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Conversion of Tricoordinate to Hexacoordinate Phosphorus. Formation of a Phosphorane−Phosphatrane System[1]

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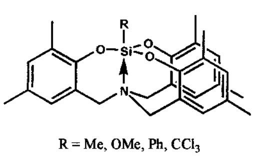
Abstract: Reaction of $RPCl_2$ with tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine (**4**) led to the formation of a tricoordinated phosphonite (**1**) when R = Ph and to a hexacoordinated phosphorane−phosphatrane (**2**) when R = Et. The X-ray structures showed that the unreacted hydroxyl group in **1** oxidatively added to phosphorus in **2** leading to the formation of three additional bonds, a P−O, a P−H, and a P−N linkage. In solution, ^{31}P measurements assisted by solid-state ^{31}P measurements revealed that each of the compounds existed in both structural forms. VT ^{31}P established equilibria where the solid-state structures predominated in each case. This is the first example of a conversion of three-coordinate to six-coordinate phosphorus on going from the solid to the solution state and the existence of these two disparate geometries in equilibrium with one another in solution. In the absence of steric protection with the use of an analogous amine (**5**) without *tert*-butyl groups, a hydrolysis reaction occurred with $PhPCl_2$. X-ray analysis revealed an anionic phenylphosphinate structure (**3**) hydrogen bonded in a cage-like arrangement with the protonated amine. Similar hydrolysis reactions take place with **1** and **2** but much more slowly.

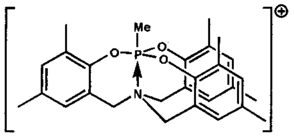
Introduction

Previously, we prepared and structurally characterized a new class of silatranes with tricyclic rings that are all six-membered.[2,3] All previous work in silatrane chemistry centered on ring systems that were five-membered.[4−6] Similarly, earlier work on phosphatranes contained only five-membered rings.[4] Our recent work in this area led to the first phosphatranes[7] composed of all six-membered rings. Examples **A**[2] and **B**[7] illustrate these formulations. The phosphatranes are cationic and, like the related silatranes, exhibit greater ring flexibility. The fluxional behavior of one of the phosphatranes[7] showed entirely analogous behavior to that of the silatranes with six-membered rings, both with respect to activation energies for intraconversion of enantiomers and the mechanism of intraconversion involving a propellor-like rearrangement of the cyclic components of the ring systems.



R = Me, OMe, Ph, CCl_3

A



Ave. P-N = 2.81(2) Å

B

The advantage of using six-membered rings supporting the coordinating nitrogen atom in its interaction with phosphorus is that a much wider range of P−N donor−acceptor distances are obtained compared to that with atranes composed of five-membered rings. In the case of the silatranes with the six-membered ring systems, the range of Si−N distances was found to vary over 0.7 Å, from 2.03 to 2.75 Å.[2] In comparison with silatranes composed of five-membered rings that possess a common set of substituents in the trans apical position, the range of the P−N distances is confined to 2.03−2.19 Å.[8−11]

In continuance of our work on hypervalent phosphorus chemistry, the present study reports the ability of phosphorus to engage in a new type of transformation. Herein reported is the first conversion of three-coordinated to six-coordinated phosphorus on going from the solid to the solution state and the existence of these two disparate geometries in equilibrium with each other in solution. The same sterically encumbered aminotriphenol that we used in a previous atrane study of silicon[3] is employed here and led to the preparation of the phenyl

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(1) (a) This paper is dedicated to Professor Herbert C. Brown, my Ph.D. thesis supervisor, on the occasion of his 90th birthday. (b) Previous paper: Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **2002**, *41*, 1645−1651.

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phosphonite **1** and the oxyphosphorane **2**. Use of a sterically less demanding aminotriphenol that was employed in earlier atrane studies of silicon[2] and phosphorus[7] resulted in the formation of the hydrolysis product **3**. X-ray analysis and ^{1}H NMR characterization were carried out as well as ^{31}P measurements in the solid and solution states.

