Inorg. Chem. **2002**, *41*, 2356–2363

Apical versus Equatorial Disposition of Substituents in Tetraoxyphosphoranes Bearing a 1,3,2-Dioxaphosphocin Ring: Implications on Apicophilicity in Trigonal Bipyramidal Phosphorus

Praveen Kommana,[†] Sudha Kumaraswamy,[†] J. J. Vittal,[‡] and K. C. Kumara Swamy*[,†]

School of Chemistry, University of Hyderabad, Hyderabad-500046, A. P., India, and Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore-117543

Received August 28, 2001

New spirocyclic (amino/amido)tetraoxyphosphoranes $CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2P(NRR')(O_2C_6Cl_4)$ [R = Me, R′ = Ph (**1**), R = R′ = *i*-Pr (**2**); R = R′ = H (**3**); R = H, R′ = Ph (**4**)] and the isothiocyanatotetraoxyphosphorane $CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2P(NCS)(O_2C_6Cl_4)$ (**5**) have been synthesized. X-ray crystallography for these compounds reveals that –N(Me)Ph, –N(*i*-Pr)$_2$, and –NCS groups occupy an *apical* position whereas –NH$_2$ and –NHPh groups occupy an *equatorial* position in a trigonal bipyramidal geometry around phosphorus. These results are in contrast with the common assumption that a sterically bulky and less electronegative substituent [e.g. –N(*i*-Pr)$_2$] should be less apicophilic than a sterically small and more electronegative substituent (e.g. –NH$_2$). The possible rationalization for these results is discussed. Variable-temperature (^{1}H, ^{31}P) NMR spectra of these compounds show some unusual features not reported before for pentacoordinate phosphorus. Probable intramolecular processes involving (i) apical–equatorial ↔ equatorial–apical exchange, (ii) apical–equatorial ↔ equatorial–equatorial exchange, and (iii) boat–chair ↔ tub (for the eight-membered ring) interconversion as well as cessation of the P–N bond rotation have been invoked to explain the spectral features.

Introduction

Pentacoordinate phosphorus has attracted considerable attention both from experimental and theoretical chemists in view of its possible role as an intermediate/transition state species in reactions at a tetrahedral P(V) center.[1,2] A trigonal bipyramidal (TBP), rather than a square (or rectangular) pyramidal geometry, is more commonly observed for pentacoordinate phosphorus compounds.[3] A knowledge of relative preferences of the substituents for the apical position (apicophilicity) in trigonal bipyramidal phosphorus may be useful in ascertaining the stereochemistry of the products in reactions involving such intermediates/transition state species. The apicophilicity of a group is assumed to depend on electronegativity, π-interactions (with phosphorus), and steric factors,[4,5] high apicophilicity being favored by high electronegativity and small size. However, it is most often observed that, in spirocyclic phosphoranes with trigonal bipyramidal phosphorus, ring constraints dominate over electronegativity effects in apical site occupancy, even for highly electronegative substituents. Thus, when phosphorus is part of a 4−7-membered ring (e.g. **I**−**IV**), the rings tend to prefer apical−equatorial sites in the solid state, irrespective of the substituents.[3a,6−7] Interesting cases of reversed apico-

* To whom correspondence should be addressed. E-mail: kckssc@uohyd.ernet.in. Fax: +91-40-3012460/3010120.
† University of Hyderabad.
‡ National University of Singapore.

(1) Selected references: (a) 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. (b) Sheldrick, W. S. *Top. Curr. Chem.* **1978**, *73*, 1. (c) Holmes, R. R. *Pentacoordinated Phosphorus-Reaction Mechanisms*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; Vol. II. (d) Bangerter, F.; Karpf, M.; Meier, L. A.; Rys, P.; Skrabal, P. *J. Am. Chem. Soc.* **1998**, *120*, 10653. (e) Wróblewski, A. E.; Verkade, J. G. *J. Am. Chem. Soc.* **1996**, *118*, 10168. (f) Bojin, M. L.; Barkallah, S.; Evans, Jr., S. A. *J. Am. Chem. Soc.* **1996**, *118*, 1549. (g) Núñez, J.; Núñez, O. *J. Org. Chem.* **1996**, *61*, 8386. (h) Michalski, J.; Skowronska, A.; Bodalski, R. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 8, pp 255−296.

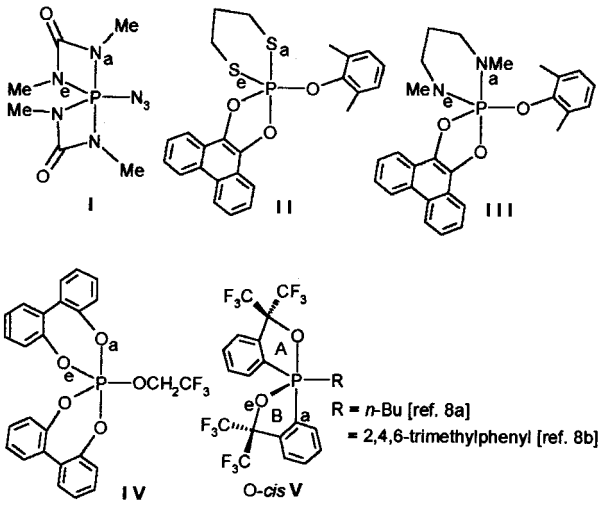
(2) Selected references: (a) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047. (b) Uchimaru, T.; Stec, W. J., Taira, K. *J. Org. Chem*. **1997**, *62*, 5793. (b) Wasada, H.; Hirao, K. *J. Am. Chem. Soc*. **1992**, *114*, 16. (c) Wasada, H.; Tsutsui, Y. *Chem. Lett*. **1995**, 825. (d) Deiters, J. A.; Holmes, R. R. *Organometallics*. **1996**, *15*, 3944.

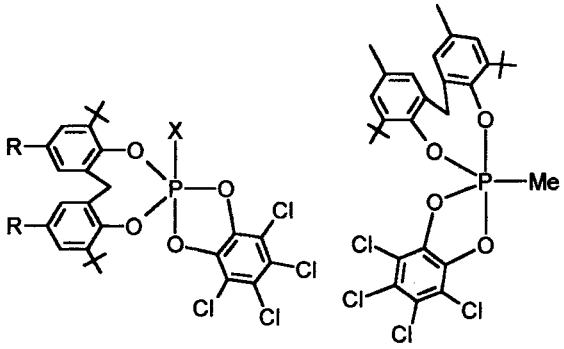
(3) For square pyramidal phosphorus, see: (a) Wunderlich, H. Mootz, D.; Schmutzler, R.; Wieber, M. *Z. Naturforsch*. **1974**, *B29*, 32. (b) Holmes, R. R. *Prog. Inorg. Chem*. **1984**, *32*, 119. (c) Shevchenko, I. V.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber*. **1992**, *125*, 1325.

