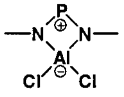
Iminophosphine Cycloaddition Reactions of a Diazaphosphoniaaluminatacyclobutane and a Novel Intramolecular Phosphiridine P→P Coordination

Neil Burford* and Daren J. LeBlanc

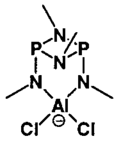
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

Received December 1, 1998

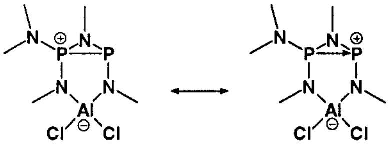
The chemistry of phosphorus is experiencing a new evolutionary phase by virtue of the development and reactivity studies of low coordinate environments.[1] Heterocycle **1**[2] (illustrations are drawn with omission of $SiMe_3$ substituents on nitrogen for clarity)



1



2



3a **3b**

contains a particularly interesting phosphorus environment which exhibits unusual reactivity.[3,4] As part of our assessment of the unusual acceptor capabilities of phosphorus in **1**,[4] we have discovered a novel reaction involving two molecules of **1**, which is facilitated by the simple anions Cl^- and CN^-. The process is mimicked by a reversible quantitative cycloaddition reaction of **1** with $(Me_3Si)_2NPNSiMe_3$ featuring a phosphiridine forming intramolecular cross-ring P→P coordinative interaction.

Equimolar reaction mixtures of **1** with PPh_4Cl or PPh_4CN exhibit similar ^{31}P NMR spectra, with the rapid appearance of a singlet at 190 ppm assigned to anion **2**, which has been isolated as the tetraphenylphosphonium salt.[5] The structure of the anion in the solid state (Figure 1a) is best described as a P_2N_2 phosphetidine (phosphazane) with a diazaaluminate bridge of the chemically equivalent phosphorus centers, consistent with analogous bridged phosphazanes.[6] The identification of $[PPh_4][AlCl_4]$, as a coproduct of the reaction, has been confirmed by X-ray crystallographic analysis,[7] and NMR studies of the reaction mixture imply a quantitative reaction of **1** with PPh_4Cl according

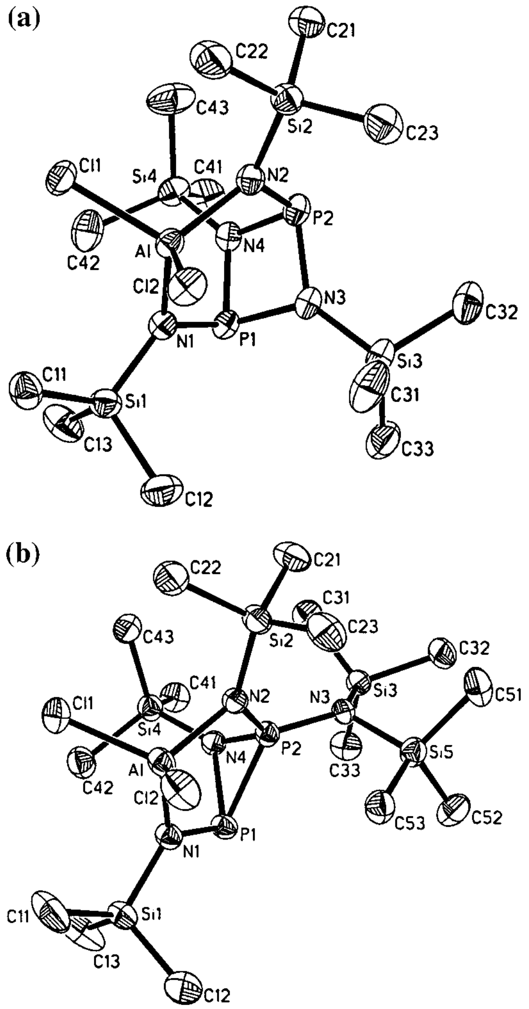


Figure 1. Solid-state structure of (a) the anion of $[PPh_4][\mathbf{2}]$ and (b) **3**. Displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

---

* Corresponding author. E-mail: Burford@is.dal.ca.

(1) Regitz, M.; Scherer, O. J., Eds. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: Stuttgart, Germany, 1990.

