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Article

Nitrogen Ligands on Phosphorus(III) Lewis Acceptors: A Versatile New Synthetic Approach to Unusual N–P Structural Arrangements

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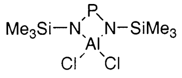
A series of Lewis acid–base adducts of phosphines with amines or pyridines have been prepared and structurally characterized, demonstrating the importance of Lewis acceptor behavior in the chemistry of electron-rich (lone-pair-bearing) centers. The neutral and cationic complexes all contain examples of N–P coordinate bonds that are void of N–P π-bonding and therefore represent definitive N–P single bonds. The structures are examples of N–P topologies that are rare or have not previously been observed, highlighting the synthetic viability of Lewis acid–base coupling in the still developing field of nitrogen–phosphorus chemistry.

Introduction

Nitrogen−phosphorus bonds are perhaps the most extensively studied after carbon−element bonds that define organic chemistry. Although nitrogen−phosphorus compounds exhibit greater structural diversity, including a wide range of coordination numbers, the limits of structure and bonding for N−P compounds have not yet been realized. The coordination chemistry of phosphines as acceptors[1] offers a new synthetic approach to some of the inaccessible bonding arrangements for N−P. Three types of adduct-forming reactions are described here involving Lewis acidic phosphines **1**, **2**, and **3**OTf with amine or pyridine ligands (The molecular drawings illustrate connectivity only, as numerous resonance contributors are possible, but the topology is paramount to this discussion). Traditional Lewis acid−base adducts **1a** and **1b** are formed from **1**,[2] triphenylphosphine ligand exchange from **2a** is responsible for the formation of **2b**, and iminophosphine **3**OTf undergoes an anion displacement reaction with quinuclidine or pyridine to give the cationic complexes **3a** and **3b**.[3] The new complexes have been isolated and structurally characterized, introducing a diverse series of compounds containing definitive single bonds between nitrogen and phosphorus.



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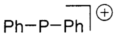
Ph−P−Ph

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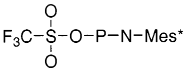
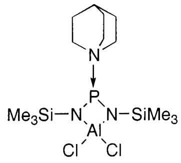
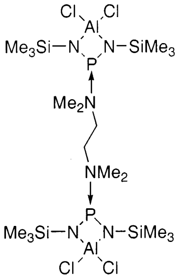

$F_3C-S(=O)_2-O-P-N-Mes^*$

3OTf



1a



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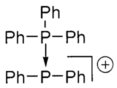

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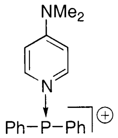

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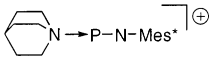
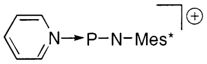


3a



3b

Experimental Procedures

General Information. Chemicals and reagents were obtained from Aldrich Chemical Co. All solvents were degassed using three freeze−pump−thaw cycles. Solids were handled in a nitrogen-filled glovebox. Sample handling and reactions were performed under oxygen- and moisture-free conditions.[4] *N*,*N*,*N*′,*N*′-Tetramethyleth-

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ylenediamine was used as supplied. Dichloromethane was dried at reflux over CaH_2, P_4O_{10}, and CaH_2 again, hexane and toluene were dried over potassium, and diethyl ether was dried over sodium/benzophenone. Deuterated solvents were dried over CaH_2. Pyridine was purified by distillation from NaOH and subsequently CaH_2. 4-(Dimethylamino)pyridine was sublimed in vacuo prior to use. Quinuclidine was obtained by treatment of 1-azoniabicyclo[2.2.2]-octane chloride with 1.0 M $NaOH_{aq}$ followed by extraction by diethyl ether and sublimation in vacuo prior to use. Compounds **5**,[5] **6a**OTf,[6] and **7**OTf[7] were prepared using literature procedures.

Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510 FT-IR spectrometer and are presented as wavenumber (cm^{-1}) maxima with ranked intensities for each absorption given in parentheses and the most intense peak given a ranking of 1. Melting point samples were placed in 1.0 mm (o.d.) Pyrex capillaries, sealed under nitrogen, and measured using an Electrothermal melting point apparatus. Solution and variable-temperature (VT) NMR spectra were recorded on a Bruker AC-250 NMR spectrometer. Solution NMR samples were flame-sealed in 5 mm Pyrex tubes. NMR spectra are referenced to the solvent, and chemical shifts are reported in parts per million relative to that of an external standard (TMS for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P, and CCl_3F for ^{19}F).

Preparative Procedures and Characterization Data. 1a. A solution of **1** (0.91 g, 3.0 mmol) in toluene (10 mL) was quickly added to a solution of quinuclidine (0.33 g, 3.0 mmol) in toluene (10 mL), and the resulting solution was stirred for 10 min. The solvent was reduced to 1 mL, *n*-hexanes (1 mL) was added to give a precipitate that was heated back into solution, and crystals of **1a** were obtained on cooling to −30 °C. Yield: 0.58 g, 1.4 mmol, 47%. Mp: 82.5−85.0 °C. Anal. Calcd (Found): C, 37.7 (37.5); H, 7.5 (7.6); N, 10.1 (10.1). IR (cm^{-1}): 1461(1), 1377(2), 1366(7), 1350(16), 1315(17), 1250(4), 1205(20), 1085(12), 1044(14), 1005(8), 985(6), 908(11), 870(5), 846(3), 760(10), 722(9), 682(19), 637(18), 577(15), 493(13). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, 205; $^{13}C\{^1H\}$, 2.9, 21.5, 25.1, 45.7; ^1H, 0.18 (18H), 1.81 (m, 6H), 2.03 (m, 1H), 2.90 (t $^3J_{HH} = 7.7$ Hz, 6H); solid-state $^{31}P\{^1H\}$ CP-MAS isotropic, 203.

1b. A solution of tetramethylethylenediamine (0.33 g, 2.8 mmol) in toluene (30 mL) was quickly added to a solution of **1** (1.71 g, 5.64 mmol) in toluene (15 mL). The mixture was stirred for 15 min, and a small amount of white precipitate was filtered from the clear solution. Clear colorless crystals identified as **1b** were obtained by concentrating the solution in vacuo. Yield: 0.99 g, 1.4 mmol, 49%. Mp: 91.0−93.5 °C. Anal. Calcd (Found): C, 29.9 (30.1); H, 7.3 (7.1); N, 11.6 (11.7). IR (cm^{-1}): 1464(2), 1404(16), 1377(9), 1267(13), 1254(6), 1248(5), 1092(10), 1002(4), 842(1), 788(7), 754(12), 742(11), 688(15), 638(14), 622(20), 576(8), 504(3), 409(17), 351(18), 310(19). NMR (CD_2Cl_2): $^{31}P\{^1H\}$, 293; $^{13}C\{^1H\}$ 2.2, 44.2; ^1H, 0.24 (36H), 2.44 (12H), 2.76 (4H); solid-state $^{31}P\{^1H\}$ CP-MAS isotropic, 234.

2bOTf. A solution of 4-(dimethylamino)pyridine (0.20 g, 1.8 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **2a**OTf (1.1 g, 1.8 mmol) in CH_2Cl_2 (20 mL), and the clear, colorless solution was stirred overnight at room temperature. The volume was reduced by half in vacuo (15 mL), and addition of *n*-hexane (20 mL) effected immediate precipitation of a fine white powder characterized as **2b**OTf. Yield: 0.39 g, 0.8 mmol, 47%. Mp: 162−164 °C. Anal. Calcd (Found): C, 52.63 (53.65); H, 4.42 (5.10). IR (cm^{-1}): 1635(8), 1569(14), 1462(1), 1404(16), 1377(2), 1351(19), 1270(4), 1264(3), 1223(6), 1147(9), 1054(10), 1031(5), 1011(12), 837(15), 747(13), 723(18), 696(11), 637(7), 518(17), 487(20). NMR: ($CDCl_3$) $^{31}P\{^1H\}$, 88 (s); $^{19}F\{^1H\}$, −82.5 (s, $^1J_{FC} = 129.4$ Hz).