(4) Trippett, S. *Phosphorus Sulfur* **1976**, *1*, 89.

(5) Corbridge, D. E. C. *Phosphorus*: *An Outline of its Chemistry, Biochemistry and Technology*, 4th ed.; Elsevier: Amsterdam, 1990; Chapter 14, pp 994−1007.

10.1021/ic010935w CCC: $22.00
Published on Web 03/30/2002

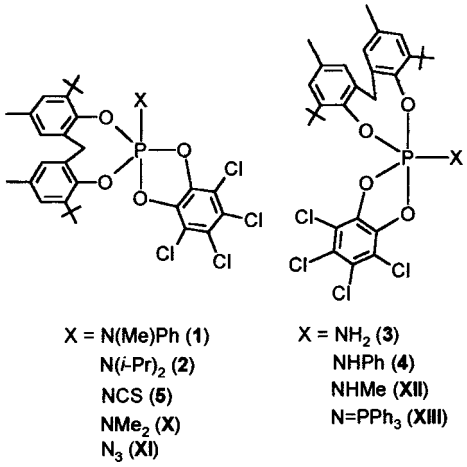




VI [R = *t*-Bu, X = Ph; ref. 10(a)] **IX** [ref. 12]
VII [R = Me, X = Ph; ref. 12]
VIII [R = *t*-Bu, X = Et; ref. 10(c)]

philicity involving a 5-membered ring system have been reported recently.[8,9] The less electronegative carbon of ring B in **V** occupies an apical position, although the rings at phosphorus still span the a−e positions.[8] A system in which the a−e and e−e dispositions for the ring are equally feasible, depending on the fifth substituent, is the sterically hindered 8-membered ring present in **VI**−**IX**.[6h,10−12] In a preliminary communication, we have pointed out that the bulkier −NMe_2 group is more apicophilic than the −NHMe group.[12] This is opposite to the general trend that a sterically more demanding group (e.g. −NMe_2; see **X** in Chart 1) should be less apicophilic than a sterically less demanding group (e.g. −NHMe; compound **XII**). We have studied this aspect in greater detail, and herein report the synthesis and X-ray structures of the new aminophosphoranes **1**−**4** (Chart 1), which *defy the steric rule* for trigonal bipyramidal phosphorus. We also report the first spirocyclic isothiocyanatophosphorane **5** with the isothiocyanate group in the apical position. The structural parameters of **1**−**5** are compared to those of **X**−**XIII**.[12] In addition, a unique exchange behavior of these aminophosphoranes observed in variable-temperature NMR (^{1}H and ^{31}P) is described.

Chart 1



X = N(Me)Ph (**1**)
N(*i*-Pr)$_2$ (**2**)
NCS (**5**)
NMe_2 (**X**)
N_3 (**XI**)

X = NH_2 (**3**)
NHPh (**4**)
NHMe (**XII**)
N=PPh_3 (**XIII**)

Results and Discussion

The new compounds **1**−**5** were synthesized by the oxidative addition of *o*-chloranil to the corresponding phosphite CH_2{6-*t*-Bu-4-Me-C_6H_2O}$_2$PX. The ^{31}P NMR spectra confirm that the pentacoordinate structure is preserved in solution.

Structural Aspects. The molecular structures of **2** and **3**·CH_2Cl_2 are shown in Figures 1 and 2, respectively. The ring conformation and the numbering scheme for **1** and **5**·$^1/_2C_6H_5CH_3$ are similar to those of **2**, while the ring conformation and the numbering scheme for **4**·$CHCl_3$ are similar to those of **3**·CH_2Cl_2.[13] Table 1 lists the important bond parameters at phosphorus for **1**−**5** and **X**−**XIII**.[14] The solid-state structures confirm that all these compounds possess essentially trigonal bipyramidal (TBP) geometry, with a maximum deviation observed for **XIII**. It is very clear

(6) Selected references: (a) Schomburg, D.; Wermuth, U.; Schmutzler, R. *Chem. Ber.* **1987**, *120*, 1713. (b) Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6092. (c) Yu, J. H.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1990**, *112*, 7451. (d) Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052. (e) Prakasha, T. K.; Burton, S. D.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 5494. (f) Kojima, S.; Kajiyama, K.; Akiba, K.-y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1785. (g) Gorg, M.; Lork, E.; Kolomeitsev, A. A.; Röschenthaler, G.-V. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *127*, 15. (h) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Inorg. Chem.* **1997**, *36*, 2044. (i) Xiao-Dong Liu, Verkade, J. G. *Inorg. Chem.* **1998**, *37*, 5189 (an unusual salt with fused five-membered rings). (j) Nakazawa, H.; Kawamura, K.; Kubo, K. Miyoshi, K. *Organometallics* **1999**, *18*, 2961 (metallophosphoranes). (k) Thirupathi, N.; Krishnamurthy, S. S.; Nethaji, M. *Inorg. Chem.* **1999**, *38*, 1093. (l) Sonnenburg, R.; Neda, I.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 412. (m) Muthiah, C.; Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Polyhedron* **2000**, *19*, 63.

(7) Highly constrained ring systems are an exception: Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800.

(8) (a) Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **1996**, *118*, 12866. (b) Kajiyama, K.; Yoshimune, M.; Nakamoto, M.; Matsukawa, S.; Kojima S.; Akiba, K.-y. *Org. Lett.* **2001**, *3*, 1873.

(9) Kobayashi, J.; Goto, K.; Kawashima, T. *The Ninth International Symposium on Inorganic Ring Systems*; Saarbrücken, Germany, July 23−28, 2000; Abstract No. P-115.

(10) (a) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525. (b) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 1243. (c) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552.

(11) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **1996**, *118*, 9841.

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

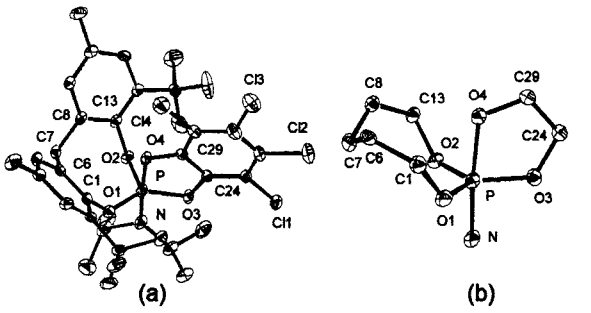


Figure 1. ORTEP drawing of **2** showing (a) all non-hydrogen atoms (only selected atoms labeled) and (b) selected atoms, highlighting the TBP geometry at phosphorus and boat−chair conformation of the 8-membered ring.