(2) Niecke, E.; Kröher, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 692−693. Niecke, E.; Kröher, R. *Z. Naturforsch.* **1979**, *34B*, 837−842. Pohl, S. *Chem. Ber.* **1979**, *112*, 3159−3165.

(3) Losier, P.; Burford, N.; Mason, S.; Sereda, S. V.; Cameron, T. S. *Phosphorus Sulfur* **1994**, *93−94*, 463−464. Burford, N.; Losier, P.; Mason, S.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 5613−5614.

(4) Burford, N.; Losier, P.; Bakshi, P. K.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1996**, 307−308.

(5) A mixture of $[PPh_4]Cl$ (0.72 g, 1.9 mmol) and KCN (0.13 g, 1.9 mmol) in CH_2Cl_2 (30 mL) was stirred at reflux for 20 min and at room-temperature overnight. The filtered solution was added to a solution of **1** (0.53 g, 1.7 mmol) in toluene (30 mL) and stirred overnight. The reaction mixture was filtered and reduced in volume to 20 mL, and pentane (25 mL) was slowly added, giving a mixture of two crystalline solids, which were Pasteur separated and characterized as $[PPh_4][\mathbf{2}]$ and $[PPh_4][AlCl_4]$. Selected characterization data for $[PPh_4][\mathbf{2}]$: dp: 145−160 °C; ^{31}P NMR (CH_2Cl_2) δ 190 (s, 2), 23 (s, PPh_4). Crystal data: $C_{36}H_{56}AlCl_2N_4P_3Si_4$, $M = 848.00$, monoclinic, $P2_1/n$, $a = 14.6485(3)$ Å, $b = 18.6224(4)$ Å, $c = 17.3207(4)$ Å, $\beta = 98.6260(10)°$, $V = 4671.47(18)$ Å^3, $T = 150(2)$ K, $Z = 4$, $\mu = 0.392$ mm^{-1}, 46 910 measured reflections, 9514 independent reflections, 6404 reflections with $I > 2\sigma(I)$, 463 refined parameters, $R[F^2 > 2\sigma(F^2)] = 0.0457$, $wR(F^2) = 0.1361$, $S = 1.022$.

(6) Scherer, O. J.; Wolmershäuser, G.; Conrad, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 404−405. Scherer, O. J.; Anselmann, R.; Sheldrick, W. S. *J. Organomet. Chem.* **1984**, *263*, C26−C29. Kumravel, S. S.; Krishnamurthy, S. S.; Cameron, T. S.; Linden, A. *Inorg. Chem.* **1988**, *27*, 4546−4550. Linti, G.; Nöth, H.; Schneider, E.; Storch, W. *Chem. Ber.* **1993**, *126*, 619−629. Scherer, O. J.; Jürgen, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503−504. Reddy, V. S.; Krishnamurthy, S. S.; Nethaji, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1933−1938.

(7) Burford, N.; LeBlanc, D. J.; Lough, A. J. *Acta Crystallogr.* **1998**, *C54*, IUC9800040.

10.1021/ic9813718 CCC: $18.00

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4][\mathbf{2}]$ and **3**

	$[PPh_4][\mathbf{2}]$	**3**
P1−P2	2.5553(11)	2.1051(13)
P1−N1	1.681(2)	1.673(3)
P1−N3	1.738(2)	−
P1−N4	1.731(2)	1.874(3)
P2−N2	1.672(2)	1.626(3)
P2−N3	1.730(3)	1.640(3)
P2−N4	1.723(2)	1.637(3)
N1−P1−N3	104.03(11)	−
N1−P1−N4	102.97(12)	108.33(14)
N3−P1−N4	82.94(11)	−
N2−P2−N3	104.82(12)	116.42(15)
N2−P2−N4	102.76(12)	114.63(15)
N3−P2−N4	83.40(12)	118.25(15)
P1−N4−P2	95.43(11)	73.34(12)
P1−N3−P2	94.95(12)	−
N4−P1−P2	−	48.15(9)
N4−P2−P1	−	58.51(10)

to reaction eq 1. We speculate that the smaller (sterically

$$2\,\mathbf{1} + 2Ph_4PCl \rightarrow Ph_4P[\mathbf{2}] + Ph_4P[AlCl_4] \qquad (1)$$

unrestricted) chloride or cyanide anions attack the more electrophilic and Lewis acidic aluminum center of **1**, in contrast to the observations for reactions of **1** with quinuclidine and *N*,*N*-tetramethylethylenediamine, which involve $N\rightarrow P$ coordinative interactions.[4] The result is formal abstraction of $AlCl_2^+$ (ultimately as $[AlCl_4]^-$) from **1**, formally releasing the $[Me_3SiNPNSiMe_3]^-$ anion which ultimately inserts into a second molecule of **1** effecting ring expansion.