Experimental Section

P,*P*-Dichlorophenylphosphine (Fluka) and *P*,*P*-dichloroethylphosphine (Aldrich) were used as supplied. Tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine (**4**) was synthesized according to a literature method.[7] Our previous procedure[3] was used to prepare tris (2-hydroxy-3-5-dimethylbenzyl)amine **5**. Triethylamine was distilled over KOH pellets. Solvents were purified according to standard procedures.[12] All the reactions were carried out in an argon atmosphere. Proton NMR spectra were recorded on a Bruker AC 200 FT-NMR spectrometer. Solution phosphorus NMR spectra were recorded on a Bruker DPX300 FT-NMR spectrometer in sweep-off mode and the solid-state phosphorus NMR spectra were recorded on a Bruker ASX300 FT-NMR spectrometer. All ^{1}H NMR spectra were recorded in CD_2Cl_2 and the solution ^{31}P NMR spectra were recorded in CH_2Cl_2. The low-temperature phosphorus NMR spectra were recorded on a Avance D600 FT-NMR spectrometer in CD_2Cl_2. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane for ^{1}H NMR or 85% H_3PO_4 for ^{31}P NMR. All were recorded at around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses: $N[CH_2(Me(t\text{-}Bu)C_6H_2)O]_2[CH_2(Me(t\text{-}Bu)C_6H_2)OH]PPh$ (1). A solution of dichlorophenylphosphine (0.500 mL, 3.68 mmol) in dichloromethane (50 mL) was added to a solution of **4** (2.00 g, 3.66 mmol) and triethylamine (1.00 mL, 7.17 mmol) in dichloromethane (120 mL) with stirring at room temperature over a period of 30 min. The reaction mixture was stirred further for 48 h. The solvent was removed and the residue extracted with diethyl ether. The ether solution was left under Argon. When the amount of solvent was nearly 10 mL, the argon flow was stopped and the remaining solution left for crystallization, after which the remainder of the solvent was decanted. The crystals were dried under a vacuum. Mp 181−184 °C (yield 1.30 g, 54%). ^{1}H NMR: 0.98 (s, 18H), 1.28 (s, 9H), 1.38 (s, 9H), 2.13 (s, 3H), 2.17 (s, 6H), 3.9 (very broad, 6H), 6.5 (s, 1H), 6.8−7.1 (m, br, 8H), 7.42 (m, 3H), 7.82 (m, 2H). ^{31}P NMR (293 K; 300 MHz): −109.3 ($^{1}J_{P-H}$ = 683 Hz), 169.3 (br, s) in a 1:9 integral ratio. ^{31}P NMR (290 K; 600 MHz): −101.4, 176.6 in a 1:8 integral ratio. ^{31}P NMR (234 K; 600 MHz): −104.7, 175.4 in a 2:11 integral ratio. ^{31}P NMR (160 K; 600 MHz) (sample frozen): −108.4, 174.3 in a 1:14 integral ratio. ^{31}P NMR (solid state): 173.3. Anal. Calcd for $C_{42}H_{54}NO_3P$: C, 77.39; H, 8.35; N, 2.15. Found: C, 77.08; H, 8.45; N, 2.08.

This compound hydrolyzes to give a salt analogous to that of **3** based on NMR comparisons. ^{1}H NMR ($CDCl_3$): 1.35 (s, 27H, *t*-Bu), 2.23 (s, 9H, Ar-CH_3), 4.04 (s, 6H, NCH_2), 6.76 (d, 1.7 Hz, 3H, Aryl), 7.07 (d, 1.7 Hz, 3H, Aryl), 7.40 (m, 3H, Ph), 7.54 (d, 1H, $^{1}J_{P-H}$ = 545 Hz), 7.55 (br, 4H, NH + OH), 7.70 (m, 2H, Ph). ^{31}P NMR ($CDCl_3$): 15.4 ($^{1}J_{P-H}$ = 545 Hz).