3aOTf. A solution of quinuclidine (0.06 g, 0.6 mmol) in benzene (15 mL) was added to a stirred solution of **3**OTf (0.25 g, 0.57 mmol) in benzene (20 mL) over a period of 15 min, giving an orange solution and precipitate. After being stirred for 1 h, the solution was decanted, and the solid was washed twice with 5 mL portions of benzene and dried under dynamic vacuum. Yield: 0.67 g, 0.12 mmol, 22%. Mp: 176−178 °C. Anal. Calcd (Found): C, 56.71 (57.10); H, 7.69 (8.38); N, 5.09 (5.12). IR (cm^{-1}): 1600(18), 1417(12), 1365(4), 1339(11), 1278(6), 1257(5), 1241(3), 1226(7), 1163(8), 1147(9), 1026(1), 1005(14), 966(15), 923(19), 891(20), 877(17), 833(21), 786(24), 763(13), 752(10), 680(25), 637(2), 571(22), 550(23), 516(16), 450(26). NMR: ^1H, 1.31 (s, 9H), 1.47 (s, 18H), 1.98 (m, 6H), 2.16 (sept, $^3J_{HH} = 3.35$ Hz, 1H), 3.43 (m, 6H), 7.40 (d, $^5J_{PH} = 1.53$ Hz, 2H); $^{13}C\{^1H\}$, 20.8 (s), 24.6 (s), 31.4 (s), 31.5 (s), 35.5 (s), 36.5 (s), 48.1 (s), 121.3 (q, $^1J_{FH} = 319$ Hz), 123.2 (s), 136.9 (d, $^2J_{PC} = 26.2$ Hz), 140.4 (d, $^3J_{PC} = 8.1$ Hz), 150.0 (s); $^{19}F\{^1H\}$, −78.8 (s); $^{31}P\{^1H\}$ 144 (s). Crystals for X-ray diffraction analysis were obtained by liquid−liquid diffusion using CH_2Cl_2 and *n*-hexane.

3bOTf. A solution of pyridine (0.13 g, 1.6 mmol) in benzene (4 mL) was added to a stirred solution of **3**OTf (0.30 g, 0.69 mmol) in benzene (25 mL), and the red solution was stirred for 1 h. Solvent was slowly removed in vacuo (overnight) to a volume of 5 mL, giving red crystals. The solution was decanted, and the crystals of **3b**OTf were washed four times with 5 mL portions of *n*-hexane and dried under dynamic vacuum. Yield: 0.11 g, 0.22 mmol, 31%. Mp: 118−120 °C. Anal. Calcd (Found): C, 55.59 (55.04); H, 6.61 (6.95); N, 5.40 (5.42). IR: 1611(16), 1597(27), 1540(28), 1496(13), 1481(9), 1415(23), 1397(21), 1362(11), 1288(2), 1265(10), 1234(1), 1223(5), 1211(13), 1167(7) 1161(6), 1039(12), 1024(3), 1008(8), 928(29), 887(25), 880(24), 771(15), 758(19), 692(18), 651(17), 638(4), 576(26), 520(20), 515(22), 429(31), 379(30). NMR (CD_2Cl_2): ^1H, 1.34 (s, 9H), 1.36 (s, 18H), 7.41 (d, $^5J_{PH} = 1.8$ Hz, 2H), 7.88 (m, $^3J_{HH} = 7.66$ Hz, $^3J_{HH} = 5.45$ Hz, $^4J_{HH} = 1.43$ Hz, $^5J_{HH} = 0.84$ Hz, 2H), 8.35 (tt, $^3J_{HH} = 7.66$ Hz, $^4J_{HH} = 1.56$ Hz, 1H), 8.82 (m, $^3J_{HH} = 5.45$ Hz, $^4J_{HH} = 0$ Hz, 2H); $^{13}C\{^1H\}$, 30.6 (s), 31.4 (s), 35.2 (s), 36.0 (s), 122.8 (s), 121.0 (q, $^1J_{FC} = 320.0$ Hz), 126.4 (s), 135.4 (d, $^2J_{PC} = 39.1$ Hz), 140.4 (s), 140.5 (s), 145.5 (s), 148.0 (s); $^{19}F\{^1H\}$, −78.9 (s, $^1J_{FC} = 320.4$ Hz); $^{31}P\{^1H\}$ 71 (s).

