1338 *Inorg. Chem.* **2000,** *39,* 1338−1339

Crystal Structures of Tris(8-dimethylaminonaphthyl)phosphane and Its Hydrochloride Salt. The First Seven-Coordinate Phosphorus Compound

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

Department of Chemistry, LGRT 701, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003-4510

Received November 8, 1999

The formation of pentacoordinate[1−3] and hexacoordinate[2−4] phosphorus is well-known. Although the number of examples of the latter coordination is relatively small, recent studies[5] have resulted in a marked increase in hexacoordination compared to pentacoordinate phosphorus.

If one considers heptacoordination, there exist two reports of phosphanes[6,7] that may be considered to be pseudoheptacoordinate as a result of the presence of six nearby ligands and a lone pair occupying a coordination site. These formulations are the phosphane $(C_{10}H_6NMe_2)_3P$,[6] which contains the dimethylaminonaphthyl ligand, and the tris(dithiacarbamato)complex $P[S_2CNMe_2]_3$.[7]

The phosphorus atom in the latter complex is surrounded by six sulfur atoms and a lone pair, resulting in a distorted capped trigonal antiprism. Three short (2.18−2.20 Å) and three long (2.87−3.02 Å) P−S distances are present. The S−P−S angles involving the short P−S distances are near pyramidal, in the range 89.3−91.4°, and those involving the long P−S distances are close to the tetrahedral value, in the range 106.1−112.2°.

Based on our interest in hypercoordination for phosphorus, we have investigated the possibility of placing seven ligands around a phosphorus atom. In the course of this work, we found it ncessary to reinvestigate the previous structural study of $(C_{10}H_6NMe_2)_3P$ reported by Corriu and co-workers[6] as a phosphane.

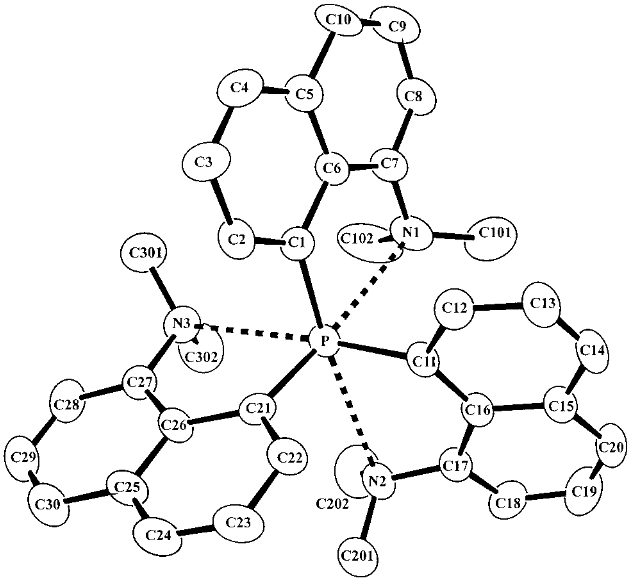

Figure 1. ORTEX[13] diagram of phosphane $(C_{10}H_6NMe_2)_3P$ (**1**) with thermal ellipsoids at the 40% probability level. All hydrogen atoms are omitted for clarity. Bond lengths (Å): P−C(21) = 1.858(8); P−C(11) = 1.859(7); P−C(1) = 1.873(7); P−N(1) = 2.820(7); P−N(3) = 2.828(6); P−N(2) = 2.885(6). Bond angles (deg): C(21)−P−C(11) = 101.7(3); C(21)−P−C(1) = 98.6(3); C(11)−P−C(1) = 99.1(3); C(21)−P−N(1) = 173.7(3); C(11)−P−N(3) = 176.2(3); C(1)−P−N(2) = 172.2(3).

Herein, we report the synthesis[8] and X-ray structure study[9] of tris(8-dimethylaminonaphthyl)phosphane (**1**) and its hydrochloride salt (**2**). Phosphane **1** is pseudoheptacoordinate if one allows a lone pair to assume a coordination site, Figure 1. The structure of **2** is the first example of a heptacoordinate phosphorus compound. It has seven associated ligands composed of three carbon atoms, three nitrogen atoms, and a proton residing in a tricapped tetrahedral geometry, Figure 2. The capping ligands are the three nitrogen atoms with P−N bond lengths averaging 2.813(6) Å. These lengths are larger than the sum of the phosphorus−nitrogen covalent radii of 1.85 Å[10] but significantly shorter than the sum of the van der Waals radii of 3.40 Å.[11] There is no interaction between the P−H unit and the chloride anion. The chloride ion is more than 6 Å away from any P−H contact. The

