Inorg. Chem. **2002**, *41*, 5235–5240

Inorganic Chemistry
Article

Pseudoheptacoordination and Pseudohexacoordination in Tris(2-*N*,*N*-dimethylbenzylamino)phosphane

A. Chandrasekaran, Natalya V. Timosheva, Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003-9336

Received February 25, 2002

The phosphane $(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3P$ (**1**) upon recrystallization from various solvents yielded the structurally different forms **1A**, **1C**, **1B$_1$**, and **1B$_2$**. Phosphane oxide $(C_6H_4\text{-}2\text{-}CH_2NOMe_2)_3PO$ (**2**) was obtained from **1** by oxidation with hydrogen peroxide. X-ray analysis provided molecular structures for **1A**, **1B$_1$**, **1B$_2$**, and **2**. Phosphanes **1A** and **1B$_1$** have pseudohexacoordinate frameworks as a result of the formation of two P–N donor interactions, **1B$_2$** has a pseudoheptacoordinate geometry due to the presence of three P–N interactions, and **2** resides in a tetrahedral geometry. The presence of the flexible dimethylaminobenzyl group in **1A**, **1C**, **1B$_1$**, and **1B$_2$** is reasoned to be responsible for this variation in coordination geometry. Phosphane oxide **2** has very strong donor oxygen atoms from *N*-oxide groups but they are involved in competition with the presence of hydrogen bonding, which results in the lack of donor coordination. High-resolution ^1H, ^{13}C, and ^{31}P NMR measurements are also reported. The results provide evidence for the low-energy threshold required to allow hypercoordinated phosphorus to alter coordination geometry.

Introduction

In recent work we reported the first example of a seven-coordinate phosphorus compound.[1] This was the hydrochloride salt of tris(8-dimethylaminonaphthyl)phosphane. It has seven associated groups composed of three carbon atoms, three nitrogen atoms, and a proton residing in a tricapped tetrahedral geometry. It is depicted as entry **9** in Chart 3 discussed later in this work. The structure of the precursor to the hydrochloride salt, i.e. tris(8-dimethylaminonaphthyl)-phosphane (compound **3** in Chart 2), revealed pseudohepta-coordination at phosphorus.[1] It contained six ligands coordinated to phosphorus in addition to a lone electron pair.To further examine the ability of phosphorus to form higher coordinated compounds, we prepared tris(2-N,N-dimethylbenzylamino)phosphane. The structure of this compound had been reported earlier and was shown by Corriu and co-workers to exhibit pseudoheptacoordination (compound 1C in Chart 1).[2]Surprisingly we found this compound to exist in other crystalline forms with interesting orientations for one of the dimethylaminomethyl groups that revealed both pseudoheptacoordinate forms, **1B$_2$** in addition to **1C**, and pseudohexacoordinate structures, **1A** and **1B$_1$**.

We believe that this represents the first example in phosphorus chemistry wherein four distinct isomeric forms undergoing a change in coordination number have been structurally characterized. The work demonstrates the ease with which phosphorus can undergo transformations to higher coordinate states and do so while involving only small energy changes. In the area of phosphoryl transfer enzymes, proposed active site transition states may well make use of higher coordinate states other than pentacoordinate ones by means of interactions with donor atoms from nearby amino acid residues. Herein, we report the synthesis, NMR measurements, and X-ray crystallographic studies of the various isomeric forms of tris(2-*N*,*N*-dimethylbenzylamino)phosphane.

Experimental Section

Phosphorus trichloride, *N*,*N*-dimethylbenzylamine (Aldrich), and *n*-butyllithium (EM Science) were used as supplied. Solvents were purified according to standard procedures.[3] All crystallizations were carried out under atmospheric conditions. Solution phosphorus-31

---

* Author to whom correspondence should be addressed. E-mail: rrh@chemistry.umass.edu.