$N[CH_2(Me(t\text{-}Bu)C_6H_2)O]_3P(H)Et$ (2). A procedure similar to that for **1** was used. The quantities were as follows: **4** (2.60 g, 4.76 mmol), triethylamine (1.4 mL, 10 mmol), and dichloroethylphosphine (0.500 mL, 4.81 mmol). Crystals were obtained from diethyl ether. They were found to have 1 molar equiv of a diethyl ether molecule in all of the data. Mp 141−145 °C dec (yield 1.80 g, 62%). ^{1}H NMR: 0.69 (dt, $^{3}J_{PCCH}$ = 38.3 Hz, $^{3}J_{HCCH}$ = 7.6 Hz, 3H), 1.25 (s, 9H), 1.27 (s, 9H), 1.35 (s, 3H), 1.36 (s, 6H), 1.40 (s, 6H), 2.13 (s, 6H), 2.16 (s, 6H), 2,32 (dq, *J* = 18.9, 7.6 Hz), 3.61 (s, br, 2H), 3.82 (br, 2.5H), 3.95 (br, 1.4H), 3.9, 6.5−7.1 (m, 6H). ^{31}P NMR (293 K; 300 MHz): −93.3 ($^{1}J_{P-H}$ = 626 Hz), 191.3 (s). ^{31}P NMR (290 K; 600 MHz): −86.1, 198.2 in a 14:1 peak height ratio. ^{31}P NMR (234 K; 600 MHz): −88.6, 198.8 in a 12:1 peak height ratio. ^{31}P NMR (160 K; 600 MHz): −91.6, 198.7 in a 12:1 integral ratio. ^{31}P NMR (solid state): −96.0. Anal. Calcd for $C_{38}H_{54}NO_3P{\cdot}C_4H_{10}O$: C, 74.41; H, 9.51; N, 2.07. Found: C, 74.95; H, 9.46; N, 2.27.

This compound hydrolyzes to give a salt analogous to that of **3** based on NMR comparisons. ^{1}H NMR (CD_2Cl_2): 1.09 (m, 3H, PCH_2CH_3), 1.36 (s, 27H, *t*-Bu), 1.62 (dqd, $^{2}J_{PH}$ = 15.5 Hz, $^{3}J_{HCCH}$ = 7.7 Hz, $^{3}J_{HPCH}$ = 2.0 Hz, 2H, PCH_2CH_3), 2.25 (s, 9H, Ar-CH_3), 3.84 (s, 6H, NCH_2), 6.84 (d, 1.8 Hz, 3H, Aryl), 6.93 (dt, $^{1}J_{PH}$ = 523.7 Hz, $^{3}J_{HPCH}$ = 2.0 Hz, 1H, PH), 7.10 (d, 1.8 Hz, 3H, Aryl), 7.80 (br, s, 4H, NH + OH). ^{31}P NMR: 33.3 ($^{1}J_{P-H}$ = 543 Hz).

$HN^+[CH_2(Me_2C_6H_2)OH]_3PhP(H)(O)O^-$ (3). Attempted synthesis of a compound analogous to **1** but with all *tert*-butyl groups replaced by methyl groups gave the expected compound similar to **1** based on phosphorus NMR. ^{31}P NMR (reaction mixture): −90.4 ($^{1}J_{P-H}$ = 680 Hz), 162.1 (s), 165.4 (s, br), 172.2 (s, br) in a 10:5:11:5 integral ratio. However, the lack of *tert*-butyl groups resulted in poor solubility in ether, preventing the separation from the amine−hydrochloride byproduct. Attempted fractional crystallization from heptane−dichloromethane gave only a fluffy solid. Also most likely due to the absence of steric protection, this compound was much more sensitive to moisture. Due to these combined effects, we were not able to isolate this product and instead only the hydrolyzed product (**3**) was isolated. Similar hydrolyzed products were observed in solution for **1** and **2** also.

A procedure analogous to that for **1** was used. The quantities were as follows: **5** (3.10 g, 7.39 mmol), triethylamine (2.1 mL, 15 mmol), and dichlorophenylphosphine (1.00 mL, 7.36 mmol). The reaction mixture was washed with water, dried over $MgSO_4$, and filtered. The filtrate was diluted with heptane (50 mL) and left for slow evaporation to obtain crystals of the hydrolyzed product **3**. This was further crystallized from a mixture of acetone−methanol (10:1, 80 mL). Mp 185−187 °C dec (yield 3.10 g, 75%). ^{1}H NMR: 2.16 (s, 9H, Ar-CH_3), 2.28 (s, 9H, Ar-CH_3), 4.04 (s, 6H, NCH_2), 6.67 (d, 1.5 Hz, 3H, Aryl), 6.90 (d, 1.5 Hz, 3H, Aryl), 7.42 (m, 3H, Ph), 7.77 (d, 1H, $^{1}J_{P-H}$ = 518 Hz), 7.87 (m, 2H, Ph), 10.1 (br, s, 4H, NH + OH). ^{31}P NMR: 15.3 (d, $^{1}J_{P-H}$ = 519 Hz). ^{31}P NMR ($CDCl_3$): 13.2 (dt, $^{1}J_{P-H}$ = 518 Hz, $^{3}J_{PCCH}$ = 31.0 Hz). Anal. Calcd for $C_{33}H_{40}NO_5P$: C, 70.57; H, 7.18; N, 2.49. Found: C, 70.52; H, 7.12; N, 2.49.

