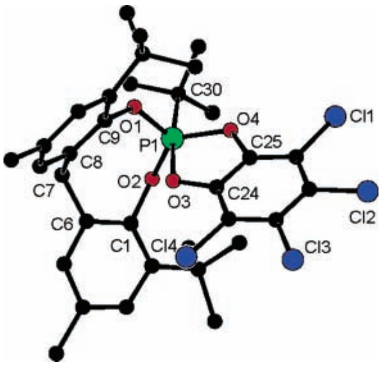


Figure 1. Molecular structure of **3**. Selected bond parameters (Å, deg): P(1)−O(1) 1.601 (2), P(1)−O(2) 1.609 (2), P(1)−O(3) 1.769 (2), P(1)−O(4) 1.674 (2); P(1)−C(30) 1.879(2), O(1)−P(1)−O(2) 116.90(8), O(1)−P(1)−O(3) 90.62(7), O(1)−P(1)−O(4) 118.92(8), O(1)−P(1)−C(30) 93.53(9), O(2)−P(1)−O(3) 88.88(7), O(2)−P(1)−O(4) 124.03(8), O(2)−P(1)−C30 92.82(9), O(3)−P(1)−O(4) 86.76(7), O(3)−P(1)−C(30) 174.22(9), O(4)−P(1)−C(30) 87.72(9). The eight-membered phosphocin ring has a boat-chair conformation.

Table 1. Solution (Toluene-d_8) and Solid-State ^{31}P NMR Data for the Phosphoranes $\{CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2\}P(R)(1,2\text{-}O_2C_6Cl_4)$

R (compd)	solution	temp (K)	solid (298 K)
Me (**4**)[a]	−15.8, −21.0, −27.2 (minor)	243 (and 233)	
	−20.7	298	−13.7
Et (**1**)	−14.2, −18.7, −25.3	246	
	−18.5 (minor), −25.3 (br)	298	−10.6 (major), −25.0 (minor)
n-Bu (**2**)	−15.3, −20.1, −25.9 (major)	242	
	−19.6, −22.6 (br)[b]	298	−26.0
t-Bu (**3**)	−22.6	233−298	−23.5

[a] Me group is equatorial in the X-ray structure.[7] [b] At 312 K, this is the only peak observed.

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(3) In the recent literature, several other examples of reversed apicophilicity wherein less electronegative substituents (rather than those with more electronegativty) occupy the apical sites are also reported. See ref 10 as well as the following: (a) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525. (b) Kajiyama, K.; Yoshimune, M.; Nakaoto, M.; Matsukawa, S.; Kojima, S.; Akiba, K.-y. *Org. Lett.* **2001**, *3*, 1873. (c) Matsukawa, S.; Kajiyama, K.; Kojima, S.; Furuta, S.-y.; Yamamoto, Y.; Akiba, K.-y. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4718. (d) Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **2002**, *124*, 7674. (e) Kommana, P.; Kumaraswamy, S.; Vittal, J. J.; Kumara Swamy, K. C. *Inorg. Chem.* **2002**, *41*, 2356. (f) Satish Kumar, N.; Kommana, P.; Vittal, J. J.; Kumara Swamy, K. C. *J. Org. Chem.* **2002**, *67*, 6653.

(4) Selected additional references (see also ref 3) on pentacoordinate phosphorus from the recent literature: (a) Skordalakes, E.; Dodson, G. G.; St. Clair Green, D.; Goodwin, A. A.; Scully, M. F.; Hudson, H. R.; Kakkar, V. V.; Deadman, J. J. *J. Mol. Biol.* **2001**, *311*, 549. (b) Sonnenburg, R.; Neda, I.; Thönnessen, H.; Jones, P. G. Schmutzler, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 412. (c) Lahiri, S. D.; Zhang, G.; D-Mariano D.; Allen, K. N. *Science* **2003**, *299*, 2067.