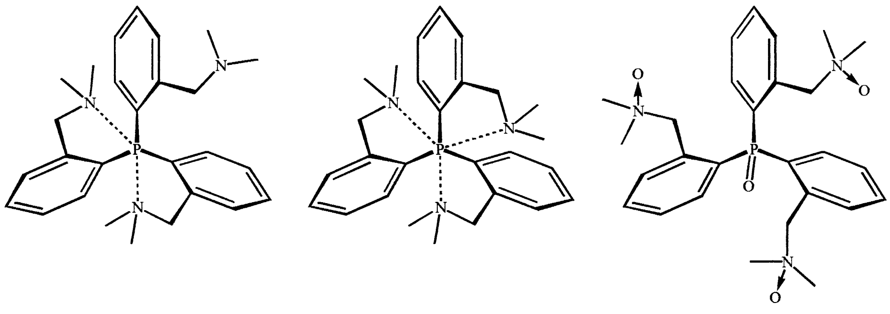
(1) Chandrasekaran, A.; Timosheva, N. V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2000**, *39*, 1338−1339.

(2) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reye, C.; Declercq, J.-P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430.

(3) (a) Riddick, J. A.; Bunger, W. B., Eds.;Organic Solvents. In *Physical Methods in Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

10.1021/ic020153i CCC: $22.00

Chart 1



NMR spectra were recorded on a Bruker DPX300 FT-NMR spectrometer in sweep-off mode, whereas the solid-state MAS ^{31}P NMR spectra were recorded on a Bruker ASX300 FT-NMR spectrometer. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane (for ^1H and ^{13}C) and 85% H_3PO_4 (for ^{31}P). All spectra were recorded at around 23 °C.

Syntheses. $(C_6H_4\text{-}2\text{-}CH_2NMe_2)_3P$(1): Phosphane **1** was synthesized by using a modification of a literature method.[2] A solution of dimethylbenzylamine (10.4 mL, 69.2 mmol) in toluene (110 mL) was added together with *n*-butyllithium (15% in hexane; 28.8 mL, 67.5 mmol) and the mixture stirred for 24 h. Then phosphorus trichloride (2.00 mL, 22.9 mmol) was added and the mixture stirred for an additional period of 18 h at ambient temperature and heated in an oil bath at 110 °C for 2 h. The toluene was removed under reduced pressure and the residue washed with aqueous potassium hydroxide solution (15 g in 100 mL). The residue was extracted with dichloromethane (100 mL), dried with anhydrous magnesium sulfate, and filtered and the solvent removed. The pasty mass was crystallized from ethanol (30 mL). Yield: 1.90 g (19.5%). The crystals obtained from ethanol were the same as those reported in the literature, which we designate here as **1C**.[2] This was definitively established since the cell parameters that we determined were the same for **1C** and that reported in the literature[2] but different from the cell parameters that we established for the other two forms reported here. However, recrystallization of this material from heptane−dichloromethane (1:1) or acetone yielded crystals of **1A**. Form **1B** was also obtained from acetone. Mp for **1A**: 99−101 °C. ^1H NMR: 2.09 (s, 18H), 3.57 (d, $J = 2.5$ Hz, 6H), 6.76 (ddd, $J = 7.6, 3.9, 1.2$ Hz, 3H), 7.07 (td, $J = 7.4, 1.2$ Hz, 3H), 7.27 (td, $J = 7.6, 1.2$ Hz, 3H), 7.49 ppm (ddd, not resolved). ^{13}C NMR: 45.14 (s), 61.78 (d, 21.2), 126.69 (s), 128.11 (s), 128.80 (d, $J = 5.1$ Hz), 134.16 (s), 137.28 (d, $J = 14.0$ Hz, quaternary), 143.34 ppm (d, $J = 23.4$ Hz, quaternary). ^{31}P NMR: −34 (CD_2Cl_2)[2], −34.9 (Et_2O), −36.1 (CH_2Cl_2), −35.1 (acetone), −35.2 (MeOH), and −35.3 ppm (EtOH). Solid-state ^{31}P NMR: −33.8 (**1A**) and −36.3 ppm (**1C**). A mixture of **1A** and **1C** in a 1:2 ratio was used as the sample for the solid-state measurement and the intensity ratio of the peaks identified each component.