X-ray Studies. The X-ray crystallographic studies were performed using a Nonius Kappa CCD difractometer and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystals of **1**−**3** were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected at 23 ± 2 °C for $\theta_{MoK\alpha} \le 25°$. All data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed on a 600 MHz Pentium III computer with SHELXS-86 for solution[13] and SHELXL-97 for refinement.[14] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on oxygen (in **1**) and on phosphorus (in **2** and **3**) were located by difference Fourier techniques and refined isotropically. The remaining hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl and hydroxyl hydrogen atoms) on the bonded atoms. The final agreement factors are based on the reflections with $I \ge 2\sigma_I$. Crystallographic data are summarized in Table 1.

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Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
formula	$C_{42}H_{54}NO_3P$	$C_{38}H_{54}NO_3P{\cdot}C_4H_{10}O$	$C_{27}H_{34}NO_3.C_6H_6O_2P$
formula wt	651.83	677.91	561.63
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
crystal size, mm^3	0.50 × 0.25 × 0.25	0.65 × 0.60 × 0.50	0.60 × 0.35 × 0.35
a (Å)	9.4521(2)	13.4625(2)	11.3043(1)
b (Å)	12.6281(2)	22.5793(4)	14.7072(2)
c (Å)	17.1232(4)	13.7246(3)	19.1561(3)
α (deg)	107.1218(11)	90.00	90.00
β (deg)	94.5036(10)	106.1372(8)	105.1107(5)
γ (deg)	95.8229(8)	90.00	90.00
V (Å^3)	1930.53(7)	4007.54(13)	3074.67(7)
Z	2	4	4
D_{calc} (g/cm^3)	1.121	1.124	1.213
$\mu_{\mathrm{MoK}\alpha}$ (cm^{-1})	1.08	1.08	1.30
total no. of reflns	6758	7025	5252
no. of reflns with $I > 2\sigma_I$	5021	5266	4078
R^a	0.0474	0.0553	0.0529
$R_w{}^b$	0.1092	0.1323	0.1417

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o{}^2) = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4\}^{1/2}$.

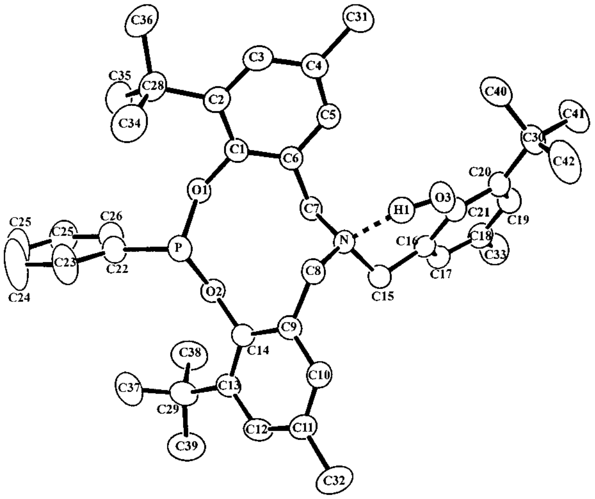

Figure 1. ORTEP diagram of **1**.