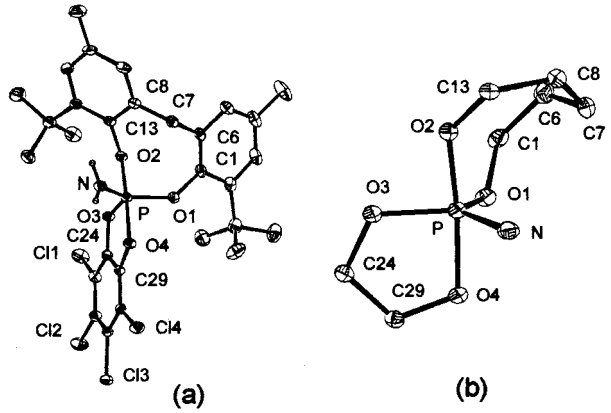
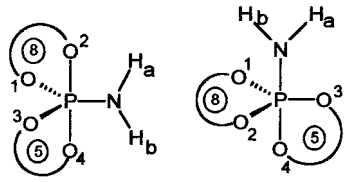


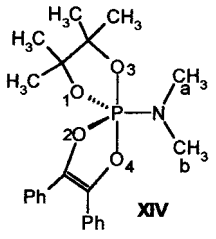
Figure 2. ORTEP drawing of **3**·CH_2Cl_2 showing (a) all non-hydrogen atoms and the NH_2 hydrogens, except the solvent with only selected atoms labeled, and (b) selected atoms, highlighting the TBP geometry at phosphorus and tub conformation of the 8-membered ring.

that the *sterically less demanding* $-NH_2$ *group in* ***3*** *occupies an equatorial position, whereas the sterically demanding* $-N(i\text{-}Pr)_2$ *in* ***2*** [*or* $-N(Me)Ph$ *in* ***1***] *occupies an apical position*. The observation contradicts the most often assumed tenet that high apicophilicity is favored by small size, and vice versa.[5,15,16]

Theoretical calculations done earlier suggest that π-donors prefer equatorial positions and that their donor orbitals will preferably lie in the equatorial plane.[2a] One would expect the $-N(alkyl)_2$ group to be a better π-donor than the $-NH_2$ group (because of the inductive effect), and hence the former should have preferred the equatorial position. This is not realized for our compounds. Information regarding the site preferences of $-NHR$ and $-NR_2$ groups on the basis of *negative hyperconjugation*[17] involving the nitrogen lone pair and an antibonding orbital of the PO_4N trigonal bipyramid is not available, for a more critical assessment of our observation.

It is unlikely that crystal packing forces are responsible for the higher apicophilicity of the $-NR_2$ group over the $-NHR$ group, because several compounds differing in the amount of steric bulk on the amino nitrogen are provided in the current study. However, one possibility is that an equatorial $-NH_2$ group is better placed for intramolecular hydrogen bonding with the apical oxygens (cf. **A** and **B**). This is best accomplished when O(2), P, O(4), N, $(N)H_a$, and $(N)H_b$ are in one plane; in fact, in the solid state they are planar with a maximum deviation of only 0.053 Å at phosphorus from the mean plane.[18] The dihedral angle between the planes comprising [P, O(2), O(4), N] and [P, N, $(N)H_a$, $(N)H_b$] is 4.1°. In the dimethylamino compound **XIV**, where such hydrogen bonding cannot exist,[19] the dihedral angle between the planes comprising [P, O(3), O(4), N] and [P, N, $(N)C_a$, $(N)C_b$] is 27.7°, clearly showing that the latter plane is tilted away from the former (apical) plane. A disconcerting feature in **3**·CH_2Cl_2, however, is that the N−H···O angles (88.6, 81.1°) are far from the normal 180°; thus it is too unlikely to be an intramolecular N−H···O bond. The NH_2 hydrogens may, however, have additional intermolecular interactions with the solvent dichloromethane (see Supporting Information for details).





Another possibility is that steric interaction between the $-NRR'$ group and the *tert*-butyl group of the aromatic part

(13) The corresponding ORTEP drawings are available as Supporting Information.

(14) Further details on the X-ray structures of **X**−**XIII** are also deposited. See ref 12.

(15) The small electronegativity differences among the amino/amido groups do not appear to have any influence, and already it is shown that in this system electronegativity rules[5] are violated (compounds **1**, **2**, **VI**, **VII**, and **X**).

(16) One of the reviewers' comments: "... If the amino group should become orthogonal to the equatorial plane, for stronger back-bonding, then actually the equatorial site is less preferable than the apical site. In the axial site only, one of the N−C bonds will be closer to one of the P-equatorial bonds and the other N−C bond can be totally free of steric interactions, whereas in an equatorial site, both N−C bonds will be forced to be closer to both P-axial bonds. When one of the N−C bonds is replaced by the N−H bond, the reduced steric effect can be compensated by back-bonding that occurs at the equatorial site." It should be noted that (i) the exact orbitals involved in back-bonding (see ref 17 also) is not clear and (ii) in **2** the nitrogen of the apical $N(i\text{-}Pr)_2$ group is planar indicating that back-bonding, if any, is possible at the apical (we use the term "apical" instead of "axial") site also. We refrain from commenting upon it further at the moment.

(17) (a) Reed, A. E.; P. von R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434. (b) Lattman, M. In *Hypervalent Compounds* in *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: Chichester, England, 1994; Vol. 3, pp 1496−1511.

(18) Note that this is also consistent with theoretical studies on $PF_4(NH_2)$ where the lone pair on nitrogen favors the equatorial plane.[2a] In the anilino compound **4** the atoms P, N, O(2), O(4), (N)H, and (N)C are also approximately in a plane with a maximum deviation of ±0.067 Å; the dihedral angle between the planes [O(2), P, O(4), N] and [P, N, (N)C, (N)H] is 3.4°.