$(C_6H_4\text{-}2\text{-}CH_2NOMe_2)_3PO$ (2): A solution of phosphane **1** (0.500 g, 1.15 mmol) and hydrogen peroxide (35%; 1.00 mL, 10.3 mmol) in methanol (30 mL) were stirred at ambient temperatures for about 18 h and then heated in an oil bath at 80 °C for 5 h. On slow evaporation, the solution turned to a thick oil that in few days partially crystallized. It was difficult to purify this material due to the high solubility in methanol and insolubility in other common solvents. ^{31}P NMR (MeOH): 40.3.

X-ray Studies. The X-ray crystallographic studies were performed by using a Nonius Kappa CCD diffractometer and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 23 ± 2 °C for $\theta_{MoK\alpha} = 25°$. All of the 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[4] and SHELXL-97 for refinement.[5] All of the non-hydrogen atoms, except those of solvents, were refined anisotropically. The hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

There were four hydrogen peroxide molecules and 1.5 water molecules in each asymmetric unit of **2**. One of the hydrogen peroxide molecules was disordered at one oxygen (O8S and O8S′) and it was refined in two positions with a 70:30 occupancy ratio. One of the water molecules (O2W) had only half occupancy.

Results and Discussion

The atom-labeling schemes for **1A**, the two molecules of **1B** that we designate as **$1B_1$** and **$1B_2$**, and **2** are given in Figures 1−4, respectively. These figures were made by using ORTEP-III for Windows.[6] The thermal ellipsoids are shown at the 50% probability level and all hydrogen atoms are omitted for clarity. Selected bond parameters are given in Tables 2−4.

Syntheses. Compound **1** was synthesized according to a literature[2] method with phosphorus tribromide and also with use of phosphorus trichloride. The latter change did not increase the yield. The reaction of **1** with hydrogen peroxide resulted in oxidation of the phosphorus atom and all nitrogen atoms to their oxides to give **2**. This compound is soluble only in methanol and presented difficulties in purification. Compound **1** crystallizes in the pseudoheptacoordinated form **1C** from methanol and ethanol or directly from the oily reaction mixture after removal of the lithium salts. However, pseudohexacoordinated form **1A** is obtained when solvents of lower polarity were used, e.g. acetone−methanol, acetone, dichloromethane, or dichloromethane−heptane. Compound **1B** was also obtained from acetone.

^{31}P NMR Spectroscopy. The solution-state phosphorus-31 NMR of **1** did not show any difference between the two

---

(4) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(5) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Gottingen: Gottingen, Germany, 1997.
(6) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 1. Crystallographic Data for Compounds **1** and **2**

compd	**1A**	**1B**	**2**
formula	$C_{27}H_{36}N_3P$	$C_{27}H_{36}N_3P$	$C_{27}H_{36}N_3O_4P \bullet 4H_2O_2 \bullet 1.5H_2O$
fw	433.56	433.56	660.65
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1/n$
cryst size, mm^3	0.60 × 0.50 × 0.25	0.50 × 0.25 × 0.25	0.75 × 0.35 × 0.30
a (Å)	9.0437(2)	9.1686(3)	11.1443(1)
b (Å)	15.2843(4)	18.2790(5)	25.4053(4)
c (Å)	19.1945(5)	15.4814(6)	12.7431(2)
α (deg)	90.00	90.00	90.00
β (deg)	103.134(1)	93.564(1)	113.3568(6)
γ (deg)	90.00	90.00	90.00
V (Å$^{3)}$	2583.8(1)	2589.55(15)	3312.23(8)
Z	4	4	4
D_{calc} (g/cm^3)	1.115	1.112	1.325
$\mu_{Mo\ K\alpha}$ (cm^{-1})	1.24	1.24	1.51
total reflns	4490	8688	5693
reflns with $I > 2\sigma_I$	3595	6908	4394
R^a	0.0605	0.0478	0.1042
$R_w{}^b$	0.1652	0.0982	0.2945

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

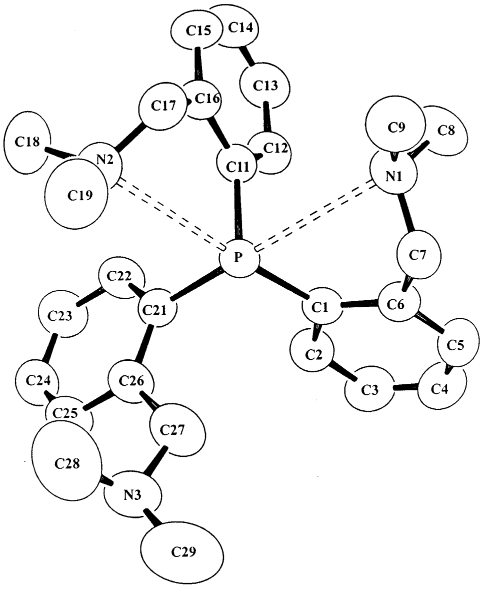


Figure 1. ORTEP diagram of **1A**.