X-ray Crystallography. Crystals for X-ray diffraction analysis were obtained by slow solvent evaporation (1 day) of the product dissolved in a 1:1 mixture (30 mL) of CH_2Cl_2 and *n*-hexane. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated radiation. The structures were solved by direct methods and refined by full-matrix least squares. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. (See the Notice to Authors.) Unit cell parameters were obtained from the setting angles of high-angle-centered reflections. The choice of space groups was based on systematically absent reflections and was confirmed by the successful solution and refinement of the

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Table 1. Crystal Data for **1a**, **1b**, **2b**OTf, **3a**OTf, and **3b**OTf

	1a	**1b**	**2b**OTf	**3b**OTf	**3a**OTf
empirical formula	$C_{13}H_{31}N_3PAlCl_2Si_2$	$C_{18}H_{52}N_6P_2Al_2Cl_4Si_4$	$C_{19}H_{20}F_3N_2O_3P$	$C_{24}H_{34}F_3N_2O_3PS$	$C_{26}H_{42}F_3N_2O_3PS$
fw	414.44	722.71	456.42	518.57	550.65
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$
a (Å)	6.900(9)	10.622(3)	10.826(3)	10.298(3)	29.469(2)
b (Å)	19.442(8)	11.580(4)	23.633(4)	16.842(4)	10.0650(6)
c (Å)	17.25(9)	9.194(5)	8.410(3)	8.835(2)	9.7745(6)
α (deg)		105.22(4)		95.69(2)	90
β (deg)	96.85(8)	95.90(4)		112.24(2)	90
γ (deg)		63.56(2)		80.66(2)	90
V (Å^3)	2298(4)	977.1(7)	2151.7(9)	1398.4(6)	2899.2(3)
Z	4	1	4	2	4
D_c (Mg m^{-3})	1.198	1.228	1.409	1.231	1.262
radiation, λ (Å)	Cu Kα, 1.54178	Cu Kα, 1.54178	Mo Kα, 0.71069	CuKα, 1.54178	MoKα, 0.71069
diffractometer	AFC5R	AFC5R	AFC5R	Rigaku AFC5R	Bruker 1KCCD
temp (K)	293(2)	293(2)	238(2)	293(2)	193(2)
R1^a ($I > 3\sigma(I)$)	0.0547	0.0424	0.068	0.057	0.0530
wR2^a ($I > 3\sigma(I)$)	0.0611	0.0471	0.070	0.060	0.1294
GOF S	1.26	1.601	1.95	1.95	1.038

[a] $R1 = (3|F_o| - |F_c|)/(3|F_o|)$. $wR2 = [(3w(F_o^2 - F_c^2)^2)/(3w(F_o^2)^2)]^{1/2}$.

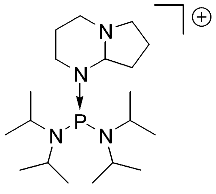
structures. All data were collected using the $\omega\angle 2\theta$ scan technique. The intensities of three representative reflections were measured after every 150 reflections. The crystal data are given in Table 1.

Results and Discussion

The donor or ligand label for electron-rich (defined as lone-pair-bearing) phosphines in coordination chemistry is somewhat restrictive in the context of the developing series of compounds involving coordinatively unsaturated phosphines as Lewis acids.[1] Complexes of phosphines with arene,[8] carbene,[9] amine,[2,10,11] imine,[3,12] phosphine,[13−16] and gallane[17] ligands have been reported, demonstrating the potential synthetic versatility of coordination chemistry for the discovery of new element−phosphorus bonds and new bonding environments for phosphorus. We have now expanded the coordination chemistry of three phosphine Lewis acceptors, **1**, **2**, and **3**OTf, using amines and pyridines as ligands.