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(8) (a) The synthesis of **1** followed the earlier method;[6] however, the product was recrystallized from acetone after an alkali treatment which gave crystals for the X-ray study. The alkali treatment consisted of the use of either 10% solutions of NaOH or KOH, followed by washing with water. (b) For the synthesis of **2**, butyllithium (10.0 mL, 1.60 n solution in hexane, 16.0 mmol) was added to a solution of *N,N*-dimethyl-1-naphthylamine (2.60 mL, 15.8 mmol) in ether (250 mL). The solution was stirred for 24 h and then cooled to −70 °C. Phosphorus trichloride (0.40 mL, 4.6 mmol) in ether (70 mL) was added dropwise over 20 min. The reaction mixture was allowed to come to room temperature and stirred for 20 h. The precipitate was filtered off. Solvent was removed from the filtrate, and the residue washed with pentane. The residue was recrystallized from heptane−dichloromethane (25:50 mL) by slow evaporation (yield 0.50 g, 16%). The crystals retained a dichloromethane molecule as a solvate. ^1H NMR ($CDCl_3$): 1.46 (s, 9 H, NMe), 2.81 (s, 9 H, NMe), 7.4 (m, 6 H, aryl), 7.7 (m, 6 H, aryl), 7.99 (d, 7.6 Hz, 3 H, aryl), 8.21 (d, 8.0 Hz, 3 H, aryl). ^{31}P (CH_2Cl_2): 11.6 ppm (J_{PH} = 691 Hz). Two types of N−Me protons are evident, i.e., those attached to C101, C201, and C301 and those attached to C102, C202, and C302.

(9) (a) Details of the experimental procedures have been described previously.[9b] Crystal data for **1**: monoclinic, $P2_1/c$, a = 9.537(3) Å, b = 16.363(4) Å, c = 18.888(4) Å, β = 100.68(2)°, V = 2897(1) Å^3, Z = 4, R = 0.0840, R_w = 0.1797. Crystal data for **2**: monoclinic, $P2_1/c$, a = 14.568(4) Å, b = 12.491(5) Å, c = 19.540(6) Å, β = 104.71(2)°, V = 3439(2) Å^3, Z = 4, R = 0.0822, R_w = 0.2122. The hydrogen atom attached to phosphorus in **2** was located from a difference Fourier and refined isotropically. In the crystal lattice of **2**, there was a dichloromethane molecule with one of the chlorine atoms disordered. The disordered chlorine was refined in three positions with equal occupancies. (b) Chandrasekaran, A.; Sood, P.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1999**, *38*, 3369.

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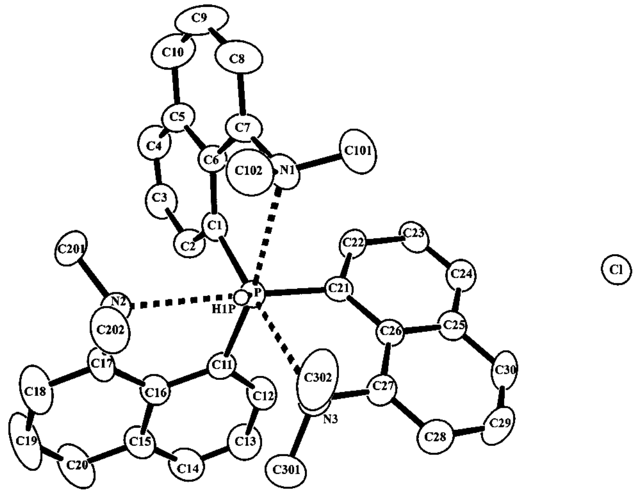

Figure 2. ORTEX[13] diagram of the cation of $(C_{10}H_6NMe_2)_3PH^+Cl^-$ (**2**) with thermal ellipsoids at the 40% probability level. The disordered dichloromethane molecule is not shown. All hydrogen atoms except the hydrogen atom bonded to phosphorus are omitted for clarity. Bond lengths (Å): P−C(11) = 1.804(7); P−C(21) = 1.808(7); P−C(1) = 1.811(8); P−H(1P) = 1.27 (fixed); P−N(1) = 2.882(6); P−N(2) = 2.775(6); P−N(3) = 2.781(6). Bond angles (deg): C(11)−P−C(21) = 107.5(3); C(11)−P−C(1) = 106.0(3); C(21)−P−C(1) = 106.9(3); C(11)−P−H(1P) = 112(3); C(21)−P−H(1P) = 111(2); C(1)−P−H(1P) = 114(3); C(11)−P−N(1) = 169.1(3); C(21)−P−N(2) = 171.9(2); C(1)−P−N(3) = 173.0(3).

shortest interaction is between the chloride ion and H(24), with a distance of 2.74 Å. H(24) is connected to C(24), Figure 2.

The synthesis of **1** reported by Corriu and co-workers[6] gave a yellow powder after attempted crystallization in benzene. The crystals these workers used for the X-ray study were from ethanol and included a molecule of HBr as well as a molecule of ethanol. Their reported X-ray analysis was that of the phosphane **1**. However, the presence of a phosphane with four basic centers led us to believe that HBr would not exist as a separate molecule.