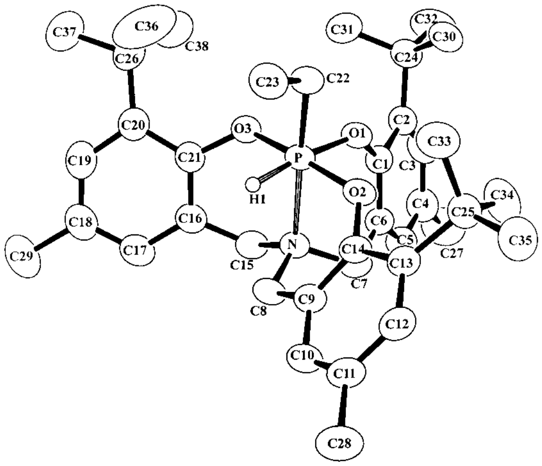

Figure 2. ORTEP diagram of **2** (solvent molecule omitted).

Results and Discussion

The atom-labeling schemes for **1**−**3** are given in the ORTEP[15] plots of Figures 1−3, respectively. The thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms are omitted for clarity as well as the solvent ether molecule for **2**. Selected bond parameters are given in Tables 2−4.

Syntheses. Although **1** and **2** were synthesized by the same type of reaction, the products are different. For **1**, reaction of the amine **4** with $PhPCl_2$ in the presence of triethylamine in dichloromethane solution yielded a tricoordinated phenylphosphonite, Scheme 1, eq 1. However for **2**, reaction of the amine **4** with $EtPCl_2$ in the presence of triethylamine in dichloromethane solution yielded a hexacoordinated oxyphosphoraneatrane (Scheme 1, eq 2). The yields were 54% and 62%, respectively. Scheme 1 depicts schememetic representations for the structures of **1** and **2** established by X-ray analysis.

With the use of methyl groups in place of the *tert*-butyl groups for the amine (**5**), a hydrolysis reaction ensued. The amine remained intact, although protonated and strongly hydrogen bonded to an anionic phenyl phosphinate (**3**), Figure 3. The hydrolysis reaction is shown in Scheme 2. The hexacoordinated intermediate is postulated based on the ^{31}P chemical shift of −90.4 ppm, which is very close to that observed for **2**.

Similar hydrolysis reactions took place with **1** and **2**, but which progressed much more slowly. Presumably the products are analogous to **3** displayed in Scheme 2 and Figure 3. Each hydrolysis process would involve two water molecules in nucleophilic attack at phoshorus and cause the cleavage of P−O bonds. The presence of the amine *tert*-butyl groups for the latter reactions to occur would reasonably impede the approach of water molecules required to engage in cleaving P−O bonds in forming the amine hydrogen bonded cage containing the protonated nitrogen atom.

Structure. The structure of **1** in Figure 1 reveals a phenylphosphonite in a three-coordinate state. The nitrogen atom is 4.019(2) Å from the phosphorus atom and is involved in hydrogen bonding with the OH group of the appended benzyl group. In contrast, the structure of **2** is six coordinate as displayed in the ORTEP III drawing in Figure 2. Here the nitrogen atom has undergone donor action at phosphorus to give an octahedral geometry with a P−N distance of 2.086(2) Å. The OH group, which is present in **1,** now makes up the octahedral arrangement in **2** by providing an additional P−O

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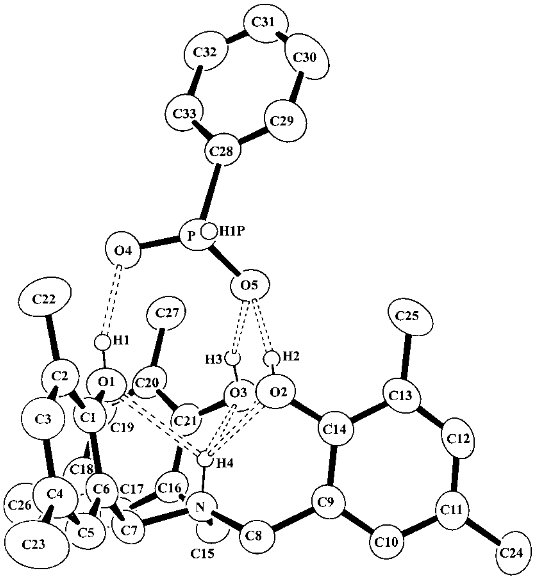


Figure 3. ORTEP diagram of **3**. Hydrogen bonds are shown with dotted lines.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**