Rapid reactions are observed at room temperature for mixtures of iminophosphine **1** with quinuclidine or tetramethylethylenediamine, as well as mixtures of iminophosphine **3**OTf with quinuclidine or pyridine. Solution ^{31}P NMR spectra of reaction mixtures show prominent species (>90%) that have been isolated by slow evaporation of the solvent. Their identities have been confirmed by spectroscopic and X-ray crystallographic characterization as **1a**, **1b**, **3a**OTf, and **3b**OTf, respectively. ^{31}P NMR spectra of the reaction between **2a**OTf and 4-(dimethylamino)pyridine (DMAP) reveal quantitative release of triphenylphosphine, and the only other signal (88 ppm) in the spectra is assigned to **2b**OTf on the basis of spectroscopic and X-ray crystallographic data for isolated material. Formation of **2b** can be described as a ligand exchange at the diphenylphosphenium center **2**.

The solid-state molecular structures of **1a** and **1b**, and the cations of **2b**OTf, **3a**OTf, and **3b**OTf, are illustrated in Figure 1. N−P bond lengths and bond angles at phosphorus are presented in Table 2 in comparison with those features for the related complexes **4**, **5**, **6**, **7**, and **8**. Although the internuclear N−P distance varies considerably from complex to complex, the interaction between phosphorus and nitrogen is definitive in all cases. The N(ligand)−P distances in **1a**, **1b**, **2b**OTf**,** **3a**OTf, and **3b**OTf are consistently longer than those in aminophosphines, which are associated with a planar geometry at nitrogen and are considered to involve a degree of N−P pπ−dπ-bonding. The coordinate bonds in the new complexes are better compared with the idealized N−P single bond [1.800(4) Å] in the phosphoramidate anion $[O_3PNH_3]^-$,[18]



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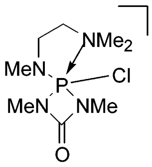

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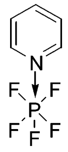

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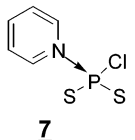

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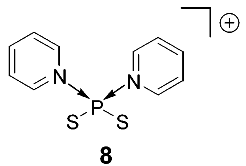