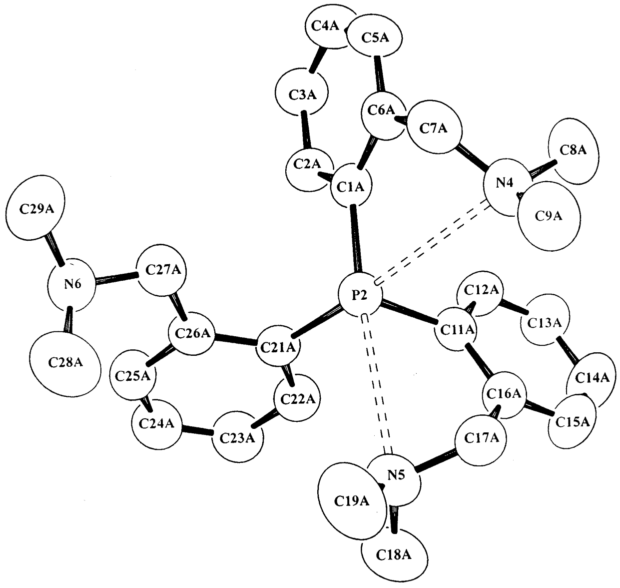


Figure 2. ORTEP diagram of **1B$_1$**.

forms that were found in the solid state (**1A** and **1C**). The values ranged between −37.8 and −39.0 ppm among various polar solvents. However, the solid-state phosphorus NMR exhibited a 2.5-ppm difference between these two different forms. The solid-state spectrum was recorded by using a mixture of **1A** and **1C** in a 1:2 ratio. This enabled the accurate determination of the chemical shift difference and at the same time unambiguous assignment of the signals to each of the forms correctly. The individual values were −33.8 (**1A**) and −36.3 ppm (**1C**) based on the observed intensities. This shows that the pseudoheptacoordinated form has a slightly greater shielding than the pseudohexacoordinated form. The ^{1}H and ^{13}C NMR assignments are consistent with the structural assessment provided by the ^{31}P measurements.

Structures. Solid-state structures of phosphanes **1A** and **1B** and phosphane oxide **2** were determined by single-crystal X-ray diffraction. The reported crystal structure of **1C** has all three nitrogen atoms facing toward the phosphorus atom, making the phosphorus pseudoheptacoordinate (Chart 1).[2] In the lattice of **1A**, one of the nitrogen atoms is facing away from the phosphorus making it pseudohexacoordinate. See Figure 1 and Chart 1. Interestingly, the crystal lattice of **1B** consists of two independent molecules, one of which is **1A** and the other being **1C** (Chart 1). We have designated these as **1B$_1$** and **1B$_2$**, as shown by the ORTEP diagrams in Figures 2 and 3, respectively. The tetrahedral structure of **2** is presented in the ORTEP plot of Figure 4 that includes molecules of crystallization of hydrogen peroxide used as a reactant and molecules of water.

Structural Comparisons. The structures of **1C** and **1B$_2$** are similar to that of tris(8-*N*,*N*-dimethylaminonaphthyl)phosphane **3**, which we reported earlier,[1] in that they all exhibit pseudoheptacoordination (Chart 2). The structures of **1A** and **1B$_1$** are similar to structures **4** and **5** where they all are in pseudohexacoordinted arrangements**.** In tris(2-formylphenyl)phosphane **4**,[7] and the tri-Schiff-base of **4** with

---

(7) Whitnall, M. R.; Hii, K. K.; Thornton-Pett, M.; Kee, T. P. *J. Organomet. Chem.* **1997**, *529*, 35.