P−O(1)	1.642(1)
P−O(2)	1.655(1)
P−C(22)	1.816(2)
O(1)−C(1)	1.402(2)
O(2)−C(14)	1.405(2)
O(3)−C(21)	1.372(2)
O(1)−P−O(2)	99.71(7)
O(1)−P−C(22)	93.64(8)
O(2)−P−C(22)	98.48(8)
C(1)−O(1)−P	128.2(1)
C(14)−O(2)−P	122.4(1)

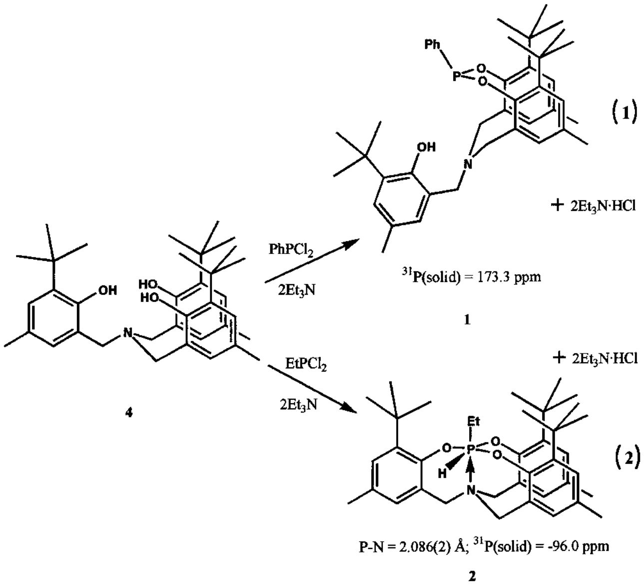
Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**

P−H(1)	1.34(2)
P−O(1)	1.674(2)
P−O(2)	1.739(2)
P−O(3)	1.750(2)
P−C(22)	1.838(2)
P−N	2.086(2)
H(1)−P−O(1)	171.0(8)
H(1)−P−O(2)	90.8(8)
H(1)−P−O(3)	91.6(8)
H(1)−P−C(22)	97.6(8)
H(1)−P−N	79.4(8)
O(1)−P−O(2)	88.15(8)
O(1)−P−O(3)	88.63(8)
O(1)−P−C(22)	91.38(9)
O(1)−P−N	91.54(7)
O(2)−P−O(3)	173.64(8)
O(2)−P−C(22)	90.43(9)
O(2)−P−N	84.36(7)
O(3)−P−C(22)	95.13(9)
O(3)−P−N	90.25(7)
C(22)−P−N	173.94(9)
C(1)−O(1)−P	134.5(1)
C(14)−O(2)−P	127.9(1)
C(21)−O(3)−P	122.8(1)

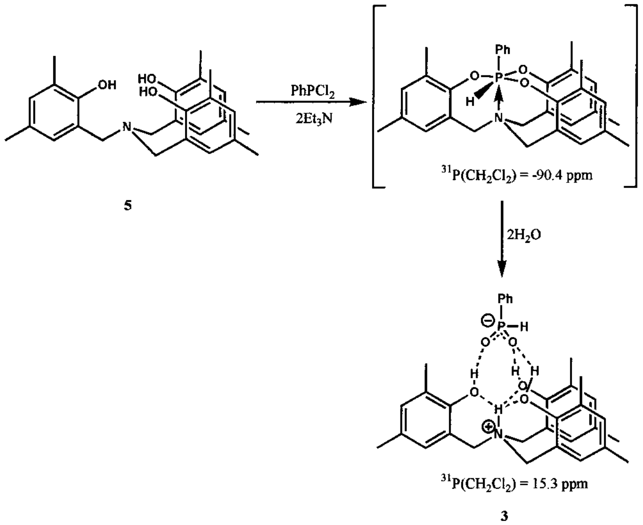
Table 4. Selected Bond Lengths [Å] and Angles [deg] for **3**

P−H(1P)	1.38(3)
P−O(4)	1.493(2)
P−O(5)	1.506(2)
P−C(28)	1.793(2)
H(1P)−P−O(4)	109.5(11)
H(1P)−P−O(5)	105.5(11)
H(1P)−P−C(28)	103.1(10)
O(4)−P−O(5)	117.35(11)
O(4)−P−C(28)	111.93(11)
O(5)−P−C(28)	108.31(11)