(5) Compound **3**$\cdot 1/2C_6H_5CH_3$: a mixture of $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2P$-(*t*-Bu) [δ(P) 189.8; prepared by treating the corresponding chloro precursor with *t*-BuMgCl] (0.42 g, 0.97 mmol) and *o*-chloranil (0.24 g, 0.97 mmol) in toluene (5 mL) was heated at 70 °C for 5 min. The solution, on standing overnight, gave crystals of **3**$\cdot 1/2C_6H_5CH_3$. Yield: 0.62 g (83%). Mp: 236−238 °C. ^1H NMR ($C_6D_5CD_3$): δ 1.30 (s, 18 H, Ar-C(C*H*$_3$)$_3$), 1.95, 2.05 (d, $^3J(PH)$ = 18.0 Hz, 9 H, P(C(C*H*$_3$)$_3$), 2.36 (s, 6 H, Ar-C*H*$_3$), 3.56 (d, $^2J(HH)$ = 13.6 Hz, 1 H, CH_AH_X), 4.84 (dd, $^5J(PH)$ = 3.0 Hz, $^2J(HH)$ = 13.6 Hz, 1 H, CH_AH_X), 7.12−7.33 (m, 4 H, Ar-*H*). The spectrum in $CDCl_3$ was nearly identical. ^{13}C NMR ($CDCl_3$): 21.1, 30.2, 30.3 (d, $^2J(PC)$ = 4.5 Hz, PC(*C*H$_3$)$_3$), 33.2, 34.6, 44.6 (d, $^1J(PC)$ = 192.0 Hz; this assignment is based on the DEPT spectrum as well as observation of a single peak in ^{31}P NMR), 125.4, 126.5, 128.3, 129.0, 133.7, 133.8, 133.9, 138.7, 138.8, 142.5, 149.1, 149.6. ^{31}P NMR ($CDCl_3$): −22.6. Anal. Calcd (after drying the sample at 0.2 mmHg for 2 h) for $C_{33}H_{39}Cl_4O_4P$: C, 58.94; H, 5.84. Found: C, 59.08; H, 5.91. The ^1H and ^{31}P NMR spectra did not change in the temperature range 233−338 K except for slight broadening at low temperatures. Compounds **1** and **2** were also prepared similarly. See Supporting Information for details. Single-crystal X-ray data were collected on a Bruker AXS SMART diffractometer (compound **3**) or an Enraf-Nonius MACH3 (compound **1**) using Mo Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined by full-matrix least-squares method with the SHELXL-97 program.[8] The solvent (CH_2Cl_2) was disordered in **1**. A plot is available in the Supporting Information. Crystal data for **1**: $C_{32}H_{37}Cl_6O_4P$, MW = 729.29, monoclinic, space group $P2_1/n$; $a = 10.842(5)$, $b = 30.340(4)$, $c = 10.832(6)$, $\beta = 92.77(2)$, $V = 3559(3)$ Å^3, $Z = 4$, $\mu = 0.56$ mm^{-1}. Data/ restraints/ parameters: 6243/0/406. R indices ($I > 2\sigma(I)$): R1 = 0.0539, wR2 = 0.1880. Crystal data for **3**: $C_{36.5}H_{43}Cl_4O_4P$, MW = 718.48, triclinic, space group $P\bar{1}$; $a = 9.5164(7)$, $b = 10.9825(9)$, $c = 17.8763(14)$, $\alpha = 84.208(2)$, $\beta = 81.966(2)$, $\gamma = 82.869(2)$, $V = 1829.0(2)$ Å^3, $Z = 2$, $\mu = 0.404$ mm^{-1}. Data/ restraints/ parameters: 6446/3/406. R indices ($I > 2\sigma(I)$): R1 = 0.0436, wR2 = 0.1091.

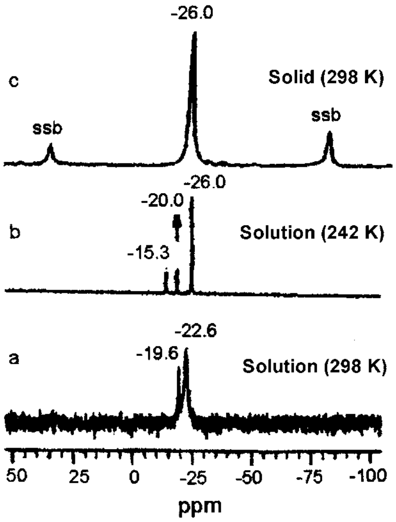
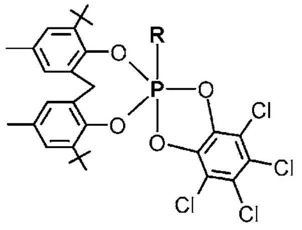
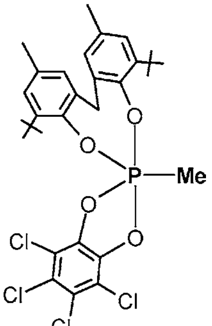