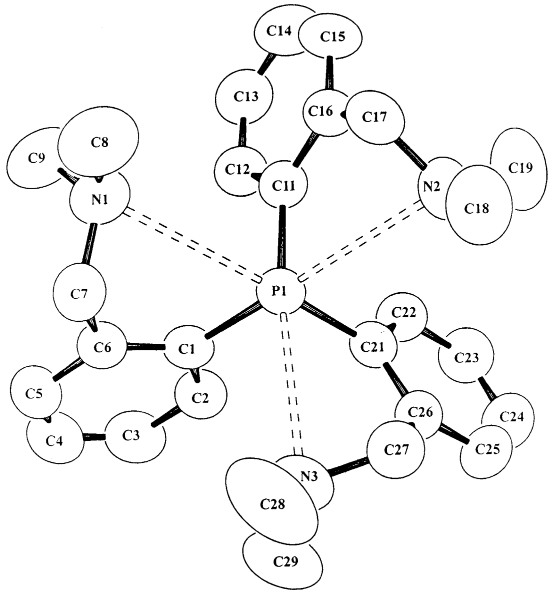


Figure 3. ORTEP diagram of **$1B_2$**.

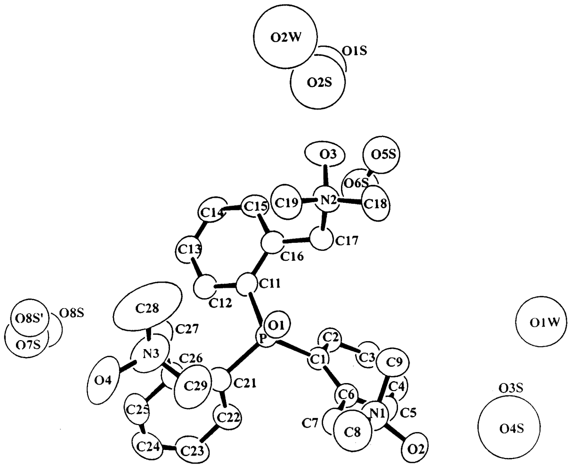


Figure 4. ORTEP diagram of **2**. The atoms with a suffix "S" belong to hydrogen peroxide and those with a suffix "W" belong to water. Atom O3S is behind atom O4S.

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

P−C(1)	1.850(2)	P−N(1)	3.024(2)
P−C(11)	1.838(3)	P−N(2)	2.986(2)
P−C(21)	1.848(2)	P−N(3)	4.415(3)
C(1)−P-C(11)	102.9(1)	C(21)−P−N(2)	80.69(9)
C(1)−P−C(21)	99.8(1)	N(1)−P−N(2)	106.67(7)
C(11)−P−C(21)	101.1(1)	C(7)−N(1)−P	79.2(1)
C(1)−P−N(1)	72.41(9)	C(8)−N(1)−P	121.9(2)
C(11)−P−N(1)	74.36(9)	C(9)−N(1)−P	116.2(2)
C(21)−P−N(1)	169.40(9)	C(17)−N(2)−P	78.3(2)
C(1)−P−N(2)	176.68(9)	C(18)−N(2)−P	127.0(2)
C(11)−P−N(2)	73.8(1)	C(19)−N(2)−P	111.1(2)

1-hydroxy-2-butylamine, i.e. **5**,[8] only two of the three donor atoms in each are directed toward the phosphorus atom while the third donor atom is oriented away from phosphorus in a manner similar to that found in **1A** and **$1B_2$**.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **1B**