In our experimental work, we found that salt formation was common. Using PCl_3 in a related synthetic procedure[8a] for **1**, we were able to obtain crystals from acetone after an alkali treatment. In our synthesis starting with PCl_3 and dimethylamino-naphthyllithium, as with **1** but without the alkali treatment,[8b] crystals of the phosphane hydrochloride **2** formed. A proton-coupled ^{31}P NMR spectrum confirmed the existence of a P−H bond, J_{P-H} = 691 Hz.

These results prompted us to reexamine the earlier reported crystal data for the phosphane (which we now label **A**) that were deposited at the Fachinformations-Zentrum, Karlsruhe, Germany.[12] We conclude that the earlier report of the X-ray analylsis[6] was not that of the phosphane **1** but that of its hydrobromide salt, **A**.

Table 1 shows the comparison of selected bond parameters for the phosphane **1**, its hydrochloride salt **2**, and the hydrobromide salt **A**. The most prominent entries that differentiate **1** from **2** are the C−P−C angles. Phosphane **1** has an average value of 99.8°, that expected for a pyramidal geometry, whereas the salt **2** has C−P−C angles averaging 106.8°, which are close to the tetrahedral value.

The parameters for **A** are very close to those for **2** and point to a tetrahedral geometry consisting of three carbon atoms and a proton. Likewise, the other parameters for **A** are close to those for the hydrochloride **2** and are not comparable to those for the phosphane **1**. Hence, it is concluded that **A**, originally reported[6] as the phosphane **1**, is in fact the phosphane hydrogen bromide salt.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $(C_{10}H_6NMe_2)_3P$ (**1**), $(C_{10}H_6NMe_2)_3PH^+Cl^-$ (**2**), and $(C_{10}H_6NMe_2)_3PH^+Br^-$ (**A**)[a]

	1	**2**	**A**[b]	**B**[c]
P−N	2.820(7)	2.775(6)	2.805(6)	2.999
	2.828(6)	2.781(6)	2.844(6)	3.010
	2.885(6)	2.882(6)	2.853(6)	3.071
H−N		2.45	2.47[e]	
C−P−C	99.8	106.8	107.2	100.7
N−P−N	104.1	97.5	97.8	
Me1−N−Me2	112.2	111.2	111.2	
P−N−Me1[d]	121.2	117.2	116.6	
P−N−Me2[d]	100.7	108.7	111.6	
C−P−N(trans)	174.0	171.3	171.6	172.1
C−P−N(cis)	78.0	77.6	77.0	75.3

[a] All are average values except those for the P−N distances. [b] Data from refs 6 and 12. [c] Data from ref 6. [d] The methyl groups of each dimethylamino group are not equivalent, which results in two sets, one set of which has P−N−Me angles that average higher than those of the other set. [e] The hydrogen was fixed at a distance of 1.25 Å from phosphorus.

The shorter P−N distances for **2**, 2.813(6) Å (av), compared to that for **1**, 2.844(6) Å (av), most reasonably are associated with the protonated phosphonium atom for **2**, which results in an enhancement in the relative phosphorus atom electrophilicity. Consistent with this rationale are the shorter P−N distances for the hydrobromide **A**, 2.834(6) Å (av), compared to the value for **1** but not as short as that for the hydrochloride **2**, presumably due to the lower electronegativity of bromine compared to chlorine.

Further evidence that the nitrogen atoms are electronically entering into interaction with the phosphorus center, despite their long P−N distances, is found by comparing the crystallographic data of the phosphane $(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3P$ (**B**) obtained by Corriu and co-workers.[6] Data available for this molecule, which contains the more flexible [2-(dimethylaminomethyl)phenyl] ligand, are listed in the last column of Table 1. The C−P−C angles for **B** average to 100.7(5)°, similar to **1**, and confirm its structure as a phosphane as reported.

Conformational flexibility of the ligand unit in **B**, e.g., rotation about the (phenyl) carbon−methylene bond, could place the nitrogen atoms outside the coordination sphere of phosphorus and allow for the absence of any donor interaction. However, for **B**, as with **1**, **2**, and **A**, the trans C−P−N angles are all quite close to a linear arrangement, varying over the range for the averages from 171° to 174° as shown in Table 1. Consistent with this less restrictive feature of the ligand in **B**, somewhat longer P−N distances are evident, the average of which is 3.027 Å, as was pointed out in the original study.[6] This comparison, however, should be made with phosphane **1**, which has the same type of phosphane structure. Here the average P−N distance is 2.844(6) Å.

Acknowledgment. The support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Fachinformations-Zentrum, Karlsruhe Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Depository number CSD-57389 refers to the number reported in the article cited in ref 6.

(13) ORTEX 5e, McArdle, P. Crystallography Centre, Chemistry Department, University College, Galway, Ireland.