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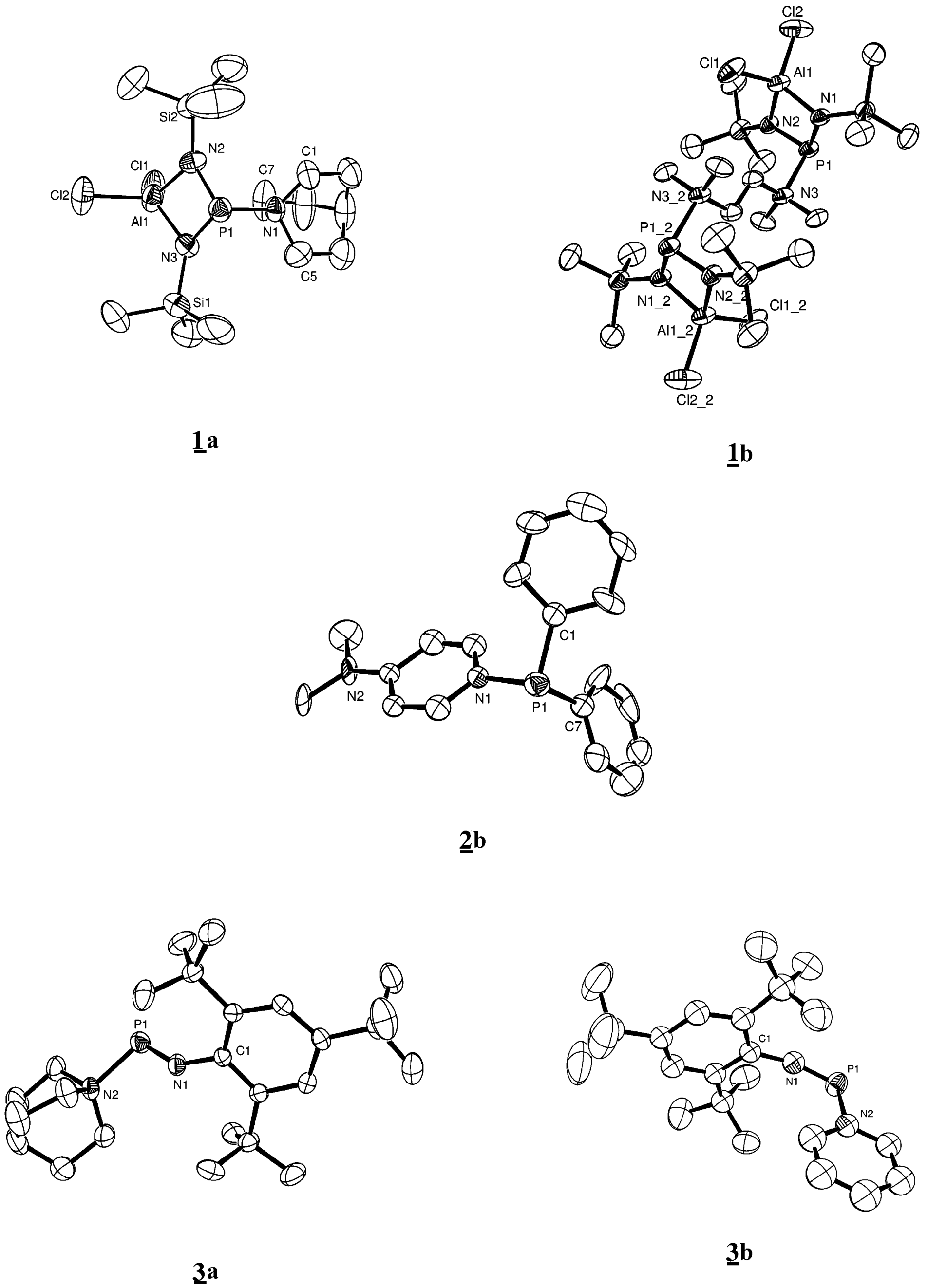

1a

1b

2b

3a

3b

Figure 1. View of the molecular structures for **1a** and **1b**, and the cations of **2b**OTf, **3a**OTf, and **3b**OTf. Ellipsoids are at the 50% probability level, and hydrogen atoms are omitted for clarity, as are the anions in **2b**OTf, **3a**OTf, and **3b**OTf.

Table 2. N−P Bond Lengths (Å) and Angles (deg) at Phosphorus for **1a**, **1b**, **2b**OTf, **3a**OTf, and **3b**OTf and Comparative Data for Related Compounds

	P−N	angles at P	ref
1a	2.038(9)	93.9(5), 99.8(4), 98.9(5)	this work
1b	2.110(6)	94.3(3), 99.2(2), 100.7(3)	this work
2bOTf	1.789(1)	104.4(6), 104.0(7), 99.3(6)	this work
3bOTf	1.958(8)	107.8(4)	this work
3aOTf	1.933(2)	103.7(1)	this work
4	1.796(3)	101.6(2), 109.3(2), 99.1(2)	12
5	1.944(2)		19
6	1.885(4)		20
7	1.849(2)		21
8	1.768(14), 1.831(3)		22

in which a quaternary nitrogen center precludes π-bonding with phosphorus.

The complexes listed in Table 2 can all be considered to involve a coordinate N−P interaction. Complex **4** is formally a pyridine-like ligand on a cationic phosphine (phosphenium)[12] and is a direct analogue of **2b**, while **5**,[19] **6**,[20] **7**,[21] and **8**[22] involve phosphorus in a higher formal oxidation state and coordination number. The N−P coordinate bonds are

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Table 3. Comparison of ^1H $\Delta\delta$ (δ(coordinated ligand) − δ(free ligand), ppm) for **1a**, **1b**, **2b**OTf, **3a**OTf, and **3b**OTf

compd	CH_3	α-^1H	β-^1H	γ-^1H
2bOTf	0.83	0.29	1.09	
1a		0.33	0.38	0.14
1b	0.20			
3bOTf		0.30	0.80	0.72
3aOTf		0.67	0.51	0.50

predictably longer in the neutral complexes **1a**, **1b**, **6**, and **7** than observed for the cations **2b, 3a**, **3b**, **4**, **5**, and **8**, presumably due to the relatively stabilized acceptor orbital at the phosphorus center in the cations.