(19) Szobota, J. S.; Holmes, R. R. *Inorg. Chem.* **1977**, *16*, 2299.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for Tetraoxyphosphoranes **1**−**5** and **X**−**XIII**

Ring Location and Labeling as in Figure 1					
param	**1**	**2**	**5**·1/2$C_6H_5CH_3$	**X**·CH_3CN	**XI**
P−O(1)	1.607(4)	1.612(2)	1.588(5)	1.601(3)	1.600(2)
P−O(2)	1.595(4)	1.599(2)	1.591(4)	1.598(3)	1.602(2)
P−O(3)	1.661(4)	1.651(2)	1.644(4)	1.657(3)	1.639(2)
P−O(4)	1.769(3)	1.783(2)	1.713(4)	1.764(3)	1.723(2)
P−N	1.727(4)	1.672(2)	1.735(5)	1.682(3)	1.757(2)
O(4)−P−N	174.6(2)	174.8(1)	175.0(3)	174.9(2)	172.7(1)
ΣN(angle, deg)	351.6	359.7		350[a]	

Ring Location and Labeling as in Figure 2				
param	**3**·CH_2Cl_2	**4**·$CHCl_3$	**XII**·$C_6H_5CH_3$	**XIII**
P−O(1)	1.599(2)	1.589(3)	1.600(3)	1.599(5)
P−O(2)	1.641(2)	1.638(3)	1.641(3)	1.660(4)
P−O(3)	1.645(2)	1.651(3)	1.646(3)	1.653(5)
P−O(4)	1.775(2)	1.753(3)	1.756(4)	1.832(5)
P−N	1.614(3)	1.630(4)	1.611(5)	1.584(5)[b]
O(4)−P−O(2)	174.5(1)	174.8(2)	175.65(17)	169.7(2)
ΣN(angle, deg)	360	358	360	

[a] Only one of the disordered carbon positions taken for calculation. [b] $Ph_3P-N = 1.571(5)$ Å.

may be greater when the −NRR′ group is placed equatorially than when it is placed apically (cf. Figures 1 and 2). In **1**, **2**, and **X**, the closest intramolecular contact between a phenyl, isopropyl, or methyl carbon of the apical amino group and a *tert*-butyl carbon is ∼3.91 Å. In **3** or **4**, where the amino/amido group is equatorial, the N*H* hydrogen is close to a *tert*-butyl carbon at 3.4−3.5 Å; this could become still less if this N*H* hydrogen is replaced by an alkyl group [as in $-NMe_2$, $-N(i\text{-}Pr)_2$, −N(Me)Ph], thus increasing steric repulsion. This could force the $-NR_2$ group to be apical. A cautionary note, however, is that other stable conformations with less steric interactions may be possible.

The P−N bond is significantly longer when the nitrogen is apical (**1**, **2**, **5**, **X**, **XI**) than when it is equatorial (**3**, **4**, **XII**, **XIII**); this is in line with the formulation of 3c−4e bonds for apical substituents and normal 2c−2e bonds for equatorial substituents.[17b] The P−N(apical) bond lengths are close to those calculated using the Schomaker−Stevenson empirical expression for a P−N single bond (1.77 Å).[20] The shorter P−N(equatorial) bonds suggest some π-character, and these are closer in length to the P−N bonds found in tri- and tetracoordinate (amino)phosphorus derivatives.[6h,21,22]

The P−O bonds also follow the expected general trend, but the P−O(4) bonds in **2**, **3**, or **XIII** are much longer than the calculated value (1.72 Å) obtained by using the Schomaker−Stevenson expression; in fact the P−O(4) bond length of 1.832 Å observed in **XIII** is among the longest P−O single (covalent) bond known.[23]

The 8-membered 1,3,2-dioxaphosphocin ring has a boat−chair conformation when located diequatorially (compounds **1**, **2**, **5**, **X**, **XI**) and a tub conformation when located apical−equatorially (compounds **3**, **4**, **XII**, **XIII**). These features for the phosphocin ring, when located diequatorially or apical−equatorially in trigonal bipyramidal phosphorus, have also been observed in similar compounds earlier.[6h,10b,11,24]

Variable-Temperature NMR Behavior. The essential features in the variable-temperature ^{31}P and ^{1}H NMR spectra for **1** are given as follows:

(i) In the ^{31}P NMR, as the temperature is raised, the two major peaks at δ −47.0 and −51.7 observed at 232 K broaden but do not disappear; at higher temperatures (>323 K) only one peak at δ −48.1, which is closer to the downfield peak (δ −47.0), is seen.

(ii) Two peaks each for the *tert*-butyl protons (δ 1.15, 1.59) and Ar−CH_3 (δ 2.12, 2.18) and two doublets for NCH_3 [δ 3.17 (^3J = 9.9 Hz), 3.57 (^3J = 12.0 Hz)] are observed at 232 K in the ^{1}H NMR spectrum. At 323 K only one set of signals [δ 1.28 (s), 2.39 (s), 3.41 (d, ^3J = 11.0 Hz)] is seen. An activation barrier of 60.4 ± 0.8 kJ mol^{-1} is estimated for this process, based on these signals.[25,26] It should however be noted that the high-temperature signals are not at the center of the two signals observed at low temperatures, as is expected for a normal exchange behavior.

(iii) Two sets of AX doublets for the $(Ar)_2CH_AH_B$ protons (set I, δ 3.31, 4.08, $^2J \sim$ 15.0 Hz; set II, δ 3.11, 4.19, $^2J \sim$

(20) See ref 5, p 46; we have used the Pauling electronegativity for this calculation.

(21) Compounds of tricoordinate phosphorus with O_2PN connectivity: (a) Keller, E.; Maurer, J.; Naasz, R.; Schader, T.; Meetsma, A.; Feringa, B. L. *Tetrahedron: Asymmetry* **1998**, *9*, 2409. (b) Müller, P.; Nury, P.; Bernardinelli, G. *Helv. Chim. Acta* **2000**, *83*, 843. (c) Kataeva, O. N.; Litvinov, I. A.; Naumov, V. A.; Mukmeneva, N. A. *Zh. Strukt. Khim.* **1989**, *30*, 166.

(22) Compounds of tetracoordinate phosphorus with PO_3N connectivity: (a) Newton, M. G.; Pantaleo, N. S.; Bajwa, G. S.; Bentrude, W. G. *Tetrahedron Lett.* **1977**, 4457. (b) Bao, J.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3814. (c) Edmundson, R. S.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1943. (d) Litvinov, I. A.; Naumov, V. A.; Arshinova, R. P. *Zh. Strukt. Khim.* **1987**, *28*, 142. (e) Hulst, R. Visser, J. M.; de Vries, N. K.; Zijlstra, R. W. J.; Kooijman, H.; Smeets, W.; Spek, A. L.; Feringa, B. L. *J. Am. Chem. Soc.* **2000**, *122*, 3135.

(23) For representative cases with long P−O bonds, see: (a) Dieckbreder, U.; Lork, E.; Röschenthaler, G.-V.; Kolomeitsev, A. A. *Heteroatom Chem.* **1996**, *7*, 281. (b) Kajiyama, K.; Kojima, S.; Akiba, K.-y. *Tetrahedron Lett.* **1996**, *37*, 8409. (c) Speier, G.; Tyeklár, Z.; Fulop, V.; Párkányi, L. *Chem. Ber.* **1988**, *121*, 1685.

(24) (a) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104. (b) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725. (c) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.

(25) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1987; p 103.