P(1)−C(1)	1.849(3)	P(2)−C(1A)	1.853(2)
P(1)−C(11)	1.845(3)	P(2)−C(11A)	1.840(3)
P(1)−C(21)	1.842(3)	P(2)−C(21A)	1.843(2)
P(1)−N(1)	3.095(3)	P(2)−N(4)	3.017(2)
P(1)−N(2)	3.032(3)	P(2)−N(5)	3.007(2)
P(1)−N(3)	3.056(3)	P(2)−N(6)	4.463(2)
C(1)−P(1)−C(11)	102.6(1)	C(1A)−P(2)−C(11A)	101.4(1)
C(1)−P(1)−C(21)	100.3(1)	C(1A)−P(2)−C(21A)	100.9(1)
C(11)−P(1)−C(21)	100.2(1)	C(11A)−P(2)−C(21A)	101.2(1)
C(1)−P(1)−N(1)	71.4(1)	C(1A)−P(2)−N(4)	72.52(9)
C(11)−P(1)−N(1)	74.7(1)	C(11A)−P(2)−N(4)	75.73(9)
C(21)−P(1)−N(1)	168.6(1)	C(21A)−P(2)−N(4)	171.76(9)
C(1)−P(1)−N(2)	175.7(1)	C(1A)−P(2)−N(5)	174.2(1)
C(11)−P(1)−N(2)	74.2(1)	C(11A)−P(2)−N(5)	72.87(9)
C(21)−P(1)−N(2)	77.69(9)	C(21A)−P(2)−N(5)	81.29(9)
C(1)−P(1)−N(3)	81.1(1)	N(4)−P(2)−N(5)	104.79(6)
C(11)−P(1)−N(3)	172.8(1)	C(7A)−N(4)−P(2)	79.2(2)
C(21)−P(1)−N(3)	73.0(1)	C(8A)−N(4)−P(2)	121.4(2)
N(1)−P(1)−N(2)	110.02(7)	C(9A)−N(4)−P(2)	116.6(2)
N(1)−P(1)−N(3)	112.38(7)	C(17A)−N(5)−P(2)	77.7(1)
N(2)−P(1)−N(3)	101.82(8)	C(18A)−N(5)−P(2)	129.3(2)
C(7)−N(1)−P(1)	76.0(2)	C(19A)−N(5)−P(2)	108.3(2)
C(8)−N(1)−P(1)	114.5(2)		
C(9)−N(1)−P(1)	125.0(2)		
C(17)−N(2)−P(1)	77.7(2)		
C(18)−N(2)−P(1)	117.7(2)		
C(19)−N(2)−P(1)	121.1(2)		
C(27)−N(3)−P(1)	77.6(2)		
C(28)−N(3)−P(1)	116.6(2)		
C(29)−N(3)−P(1)	121.7(2)		

Table 4. Selected Bond Lengths [Å] and Angles [deg] for **2**

P−O(1)	1.487(3)	O(3)−N(2)	1.390(6)
P−C(1)	1.816(4)	O(4)−N(3)	1.390(9)
P−C(11)	1.818(4)	P- -N(1)	4.152(4)
P−C(21)	1.820(5)	P- -N(2)	4.224(4)
O(2)−N(1)	1.401(6)	P- -N(3)	4.148(5)
O(1)−P−C(1)	112.4(2)	O(1)−P−C(21)	113.5(2)
O(1)−P−C(11)	111.9(2)	C(1)−P−C(21)	105.6(2)
C(1)−P−C(11)	107.4(2)	C(11)−P−C(21)	105.5(2)

The crystal structures of tris(2-(2′-benzothiazolyl)phenyl)phosphane (**6**) and its phosphane oxide (**7**) also have been studied.[9] The P−N distances in phosphane **6** indicate pseudoheptacoordination. For the corresponding phosphane oxide **7**, only one short P−N distance is observed.[9] With one donor nitrogen atom, the structure is pentacoordinate.

In compound **2**, all the donor oxygens from the amine *N*-oxide groups are oriented away from the phosphorus, resulting in a tetrahedral structure. The *N*-oxide oxygens are hydrogen bonded to three hydrogen peroxide molecules, thus revealing a competition between hydrogen bonding and donor interactions.[10] The orientation of the groups is similar to that found in tris(2′-(1-dimethylaminoethyl)phenyl)phosphane oxide (**8**), where all the dimethylamino groups are oriented away from the phosphorus atom.[11]

Donor Coordination. Table 5 summarizes the extent of donor atom coordination at phosphorus as measured by the N−P distances for the compounds studied here along with their coordination geometries as well as that for **3**−**8** and analogous seven-coordinate phosphorus compounds, **9** and

---

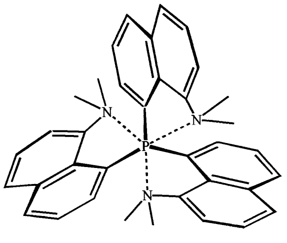
(8) Brunner, H.; Deml, I.; Dirnberger, W.; Nuber, B.; Reisser, W. *Eur. J. Inorg. Chem.* **1998**, 43.