Consistent with a bonding model retaining a lone pair of electrons at the phosphine acceptor site, all complexes exhibit a distinctly pyramidal geometry at phosphorus. The bis-acid arrangement of **1b** shows equivalent N−P interactions at each end of the bifunctional donor. The geometry at the phosphorus centers in complexes **1a**, **1b**, **2b**, and **4** is typical of a phosphine, consistent with the retention of a nonbonding pair (lone pair) of electrons, and validating the Lewis acid assignment for the phosphine in these complexes.

Interpretation of the ^{31}P NMR chemical shifts for complexes **1a**, **1b**, **2b**OTf, **3a**OTf, and **3b**OTf with those of the free Lewis acids is speculative on the basis of the limited data available. Nevertheless, it is important to note that solution chemical shifts are typically deshielded from those of the free phosphine acid. Solution ^1H NMR spectra of complexes **1a**, **1b**, **2b**OTf**, 3a**OTf, and **3b**OTf show that the protons associated with the ligand are consistently deshielded with respect to those for the free ligand (Table 3). The δ(^1H) and δ(^{13}C) resonances corresponding to the ligand show no indication of coupling with phosphorus in the complexes.

The compounds described above represent important examples of structural arrangements for N−P that have not been previously observed or are rare. Potential structural options for N−P can be illustrated by the topological catalogue of coordination numbers for nitrogen and phosphorus presented in Figure 2. Illustration **1.1** describes the diatomic molecule, and **3.3** represents an aminophosphine, one of the most common arrangements in N−P chemistry. Iminophosphoranes (phosphine imides),[23] represented by **2.4**, are well established, and the chemistry of iminophosphines[24] has developed rapidly in recent years to highlight the importance of **2.2**. We have exploited the Lewis acidity of coordinatively unsaturated phosphines to prepare and isolate compounds exhibiting the first examples of representatives **3.2**, **4.2**, and **4.3**, demonstrating coordination chemistry of phosphorus(III) as a versatile synthetic approach.

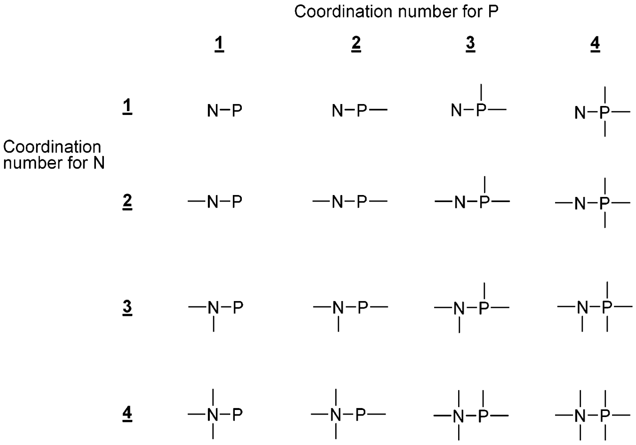

Figure 2. Structural topologies for the N−P(III) unit.

Conclusions

A series of Lewis acid−base adducts of phosphorus(III) compounds with amines or pyridines have been prepared and structurally characterized. Complexes of **1**, **2**OTf and **3**OTf demonstrate the synthetic value of the Lewis acceptor behavior of electron-rich (lone-pair-bearing) centers and contain examples of N−P coordinate bonds that are void of N−P π-bonding. The structures are examples of N−P topologies that are rare or have not previously been observed, highlighting the synthetic importance of Lewis acid−base coupling in the still developing field of N−P(III) chemistry.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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