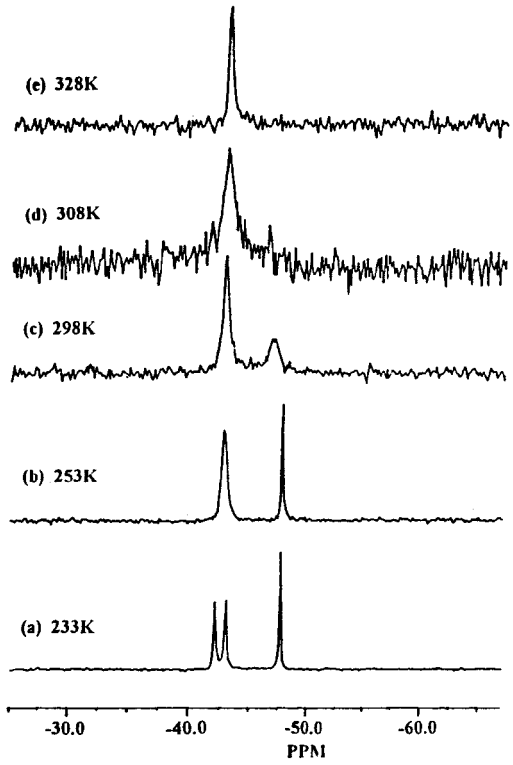


Figure 3. Variable-temperature ^{31}P NMR spectra for **X**.

14.8 Hz) are observed in the ^{1}H NMR spectrum at 232 K; these signals broaden on raising the temperature (until 323K), but the high-temperature limit (single peak) could not be reached.

In the case of **2**, there was essentially no change with temperature in the ^{1}H NMR chemical shifts of the $C(CH_3)_3$, $ArCH_3$, or $(Ar)_2CH_AH_B$ protons; in the ^{31}P NMR spectrum the single peak at -42.0 ± 0.3 ppm also remained unchanged in the temperature range 223−313 K. Only the signals of $NCH(CH_3)_2$ protons showed up as two doublets at <243 K [δ 1.31, 1.75, ^3J(H−H) ∼ 5.0 Hz] which merged into a single broad peak (δ 1.50) at 298 K. The coalescence in this case is symmetrical with the activation barrier for the process calculated as 57.9 kJ mol^{-1}.

Earlier, we have very briefly alluded to the unsymmetrical coalescence in the variable-temperature NMR spectra of **X**.[12] The ^{31}P NMR spectra of **X** at different temperatures are shown in Figure 3. After the symmetrical coalescence of the two downfield signals (δ −42.2, −43.1), the upfield peak (δ −47.1) 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. Thus, both symmetrical (between the peaks at δ −42.2 and −43.1) and unsymmetrical coalescences are observed. The spectra recorded at different temperatures while cooling and while warming were identical. The ^{1}H NMR spectra (Figure 4) corroborate the essential features observed in the ^{31}P NMR spectra: Three doublets at δ 2.28 [^3J(P−H) 10.7 Hz], 2.50 [^3J(P−H) 11.0 Hz], and 2.98 [^3J(P−H) 16.6 Hz] are observed for the $-NMe_2$ protons at 233 K. Those at δ 2.28 and 2.98 undergo symmetrical coalescence at ca. 253 K ($\Delta G^{\ddagger} = 50 \pm 1$ kJ mol^{-1}). At higher temperatures the doublet at δ 2.50 also broadens, and finally only one doublet at δ 2.75 [^3J(P−H) 12.5 Hz] is observed at 328 K. Of the three *tert*-butyl signals (δ 1.08, 1.31, 1.45), the two upfield signals coalesce symmetrically to give a single peak (δ 1.20) at ca. 250 K ($\Delta G^{\ddagger} = 50 \pm 1$ kJ mol^{-1}). The third signal (δ 1.45) broadens and decreases in intensity, and finally at 338 K, only one peak (δ 1.28) closer to the center of the coalesced peaks is observed. Other regions in the spectra are less clear.

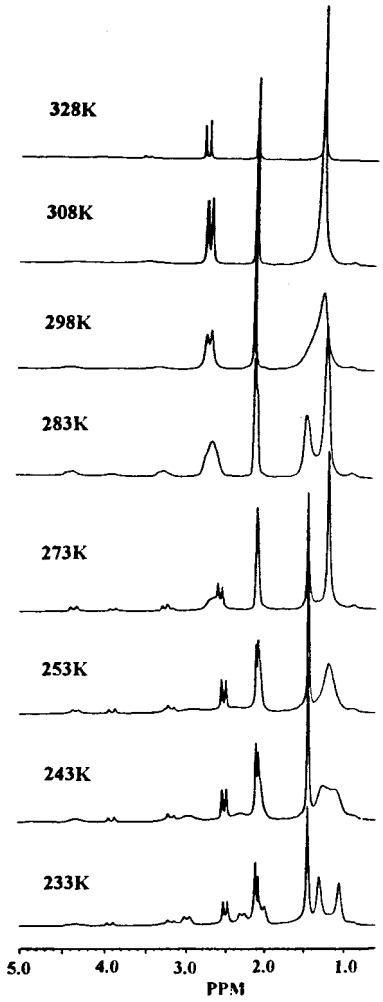


Figure 4. Variable-temperature ^{1}H NMR spectra for **X** in the region 0.8−5.0 ppm.

As regards **3** in which the $-NH_2$ group is equatorial, two closely spaced peaks at δ −50.6 and −50.9 (intensity ratio ca. 6:1) are observed in the ^{31}P NMR at 236 K; the low-intensity peak essentially disappears at higher temperatures, and at 328 K a single peak at δ −50.4 is observed. In the ^{1}H NMR (Figure 5), at <243 K two peaks for $C(CH_3)_3$ and three peaks for $ArCH_3$ are seen. At 293 K, there is a distinct

(26) An activation barrier of 50.8 kJ mol^{-1} in the monocyclic phosphorane $(2,6\text{-}Me_2C_6H_3O)_3P[(OC_6H_4)_2CH_2]$ which has a 1,3,2-dioxaphosphocin ring is ascribed for the a−e ↔ e−a exchange process involving this ring. See ref 24a. In a tricoordinate P(III) compound bearing a similar 1,3,2-dioxphosphocin moiety, unequal population of isomers (assigned to two diasteroisomeric conformers) exhibiting fluxionality was observed; activation barriers of 51−53 kJ mol^{-1} on the basis of NMR were calculated for ring inversion. See: Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; Chapter 3.