(9) Allen, D. W.; Hibbs, D.; Hursthouse, M. B.; Malik, K. M. A. *J. Organomet. Chem.* **1999**, *572*, 259.

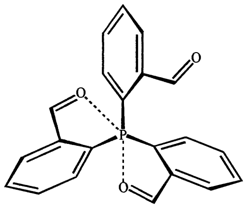
(10) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2000**, *39*, 5683−5689.

(11) Dem'yanovich, V. M.; Shishkina, I. N.; Potekhin, K. A.; Balashova, E. V.; Struchkov, Yu. T.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1998**, *360*, 645.

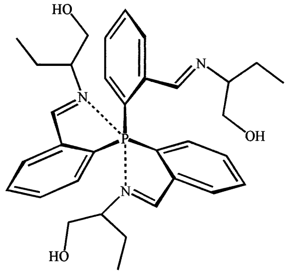
Chart 2



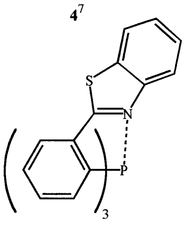
3[1]



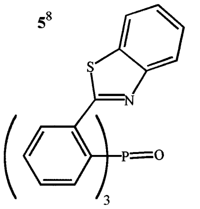
4[7]



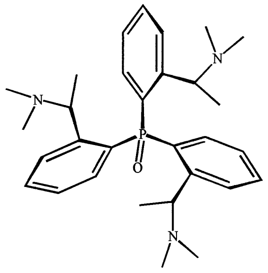
5[8]



6[9]



7[9]



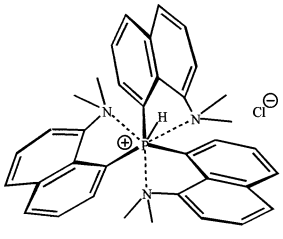
8[11]

Table 5. Nitrogen−Phosphorus Donor−Acceptor Distances (Å) and Coordination Geometries

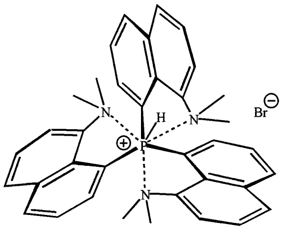
compd				av	%[a]
		pseudohexacoordination			
1A	2.986(2)	3.024(2)		3.005	25.5
$1B_1$	3.007(2)	3.017(2)		3.012	25.0
4[b]	2.795	2.835		2.815	35.2
5(1)	2.776	2.882		2.815[c]	37.7
5(2)	2.719	2.883			
		pseudoheptacoordination			
1C	2.999	3.010	3.071	3.027	24.1
$1B_2$	3.032(3)	3.056(3)	3.095(3)	3.061	21.9
3	2.820(7)	2.828(6)	2.885(6)	2.844	35.9
6	2.851(5)	2.966(5)	3.105(5)	2.974	27.5
		heptacoordination			
9	2.775(6)	2.781(6)	2.882(6)	2.813	39.9
10	2.805(6)	2.844(6)	2.853(6)	2.834	36.5
		pentacoordination			
7	2.888(7)				33.0
		tetracoordination			
2	4.148(5)	4.152(4)	4.224(4)	4.175	
8	4.395	4.517		4.456	

[a] The % refers to the degree of structural displacement from a tricoordinate geometry toward a higher coordinate form as a result of donor action indicated by the heading for each class of phosphanes in this table. The % is obtained by interpolation of the extent of the donor distance traversed from the sum of the van der Waals radii[13] to the sum of the covalent radii[14] for phosphorus and the donor atom. The sums that were used are 3.40 and 1.85 Å for P−N, respectively. For P−O, the sums were 3.335 and 1.83 Å. [b] The donor in **4** is an oxygen atom. [c] This is an average value for the P−N distances for the two independent molecules in the unit cell of **5**.