Figure 2. ^{31}P NMR spectra of **2** (a) at 298 K in solution state ($C_6D_5CD_3$), (b) at 242 K in solution state ($C_6D_5CD_3$), and (c) at 298 K in the solid state.

details[10]) showed two very broad signals [δ(P, solid, 298 K) −10.6, −25.0] compared to **2**−**4**. For the methyl compound **4**, a fairly sharp solid-state signal, close to the downfield peak observed at low temperatures in solution, is observed. These data suggest that the upfield ^{31}P NMR signals for these compounds in solution at low temperatures are most likely due to the isomer with apical C(alkyl) with compound **1** showing a borderline behavior. For **4** also, at temperatures above 298 K, the solution-state NMR suggests an apical disposition of the methyl group.


R = Et (**1**), *n*-Bu (**2**), *t*-Bu (**3**)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It is interesting to note that there are three distinct ^{31}P NMR signals in solution at low temperatures for **1**, **2**, and **4** in the pentacoordinate region (see Supporting Information for more details). To our knowledge, such a phenomenon in systems containing pentacoordinate phosphorus is rare.[11] Since it is clear that the eight-membered phosphocin ring can (i) occupy either diequatorial or apical-equatorial sites in trigonal bipyramid readily and (ii) have two favored conformations (boat-chair and tub),[3e,12] there are four possible isomers; three of these are observed in the ^{31}P NMR spectrum (solution; Figure 3). Although ^{1}H NMR spectra also showed multiple resonances, because of the overlapping and broad signals with poor resolution in the temperature region studied, a detailed analysis was not possible.

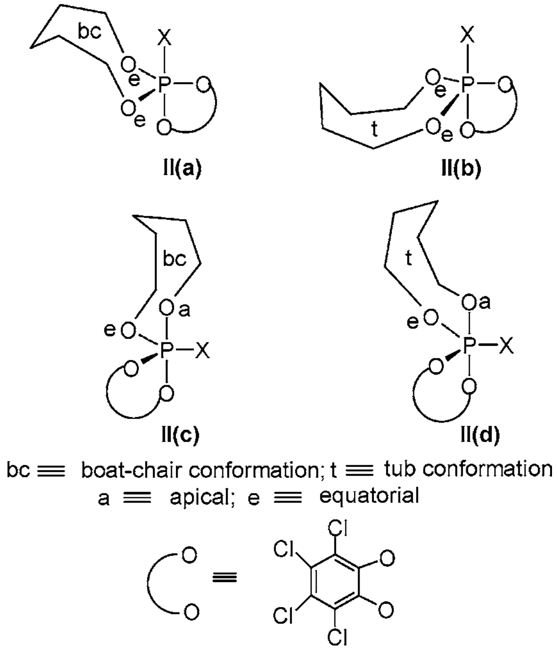

Figure 3. Four possible isomers for the compounds **1**, **2**, and **4**.

Theoretical calculations on four possible combinations **IIa**−**d** for R = Me and *t*-Bu have been carried out at the B3LYP/3-21G* level using the Gaussian 94 program package (the conclusions arrived at were also verified by using the DZP basis set, which is equivalent to Gaussian 6-31G* using the ADF program).[13] With R = *t*-Bu, the experimentally isolated structure is found to be the thermodynamically stable structure as well. However, with R = Me, it is found that the structure with methyl apical and the eight-membered ring diequatorial with a boat-chair structure is (thermodynamically) marginally favored over the observed solid-state structure in which methyl is equatorial. However, the

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(6) In many cases the magnitude of ^{1}J(PC) for apically located carbon is small;[3d] the large value of ^{1}J(PC) in **3** is characteristic of pentacoordinate phosphorus compounds where all the equatorial positions are occupied by electronegative substituents. See: Kobayashi, J.; Goto, Kawashima, T.; Schmidt, M. W.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 3703.

(7) Kumaraswamy, S.; Muthiah, C.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **2000**, *122*, 964.