Scheme 1



Scheme 2



bond and a P−H bond. A calculation of the extent that the P−N distance is displaced from the sum of the van der Waals radii[16] of 3.47 Å to the sum of the covalent radii[17] of 1.85 Å for phosphorus and nitrogen provides an estimate of the octahedral character of **2** of 85%. Examination of the bond angles for **2** in Table 3 supports this contention. As expected in the higher coordinate structure **2**, the P−O bond distances are longer than those for **1** by 0.072 Å. Further it is noted that the bond angles for **1** are substantially smaller than the tetrahedral angle, averaging 97.28 °. This compression of angles toward trigonal planar is likely associated with the space required for the lone pair at phosphorus to give a pseudotetrahedral geometry for **1**.

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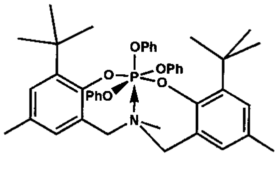
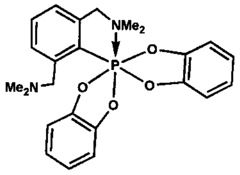
It is instructive to compare the P−N electron pair donor distances for **2** with those of **C**[18] and **D**,[19] which also are octahedral. For phosphorane **C**, the P−N distance is 2.143(3) Å, which is 0.057 Å longer than that for **2**, while the P−N distance for **D** is 2.063(4) Å, which is 0.023 Å shorter than that for **2**. The order observed for the P−N distances is not expected based on electronegativity considerations. **C** is a PO_5 system, **D** a PO_4 system, and **2** a PO_3 system. The longer P−N distance for **C** most likely is associated with the presence of a bicyclic ring system in comparison to the tricyclic atrane ring formation for **2** that results in a greater contribution in strengthening the interaction compared to the opposite effect that electronic factors would allow.



P-N = 2.143(3) Å; 73.4% octa

C[18]

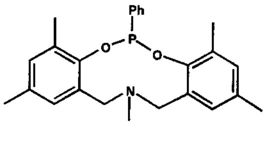


P-N = 2.063(4) Å

D[19]

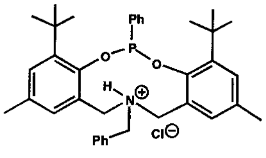
The P−O bond distances (Table 4) for the anionic phenylphosphinate that is hydrogen bonded to the protonated amine in **3** (Figure 3) are nearly equal to one another at an average value of 1.500 Å. Delocalization over the O−P−O unit has resulted in extensive double bond character. This compares with the longer P−O distances (Table 2) for the phenylphosphonite in **1,** near the single bond distance, averaging 1.649 Å. Literature values for the single and double P−O bonds are 1.63 and 1.5 Å, respectively.[20]

NMR Spectroscopy. The comparison of the solid- and solution-state ^{31}P NMR spectra that we obtained allows us to establish an unprecedented transformation for phosphorus, from three to six coordinate, and to show that an equilibrium exists in solution between these two forms for **1.** The solid-state ^{31}P chemical shift for **1** of 173.3 ppm is in the expected region for a tricoordinated phosphinate[21] in agreement with the X-ray analysis. We note that for the related phosphonites **E**[18] and **F**,[18] the solution ^{31}P shifts are close to that of **1**. The solid-state ^{31}P



^{31}P, 168.6 ppm

E[18]

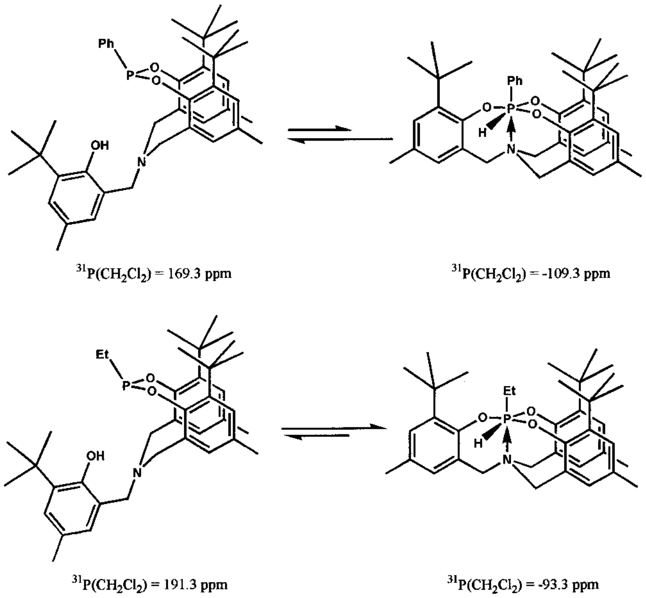


^{31}P, 177.8 ppm

F[18]