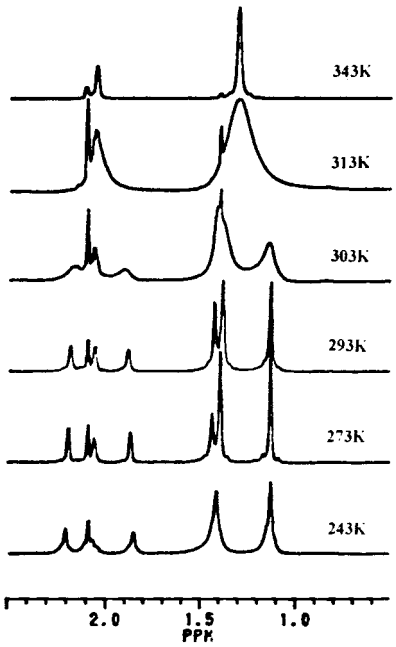


Figure 5. Variable-temperature ^{1}H NMR spectra for **3** in the region 0.5−2.5 ppm.

separation of peaks in this region, three peaks each for C(CH_3)$_3$ (δ 1.12, 1.39, 1.43) and ArCH_3 (δ 1.86, 2.08, 2.19) being observed. These peaks get broader at >303 K and merge into broad singlets centered at δ 1.29 and 2.04, respectively, on reaching 293 K. However, the coalescence does not appear to be symmetrical. At 343 K these peaks are sharp. There are two $-NH_2$ doublets at 236 K (δ 2.65, 2.95), which merge at higher temperatures to give only one doublet [δ 3.10, ^3J(P−H) 17.3 Hz at 343 K; not shown in Figure 5], but because of the presence of other peaks, the coalescence pattern is less clear.

For the P−NHPh compound (**4**), only one sharp ^{31}P NMR signal (δ −57.4 ± 0.2) is observed in the temperature range 243−303 K. In the ^{1}H NMR, two signals each for C(CH_3)$_3$ (δ 1.20, 1.56) and ArCH_3 (δ 1.85, 2.15) are observed at 243 K whereas only one signal each (δ 1.40 and 2.20, respectively) is observed at 323 K. An energy of activation ($\Delta G^{\ddagger}$) of 62.1 ± 0.8 kJ mol^{-1} is calculated for the process. The ^{1}H NMR spectrum of the −NHMe compound **XII** in the *tert*-butyl region is analogous to that of **4** with $\Delta G^{\ddagger} \sim$ 62.1 kJ mol^{-1}. The Ar−CH_3 region is a bit unclear due to interference by the −NHCH_3 protons. In the ^{31}P NMR, at low temperatures (256−298 K), two closely spaced signals at δ −52.2 and −52.5 ppm of unequal intensity (ratio ∼1:6) are observed; at higher temperatures (>310 K), only one peak is observed at δ −52.4.

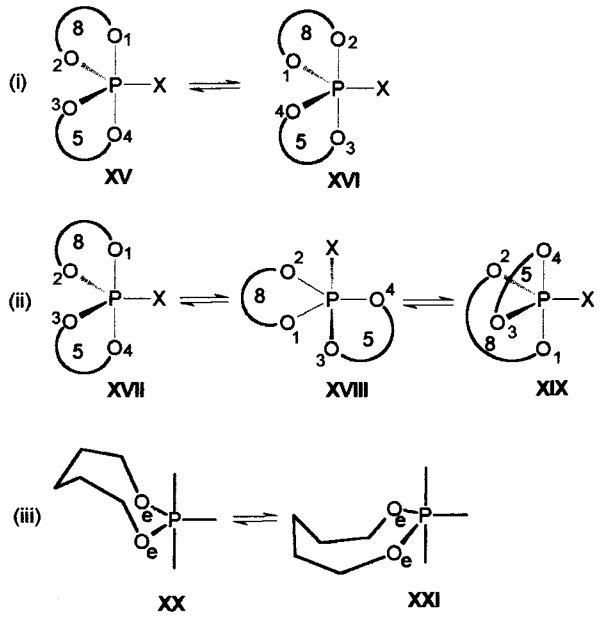
Three possible intramolecular processes that may be operating in this system are given in Scheme 1:

(i) an a−e ↔ e−a exchange process for the two rings, possibly of low energy, with X as the pivotal ligand;

(ii) an a−e ↔ e−e (or e−e ↔ a−e) exchange process involving the 8-membered ring, with O(2) pivotal, where a similar process could be considered for the 5-membered ring also, except being of higher energy;

(iii) boat−chair to tub conformational change for the

Scheme 1



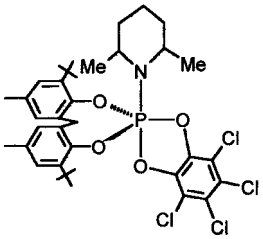
8-membered ring located e−e (shown in Scheme 1) and tub to boat−chair for the eight-membered ring located a−e (not shown in Scheme 1).

Due to steric factors it should be more difficult for the above exchange processes to occur in compound **2**; the observation of only one signal in the ^{31}P NMR spectrum (as well as single peaks for the *tert*-butyl and ArCH_3 protons in the ^{1}H NMR spectrum) throughout the temperature range studied is consistent with this assumption.[27] At low temperatures, the P−N bond rotation is frozen and, hence, two doublets for the methyl protons of the isopropyl groups [CH(CH_3)$_2$] are observed in the ^{1}H NMR spectrum of **2**. Because of the lesser steric bulk of the $-NMe_2$ group, the P−N bond rotation is not frozen in **X**. The low-temperature symmetrical coalescence observed for **X** is likely to be due to the boat−chair ↔ tub process iii, with the $-NMe_2$ group apical. We ascribe the unsymmetrical coalescence in **1** and **X** to the a−e↔ e−e exchange ii. In this process, the local environment at phosphorus is likely to change significantly [the O(1)−P−O(2) angle could vary from 117.0° in the e−e isomer to 95° in the a−e isomer; there will also be large changes in the P−N bond lengths], and hence, the ^{31}P NMR chemical shifts can be expected to show a wide difference for the two isomers of **1** and **X**.

On the basis of the above arguments, we assign the downfield signal(s) in the ^{31}P NMR spectra of **1** and **X** to the N(apical) isomer and the upfield signal to the N(equatorial) isomer. This is also consistent with the δ(P) values of **2** as well as **6** (which has an amino group similar in bulk to **2**).[28] For the N(equatorial) isomer of **1** or **X** observed at low temperatures in the NMR spectra, the a−e ↔ e−a

(27) These spectral features are also possible if the a−e ↔ e−a exchange i occurred in a situation where the −N(*i*-Pr)$_2$ group was equatorial, because the two trigonal bipyramids **XV** and **XVI** are equivalent. This possibility, however, is inconsistent with the solid-state structure of **2**. It is true that X-ray data need not always support NMR results and vice versa (as pointed out by a reviewer); the arguments presented here offer a possible explanation of the results.

exchange probably occurs rapidly, making its *tert*-butyl protons equivalent.