(8) Shedrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

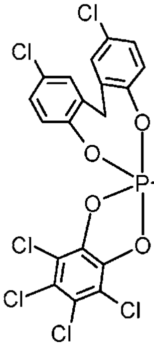
(9) A distortion of ca. 8% and 12% for **1** and **3** from trigonal bipyramidal geometry towards rectangular pyramid based on the dihedral angles is calculated using Holmes' program. See: Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(10) This result is similar to that obtained by Holmes and co-workers. See: Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552.

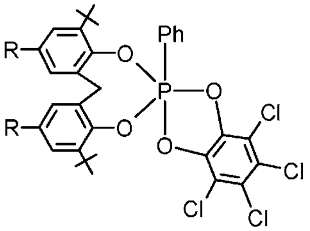
(11) In ref 3d, synthesis of two isomeric pentacoordinate phosphoranes is reported. Multiple signals due to the presence of both penta- and hexacoordinate phosphorus species (but not due to pentacoordinate isomers) are observed. See: Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem.. Soc.* **1997**, *119*, 11434.

(12) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Inorg. Chem.* **1997**, *36*, 2044.

difference in energy between **IIa** and **IId** for the *tert*-butyl compound (42.8 kJ mol^{-1}) is nearly six times that for the methyl compound (7.4 kJ mol^{-1}), although **IIa** is favored in both. This suggests that *for R= t-Bu the apical occupancy is far more preferred than for R = Me*. Steric reasons can be attributed to the instability of the structures **IIc** and **IId** where the alkyl hydrogens and the CH_2 hydrogens are within van der Waals distance. The role of steric factors is also evident by the fact that the phenyl group is equatorial in **III** but apical in **IV**.[3a,7,10]



III



IV [R = Me, *t*-Bu]

In a trigonal bipyramidal molecule, there are three 90° interactions (with the three equatorial groups) for the apical substituents compared to two (with the two apical groups) for the equatorial ones. These 90° interactions are considered to be more important than the 120° interactions among the three equatorial substituents. However, the 90° interactions are maximum only for the atoms (e.g., N, O, C) directly connected to the central atom (e.g., P). In a majority of systems, the apical atoms bear one or more R groups (like those in OR, NR_2, CR_3) that can be oriented away from the equatorial ones, and in such cases a sterically bulky group can occupy an apical site. This is one possible rationale for the result reported here.[14,15]

Acknowledgment. We thank (i) the Department of Science and Technology (DST), New Delhi for financial support, (ii) DST (New Delhi) and NUS (Singapore) for Single Crystal Diffractometer facilities, (iii) SIF, IISc (Bangalore, India) for the Solid State NMR facility, (iv) Prof. R. R. Holmes for the program to calculate the distortion from TBP to RP geometry, and (v) the Center for Modeling, Simulation and Design (UPE program) for computational facilities.

Supporting Information Available: An ORTEP drawing with selected bond parameters for **1**, CIF files for compounds **1** and **3**, solid-state and variable temperature ^{31}P NMR spectra for **1** and **4**, and additional details on theoretical calculations and synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The molecules in the present study are fairly large in terms of theoretical calculations, and for *C*1 symmetry the number of parameters was too large for our system to handle at the 6-31G* level. See Supporting Information for details and references as well as calculated ^{31}P NMR chemical shifts.

(14) If this is so, the apical site occupancy of the ethyl/phenyl carbon instead of an oxygen, reported by Holmes et al.[10] and by us[7] in analogous systems may be rationalized.

(15) One of the referees comments: "Apicophilicity of alkyl groups in this system may be controlled by the eight-membered phosphocin ring which is designed to prefer diequatorial position due to a combination of ring strain and steric hindrance, but by combination with rigid five-membered ring here, the preference for diequatorial and apical-equatorial conformation is seen and this delicate equilibrium is affected by the steric hindrance of alkyls." This point needs to be tested further by replacing the five membered-ring with acyclic substituents. In $\{CH_2(6\text{-}t\text{-}Bu\text{-}4\text{-}Me\text{-}C_6H_2O)_2\}P(OCH_2CF_3)_3$ (cf. ref 10) the eight-membered ring is diequatorial, but compounds with different acyclic substituents in this series are yet to be checked.