To obtain a better understanding of eq 1, we have examined the reaction of **1** with $(Me_3Si)_2NPNSiMe_3$, which analogously results in the insertion of the iminophosphine (N═P) unit into the N−P bond or N−Al bond (considering the precedent for lability of the N−Al bond)[3] of **1** to give cycloadduct **3** (eq 2).[8]

$$(Me_3Si)_2NPNSiMe_3 + \mathbf{1} \rightleftharpoons \mathbf{3} \qquad (2)$$

The solid-state structure of **3** (Figure 1b) reveals a bicyclic arrangement imposed by a cross-ring P−P interaction that defines an azadiphosphiridine (PPN) heterocycle.

As documented by the comparative structural parameters in Table 1, adduct **3** can be considered as the formal addition of a $[SiMe_3]^+$ unit at N3 of anion **2** which results in significant structural changes, including opening of the phosphetidine heterocycle, contraction of all three P2−N bonds, close to planarisation of P2 within the N2, N3, N4 triangle [sum of the N−P2−N angles is 349.30(15)°], an extension of the P1−N4 bond, acute reduction of the P1−N4−P2 angle, and substantial shortening of the P−P vector. The P1−P2 bond distance [2.1051(13) Å] and P1−N4−P2 angle [73.34(12)°] of **3** are the smallest yet observed for crystallographically characterized azadiphosphiridines.[9]

The cluster-like cycloadduct **3** results from an unprecedented ring-opening and three bond forming cycloaddition. ^{31}P NMR spectra reveal that **3** achieves retro-dissociation equilibrium in solution (with ring contraction to give **1**) above RT according to eq 2, and only at −63 °C are the two doublets assigned to **3** observed independently, indicating quantitative association. The new heterocycle can be interpreted in terms of two resonance structures: a phosphine (P1) phosphonium (P2) aluminate **3a** or a phosphenium (P1) aluminate with an intramolecular phosphine (P2) coordination **3b** representing a new contribution to the developing coordination chemistry of phosphorus as an acceptor.

The donor or ligand label for electron rich sites such as phosphines is becoming somewhat of a misnomer with the realization of $N\rightarrow P$,[10] $P\rightarrow P$,[11] $O\rightarrow P$,[12] and $S\rightarrow P$[13] coordination complexes as well as π-arene complexes[14] and examples of halide ion addition to halophosphines to give $[PX_4]^-$ salts.[15] Compound **3** is a new dramatic illustration of such an interaction, effecting a fold in the six-membered ring and planarization of the phosphine donor.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Killam Trust of Dalhousie University for funding, the Atlantic Region Magnetic Resonance Centre for the use of instrumentation, and Dr. Alan Lough of the University of Toronto for collecting the X-ray data.

Supporting Information Available: Complete crystallographic details, in CIF format, for $[PPh_4][\mathbf{2}]$ and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9813718

---

(8) $(Me_3Si)_2NPNSiMe_3$ (2.74 g, 9.84 mmol) in toluene (30 mL) was added to **1** (2.80 g, 9.23 mmol) in toluene (30 mL) and stirred for 1 h. The volume was reduced to 15 mL, and pentane (20 mL) was slowly added, giving a white crystalline material characterized as **3** (yield = 1.40 g, 24%). Anal. Calcd: C, 30.97; H, 7.80; N, 9.63; Cl, 12.19. Found: C, 30.98; H, 7.88; N, 9.68; Cl, 12.11. Mp 98−105 °C; ^{31}P NMR (CH_2Cl_2), 37 °C, δ 380 [s, 1], 327 [s, $(Me_3Si)_2NPNSiMe_3$], 14 (d, $J_{P-P} = 94$ Hz), −9 (d, J_{P-P} unresolved); −63 °C: δ 11 (d, $J_{P-P} = 91$ Hz), −10 (d, $J_{P-P} = 91$ Hz). Crystal data: $C_{15}H_{45}AlCl_2N_4P_2Si_5$, $M = 581.82$, monoclinic, *Cc*, $a = 22.2416(14)$ Å, $b = 8.9070(7)$ Å, $c = 18.5029(13)$ Å, $\beta = 119.5280(10)°$, $V = 3189.4(4)$ Å^3, $T = 150(2)$ K, $Z = 4$, $\mu = 0.531$ mm^{-1}, 11 799 measured reflections, 6229 independent reflections, 4795 reflections with $I > 2\sigma I$, 295 refined parameters, $R[F^2 > 2\sigma(F^2)] = 0.0414$, $wR(F^2) = 0.0910$, $S = 0.979$.