6 [δ(P) -40.0]

For the $-NH_2$ or the $-NHR$ compounds **3**, **4**, and **XII**, either a single peak (**4**) or two closely placed peaks (**3**, **XII**) of differing intensity observed in the ^{31}P NMR spectrum suggest that the local environment at phosphorus is not changed significantly. We ascribe these spectral features to exchange processes i and iii with only the N(equatorial) isomer being present. The coalescence of the two peaks (^1H or ^{31}P NMR) is again not symmetrical, suggesting that one isomer/conformer is preferentially present at higher temperatures.

Summary

We have provided a number of examples of compounds containing a PO_4N framework in a TBP geometry, which demonstrate that the familiar steric or electronegativity rule for the apicophilicity of an amino/amido group is not followed in these cases. The possible rationalization for this is discussed. In addition, new features in the exchange behavior of pentacoordinate phosphorus are observed in the NMR spectrum (^1H, ^{31}P). Thus, this study is expected to significantly enhance our understanding of the structural preferences of pentacoordinate phosphorus, which in turn are important in the context of nucleophilic substitution reactions at a tetrahedral phosphorus(V) center.

Experimental Section

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[29] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^1H, ^{13}C, and $^{31}P\{H\}$ NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ or $C_6D_5CD_3$ solutions (unless stated otherwise), with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). Variable-temperature ^1H and ^{31}P NMR spectra were recorded in $C_6D_5CD_3$. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer or obtained from the Indian Association for the Cultivation of Science (Kolkata, India).

The chloro precursor $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2PCl$ was prepared by a literature procedure and sublimed prior to use.[30] The P(III) precursors $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2PX$ [X = NH_2, NHPh, NMe(Ph), N(*i*-Pr)$_2$, NCH(Me)$CH_2CH_2CH_2CHMe$, NCS] were prepared by the reaction of the chloro compound with an appropriate amine or sodium thiocyanate in toluene or acetonitrile; detailed procedures and spectroscopic data are given in the Supporting Information.

Reaction of P(III) Compounds with *o*-Chloranil. Synthesis of 1. A mixture of the P(III) precursor $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2$-PN(Me)Ph (0.229 g, 0.48 mmol) and *o*-chloranil (0.119 g, 0.48 mmol) in toluene (5 mL) was heated to dissolve the solids (~10 min) and left stirring overnight at room temperature. The solution was concentrated to ~1 mL, heptane (0.5 mL) was added, and dissolution of the solids was effected by warming. Slow evaporation of the solvent afforded crystals of **1** after 2 d. Yield: 0.195 g (56%). Mp: 218−220 °C. ^1H NMR ($CDCl_3$): 1.21, 1.46 (2 br s, 18 H, C(C*H*$_3$)$_3$), 2.32 (s, 6 H, ArC*H*$_3$), 3.48 (d, ^3J = 9.9 Hz, 3 H, NC*H*$_3$), 4.15 (br, 2 H, ArC*H*$_2$), 6.85−7.70 (m, 9 H, Ar *H*) ppm. ^{31}P NMR ($CDCl_3$): −47.9, −50.6 (ca. 5:1) ppm. Anal. Calcd for $C_{36}H_{38}Cl_4NO_4P$: C, 59.93; H, 5.31; N, 1.94. Found: C, 59.89; H, 5.25; N, 1.85.

Synthesis of 2. A mixture of the P(III) precursor $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2PN(i\text{-Pr})_2$ (0.38 g, 0.81 mmol) and *o*-chloranil (0.20 g, 0.81 mmol) in toluene (5 mL) was heated at 90 °C for 10 h. Upon cooling of the solution, crystals of **2** separated out. Yield: 0.49 g (85%). Mp: 194−196 °C. ^1H NMR ($CDCl_3$): 1.10 (s, 18 H, C(C*H*$_3$)$_3$), 1.50 (br, 12 H, CH(C*H*$_3$)$_2$), 2.30 (s, 6 H, ArC*H*$_3$), 3.50 (v br, 2 H, C*H*(CH$_3$)$_2$), 3.57 (d, ^2J = 13.0 Hz, 1 H, C*H*$_A$H$_X$), 4.56 (dd, $J \sim$ 3.2, 13.0 Hz, 1 H, CH$_A$*H*$_X$), 6.91−7.15 (2 s, 4 H, Ar *H*) ppm. ^{31}P NMR ($CDCl_3$): −41.9 ppm. Anal. Calcd for $C_{35}H_{44}Cl_4NO_4P$: C, 58.75; H, 6.20, N, 1.96. Found: C, 58.58; H, 6.12; N, 1.89.

Synthesis of 3·CH_2Cl_2. A mixture of the P(III) precursor $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2PNH_2$ (0.388 g, 1.0 mmol) and *o*-chloranil (0.247 g, 1.0 mmol) in toluene (2 mL) was heated at 60 °C for 10 min and left overnight at room temperature. The solid obtained was crystallized from a mixture of dichloromethane (2 mL) and heptane (1.5 mL) to give **3**·CH_2Cl_2. Yield: 0.56 g (78%). Mp: 160−162 °C (frothing). ^1H NMR ($CDCl_3$): 1.18, 1.37, 1.43 (3 s, 18 H, C(C*H*$_3$)$_3$), 2.21, 2.28, 2.33 (3 s, 6 H, ArC*H*$_3$), 3.51 (d, ^2J = 14.9 Hz, 1 H, C*H*$_A$H$_X$), 3.52−3.80 (br, 2 H, N*H*$_2$), 4.60 (d, $^2J \sim$ 14.9 Hz, 1 H, CH$_A$*H*$_X$), 5.30 (s, 2 H, C*H*$_2$Cl$_2$), 6.92−7.20 (m, 4 H, Ar *H*) ppm. ^{31}P NMR ($CDCl_3$): −50.1 ppm. Anal. Calcd (after powdering and drying in vacuo for 3 h) for $C_{29}H_{32}Cl_4NO_4P$: C, 55.17; H, 5.11; N, 2.22. Found: C, 55.38; H, 5.09; N, 2.28.