Chart 3



9[1]



10[1]

10[1]. Compounds **3**, **9**, and **10** contain the dimethyaminonaphthyl group that imparts a greater steric rigidity compared to that present with the use of the dimethylaminobenzyl group found in **1A**, **$1B_1$**, **$1B_2$**, and **1C**[2,12] (Chart 1). Due to the ability of the dimethylaminomethyl group to rotate about the methylene carbon bond, weakly coordinated structures are obtained as noted in Table 5. In the last column of Table 5, the percent displacement from the lower coordinate form to that resulting from donor coordination is given.

Compounds **1A** and **$1B_1$** form pseudohexacoordinate structures and **$1B_2$** and **1C** form pseudoheptacoordinate structures due to the ability of the dimethylaminomethyl group to rotate out of the coordination sphere of phosphorus. By contrast, **9** and **10** (Chart 3) exist as the first examples of seven-coordinate phosphorus compounds[1] although **3**[1] resides in a pseudoheptacoordinate framework. This results in slightly longer N−P donor distances in the less restricted entities.[12] The range of P−N distances in Table 5 for **1A**, **$1B_1$**, **$1B_2$**, and **1C** is 2.986−3.095 Å while the P−N distances for **3**, **9**, and **10** are somewhat shorter, in the 2.775−2.885 Å range. Correspondingly, the latter are displaced further from the phosphane geometries toward the higher coordinate structures than that found for the former set of compounds. The range for **3**, **9**, and **10** is 35.9−37.9% while that for **1A**, **$1B_1$**, **$1B_2$**, and **1C** is 21.9−25.5% as displayed in Table 5.

Phosphanes **4** and **5** (Chart 2) also have less rigid groups but have donor distances in the shorter range, 2.719−2.829 Å, as shown in Table 5. A greater donor character supplied by oxygen coordination in **4** and the presence of hydrogen bonding in **5** may account for the shortening. The displacements toward the higher coordinate structures from the tricoordinate forms reflect this. These are comparable to those found in **3**, **9**, and **10**, all in the range of 35.2−37.9%.

Phosphane **6** encumbered with a rigid group exhibits pseudoheptacoordination. In comparison, the analogous phosphoryl compound **7** is pentacoordinate as a consequence of decreased electrophilicity at phosphorus provided by the presence of the phosphoryl group. Likewise, the phosphane oxides **2** and **8** portrayed in Charts 1 and 2, respectively, have no P−N distances shorter than the van der Waals sum[13] and reside in tetracoordinate geometries even though they possess groups capable of rotating into the coordination sphere of phosphorus.

---

(12) Corriu and co-workers made this point earlier[2] but the structure they analyzed as **3** actually turned out to be **10** on later analysis.[1] Consequently, they were comparing **1C** with **10**.

(13) Sutton, L., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publications 11 and 18; The Chemical Society: London, UK, 1958 and 1965.

(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

The fact that the crystal structure of **1B** that contains the flexible dimethylaminobenzyl group has both the pseudoheptacoordinate and pseudohexacoordinate forms present in the same unit cell shows their closeness in relative energy, in this case governed by crystal lattice effects. Both of these geometries are also found independently in the crystal structures of **1A** and **1C** obtained from the same synthesis but with the use of different crystallizing solvents. The literature shows that **1C** has only one signal for the dimethylamino protons in solution, indicating that an equilibrium exists between the open and higher coordinate closed form. With the use of the more rigid dimethylaminonaphthyl group for **3**, **9**, and **10**, the higher coordinate closed forms are obtained: pseudo-seven-coordinate for **3** and seven-coordinate for **9** and **10**. In solution, two signals are observed for the dimethylamino protons[1] consistent with retention of the geometries found in the solid state. The appearance of these signals demonstrates the presence of structures that are more rigid than those that exist for the phosphanes with the more flexible dimethylaminobenzyl groups.

Acknowledgment. The support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly acknowledged as is the X-ray Structural Characterization Laboratory at the Chemistry Department supported by the University of Massachusetts and the National Science Foundation (grant CHE-9974648). We also acknowledge Dr. L. Charles Dickinson for recording the solid-state MAS ^{31}P NMR spectra

Supporting Information Available: Further crystallographic details and X-ray crystallographic files in CIF format for **1**, **1B**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020153I