(9) Niecke, E.; Gudat, D.; Symalla, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 834−835. Niecke, E.; Nickloweit-Lüke, A.; Rüger, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 385−386. Roques, C.; Mazieres, M. R.; Majoral, J. P.; Sanchez, M. *Tetrahedron Lett.* **1988**, *29*, 4547−4550. Niecke, E.; Nickloweit-Lüke, A.; Rüger, R.; Krebs, B.; Grewe, H. *Z. Naturforsch.* **1981**, *36B*, 1566−1574. Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Organometallics* **1986**, *5*, 2376−2377. Barion, D.; Gärtner-Winkhaus, C.; Link, M.; Nieger, M.; Niecke, E. *Chem. Ber.* **1993**, *126*, 2187−2195. Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1034−1036. Niecke, E.; Lysek, M.; Symalla, E. *Chimia* **1986**, *40*, 202−205. Niecke, E.; Kramer, B.; Nieger, M.; Severin, H. *Tetrahedron Lett.* **1993**, *34*, 4627−4630.

(10) Bouhadir, G.; Reed, R. W.; Reau, R.; Bertrand, G. *Heteroatom Chem.* **1995**, *6*, 371−375. Reed, R.; Reau, R.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 399−401. Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 4945−4952. Liu, X. D.; Verkade, J. G. *Inorg. Chem.* **1998**, *37*, 5189−5197. Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reyé, C.; Declercq, J. P.; Dubourg, A. *J. Organomet. Chem.* **1996**, *511*, 171−175.

(11) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Wu, G. *Organometallics* **1997**, *16*, 4712−4717. Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460−5467. Kaukorat, T.; Neda, I.; Schmutzler, R. *Coord. Chem. Rev.* **1994**, *137*, 53−107. Vogt, R.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1993**, *126*, 1271−1281. Ernst, L.; Jones, P. G.; Look-Herber, P.; Schmutzler, R. *Chem. Ber.* **1990**, *123*, 35−43. Bettermann, G.; Schmutzler, R.; Pohl, S.; Thewalt, U. *Polyhedron* **1987**, *6*, 1823−1831. Niecke, E.; David, G.; Detsch, R.; Kramer, B.; Nieger, M.; Wenderoth, P. *Phosphorus Sulfur* **1993**, *76*, 25−28. Sanchez, M.; Réau, R.; Dahan, F.; Regitz, M.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1996,** *35*, 2228−2230. David, G.; Niecke, E.; Nieger, M.; Radseck, J.; Schoeller, W. W. *J. Am. Chem. Soc.* **1994**, *116*, 2191−2192. Alder, R. W.; Ellis, D. D.; Hogg, J. K.; Martin, A.; Orpen, A. G.; Taylor, P. N. *J. Chem. Soc., Chem. Commun.* **1996**, 537−538. Alder, R. W.; Ellis, D. D.; Orpen, A. G.; Taylor, P. N. *J. Chem. Soc., Chem. Commun.* **1996**, 539−540.

(12) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3862−3867.

(13) Holmes, R. R. *Acc. Chem. Res.* **1998**, *31*, 535−542.

(14) Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1995**, *14*, 1578−1585.

(15) Christe, K. O.; Dixon, D. A.; Mercier, H. P. A.; Sanders, J. C. P.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.* **1994**, *116*, 2850−2858. Dillon, K. B.; Platt, A. W. G.; Schmidpeter, A.; Zwaschka, F.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.*, **1982**, *488*, 7−26. Sheldrick, W. S.; Schmidpeter, A.; Zwaschka, F.; Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1981**, 413−418.