Synthesis of 4·$CHCl_3$. A mixture of the P(III) precursor $CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2PNHPh$ (1.88 g, 4.07 mmol) and *o*-chloranil (1.00 g, 4.07 mmol) was dissolved in chloroform (20 mL) by warming to 50 °C for 15 min. Cooling the resulting solution to 0 °C afforded crystalline **4**·$CHCl_3$. Yield: 2.39 g (71%). Mp: 158−160 °C. ^1H NMR ($CDCl_3$): 1.34, 1.37 (2 br s, 18 H, C(C*H*$_3$)$_3$), 2.28 (s, 6 H, ArC*H*$_3$), 3.61 (d, ^2J = 15.1 Hz, 1 H, C*H*$_A$H$_X$), 4.77 (d, $^2J \sim$ 15.1 Hz, 1 H, CH$_A$*H*$_X$), 5.48 (d, ^2J = 21.9 Hz, 1 H, N*H*), 6.96−7.26 (m, 9 H, Ar *H*) ppm. ^{31}P NMR ($CDCl_3$): −57.7 ppm. Anal. Calcd (after powdering and drying in vacuo for 3 h) for $C_{35}H_{36}Cl_4NO_4P$: C, 59.42; H, 5.13; N, 1.98. Found: C, 59.48; H, 5.18; N, 2.04.

(28) Compound **6** was prepared by treating the corresponding P(III) precursor [Mp 222−224 °C; δ(P) ($CDCl_3$) 142.1] with an equimolar quantity of *o*-chloranil. Data for **6** are as follows. Mp: 276−278 °C (dec). ^1H NMR ($CDCl_3$): 1.14 (d, ^3J = 7.6 Hz, 6 H, CHC*H*$_3$), 1.31 (s, 18 H, C(C*H*$_3$)$_3$), 1.20−1.80 (br, 6 H, (C*H*$_2$)$_3$), 2.27 (s, 6 H, ArC*H*$_3$), 3.41 (d, ^2J = 13.9 Hz, 1 H, (Ar)$_2$C*H*$_A$H$_X$), 4.08 (br m, 2 H, C*H*-N), 4.66 (d, ^2J = 13.9 Hz, 1 H, (Ar)$_2$CH$_A$*H*$_X$), 6.88, 6.99 (two s, 4 H, Ar-*H*) ppm. ^{31}P NMR ($CDCl_3$): −40.0 ppm. Anal. Calcd for $C_{36}H_{44}Cl_4NO_4P$: C, 59.43; H, 6.10; N, 1.94. Found: C, 59.65; H, 6.14; N, 1.98.

(29) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, U.K., 1986.

(30) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082.

Table 2. Crystal Data for **1**−**5**

param	**1**	**2**	**3**·CH_2Cl_2	**4**·$CHCl_3$	**5**·1/2$C_6H_5CH_3$
emp formula	$C_{36}H_{38}Cl_4NO_4P$	$C_{35}H_{44}Cl_4NO_4P$	$C_{30}H_{34}Cl_6NO_4P$	$C_{36}H_{37}Cl_7NO_4P$	$C_{33.5}H_{38}Cl_4NO_4PS$
fw	721.44	715.48	716.25	826.79	723.48
cryst system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/c$	$P\bar{1}$
a/Å	10.219(1)	22.4934(11)	20.718(11)	11.187(3)	9.563(2)
b/Å	11.192(6)	16.9072(8)	17.009(11)	13.151(10)	12.993(2)
c/Å	17.157(3)	20.7734(10)	19.877(9)	26.571(15)	15.994(3)
α/deg	105.74(4)	90	90	90	72.986(18)
β/deg	101.57(2)	114.599(1)	103.89(4)	90.76(3)	78.85(4)
γ/deg	104.65(3)	90	90	90	73.25(3)
V/Å^3	1749.3(10)	7183.1(6)	6800(6)	3909(4)	1806.7(6)
Z	2	8	8	4	2
D_{calc}/g cm^{-3}	1.370	1.323	1.399	1.405	1.330
μ/mm^{-1}	0.424	0.412	0.588	0.588	0.466
F(000)	752	3008	2960	1704	754
data/restraints/params	6143/0/424	6326/0/406	5955/0/395	6865/0/472	6348/3/405
S	1.182	1.055	1.088	1.018	1.057
R1[a] [$I > 2\sigma(I)$]	0.0584	0.0528	0.0484	0.0654	0.0860
wR2[a] (all data)	0.2146	0.1345	0.1523	0.2099	0.2582
max/min resid electron dens/e Å^{-3}	0.669/−0.382	0.525/−0.279	0.759/−0.764	0.687/−0.758	0.721/−0.993

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o]^{0.5}$.

Synthesis of 5·1/2$C_6H_5CH_3$. This was prepared using CH_2{6-*t*-Bu-4-Me-C_6H_2O}$_2$PNCS (0.376 g, 0.88 mmol) under experimental conditions similar to that for **1**. Yield: 0.396 g (62%). Mp: 178−180 °C. ^{1}H NMR (after powdering and drying in vacuo for 3 h; $CDCl_3$): 1.29 (s, 18H, C(C*H*$_3$)$_3$), 2.36 (s, 6H, ArC*H*$_3$), 3.40−3.60 and 4.20−4.40 (br, 2 H, ArC*H*$_2$), 7.07, 7.20 (2 s, 4H, Ar *H*) ppm. ^{31}P NMR ($CDCl_3$): −59.0 ppm. The sample was rather unstable in our hands, and hence variable-temperature NMR spectra were not recorded. Anal. Calcd (after powdering and drying in vacuo for 3 h) for $C_{30}H_{30}Cl_4NO_4PS$: C, 53.51; H, 4.49; N, 2.08. Found: C, 53.95; H, 4.34; N, 2.01.

X-ray data were collected on an Enraf-Nonius-MACH3 at 293 K (**1**, **3**−**5**) or Bruker AXS SMART diffractometer at 296 K (**2**) using Mo Kα (λ = 0.710 73 Å) radiation and capillary mounting. The structures were solved by direct methods;[31] all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms bonded to carbon, the riding model was used. The hydrogen atoms bonded to nitrogen were located in a difference map. In the structure of **4**·$CHCl_3$, the hydrogen of the solvent could not be fixed due to disorder. In the structure of **5**·$^1/_2C_6H_5CH_3$, the solvent molecule is highly disordered; only the ring carbon atoms (not the methyl carbon) were located by a difference map and refined. The corresponding hydrogen atoms were not included in the refinement. Thus, the *R* values are a bit high for this compound; however, for the theme of the paper the essential features at the phosphorus center are fairly clear. The crystal data for the new compounds **1**−**5** are summarized in Table 2; details on the other compounds are already deposited.

Acknowledgment. This work was supported by the Department of Science and Technology (DST), New Delhi. P.K. thanks the CSIR for a fellowship. The National Single Crystal Diffractometer Facility at the University of Hyderabad funded by the DST (New Delhi) is gratefully acknowledged.

Supporting Information Available: X-ray structure determination and crystal data for **1**−**5** including the full ORTEP diagrams and CIF files, additional variable-temperature NMR spectra for **1**−**4**, and text describing characterization data for the P(III) precursors to compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010935W

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