chemical shift for **2**, which appears at a much higher field at −96.0 ppm, is in the upper part of the region associated with ^{31}P shifts of oxyphosphoranes that are hexacoordinated as a result of donor coordination. For example, the pentaoxyphosphorane **C**[18] has a ^{31}P shift of −136.1 ppm. As with **1**, the chemical shift is in agreement with the X-ray analysis.

Scheme 3



The solution NMR, however, presents a different story. The ^{31}P spectra of both phosphonite **1** and phosphorane **2** in solution show the presence of two lines. For example, at 293 K for **1** one line is at 169.3 ppm, very close to that shown in the solid state, and one upfield at −109.3 ppm in the hexacoordinate oxyphosphorane region, close to that observed in the solid state for hexacoordinate **2**. Like that observed for **1**, the ^{31}P NMR spectrum for phosphorane **2** shows two resonances, one in each of the two regions. At 293 K, one line appears downfield at 191.3 ppm and the other appears upfield at −93.3 ppm, corresponding to the three- and six-coordinate structural forms, respectively. Scheme 3 portrays the equilibria between the three-coordinate and six-coordinate structures for **1** (upper) and **2** (lower) established by ^{31}P NMR measurements. The arrows indicate the forms that predominate in solution at room temperature and are in agreement with those found by X-ray analysis. ^{31}P solution-state chemical shifts obtained at 293 K are included. These values result from use of the 300 MHz instrument, the same instrument that was used for the ^{31}P solid-state measurements. In addition, there is strong P−H coupling for the resonances assigned to the hexacoordinated forms in solution. The J_{P-H} value for **1** is 683 Hz and that for **2** is 626 Hz.

The variable-temperature ^{31}P NMR spectra for **1** indicate that the amount of the tricoordinate form increases with increasing temperature over the range from 234 to 293 K as noted in the Experimental Section. These results suggest that an equilibrium exists between the tricoordinate and hexacoordinate forms for **1**. For **2**, the ^{31}P spectrum is essentially unchanged with temperature on going from 160 to 290 K and the hexacoordinate form predominates. The form that predominates in solution is consistent with the structural form observed via the X-ray analyses. It may simply be that the phenyl group attached to phosphorus in **1** experiences a steric effect from the close proximity of the neighboring *tert*-butyl groups associated with the amine, thus preventing it from achieving hexacoordination in a phosphorane−phosphatrane environment.

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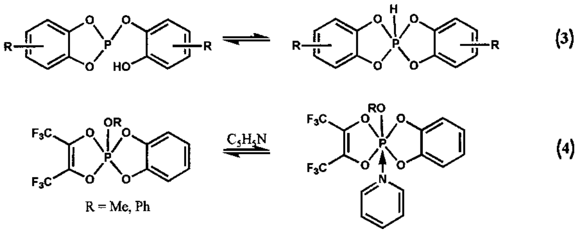
Scheme 4



Comparisons with Other Phosphorus Conversions. Literature[22] dealing with spirophosphoranes, primarily during the 1970s, discussed the conversion and possible equilibria between pentacoordination and hexacoordination and also between tricoordination and pentacoordination. Examples of these conversions are illustrated in eqs 3[22b] and 4,[22c] Scheme 4. In the present work, the presence of an additional coordinating agent, the amine nitrogen atom, supplies the third attachment to phosphorus that allows tricoordinate phosphorus to proceed to a hexacoordinate state in forming the phosphorane−phosphatrane system. This is the first such transformation. The increased electrophilicity enjoyed by phosphorus on traversing from the tricoordinate state in **1** toward the higher valent state found in **2** promotes the coordination of the nitrogen atom to allow hexacoordination to be achieved.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**−**3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA012579M

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