Inorg. Chem. **2000,** *39,* 3037−3041 **3037**

Syntheses and Structures of Heterobicyclic Bis(*tert*-butylamido)cyclodiphosph(III)azane Compounds Having Phosphorus(III) and Arsenic(III) Centers

Ingo Schranz, Luke P. Grocholl, and Lothar Stahl*

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202-9024

Richard J. Staples

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

Alison Johnson

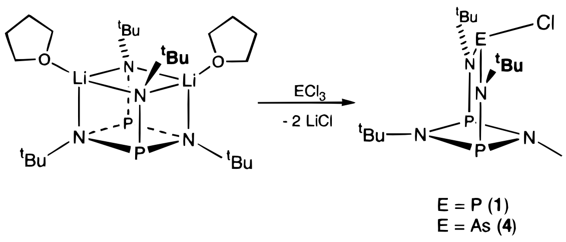
Department of Chemistry, St. Cloud State University, St. Cloud, Minnesota 56301-4498

Received December 7, 1999

Syntheses and single-crystal X-ray diffraction studies of heterobicyclic cyclodiphosphazanes having central phosphorus(III) and arsenic(III) atoms are described. Interaction of PCl_3 or $AsCl_3$ with *cis*-$[(^tBuNP)_2(^tBuNLi{\bullet}THF)_2]$ produced the isomorphous $\{[(^tBuNP)_2(^tBuN)_2]ECl\}$; E = P(**1**), As(**4**), respectively. These C_s-symmetric molecules crystallize with two molecules in the monoclinic space group $P2_1/m$. Unit cell dimensions of **1** are (293 K) a = 9.777(1) Å, b = 11.745(1) Å, c = 9.986(2) Å, and β = 97.44(1)°; those of **4** are (213 K) a = 9.688(3) Å, b = 11.873(3) Å, c = 9.975(3) Å, and β = 97.80(3)°. When $\{[(^tBuNP)_2(^tBuN)_2]PCl\}$ was treated with NaN_3 or $LiN(SiMe_3)_2$, $\{[(^tBuNP)_2(^tBuN)_2]PN_3\}$(**2**) and $\{[(^tBuNP)_2(^tBuN)_2]PN(SiMe_3)_2\}$(**3**), respectively, were obtained. Compound **2** crystallizes in the monoclinic space group $P2_1/m$ and has unit-cell dimensions (213 K) of a = 9.496(7) Å, b = 12.455(7) Å, c = 10.043(6) Å, and β = 97.23(4)°, Z = 2.

No congeners in the periodic table of the elements form compounds of a greater structural variety than nitrogen and phosphorus.[1] This is due in part to the ability of these nonmetals to form single, double, and triple bonds with each other. It is, however, also due to the strength of P−N bonds, which render most phosphorus−nitrogen compounds exceptionally thermally stable. While the unsaturated cyclophosphazenes and their polymeric products are the oldest and best-known class of P−N compounds,[2] the saturated phosphazanes also have a well-established chemistry.[3]

We are investigating bis(amino)cyclodiphosphazanes,[4] **A**, as N-donor ligands for main-group and transition elements.[5] Recently we reported the syntheses of antimony(III) (**5**) and bismuth(III) compounds of **A** with intramolecular base stabilization.[6] The smaller group 15 elements are not expected to exhibit interactions with the cyclodiphosphazane ring, but they should form molecules of even greater stability. Below we describe syntheses and X-ray structures of the first fully characterized arsenic and monophosphorus derivatives of a bis(amido)-cyclodiphosphazane.



(1)

Experimental Section

General Considerations. All operations were performed under an atmosphere of argon or prepurified nitrogen on conventional Schlenk

---

* Author to whom correspondence should be addressed.

(1) (a) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 5th ed.; Elsevier: Amsterdam, 1995. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements, 2nd ed.; Butterworth-Heinemann: Oxford, 1998.*

(2) (a) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (c) Allen, C. E. *Coord. Chem. Rev.* **1994**, *130*, 137.

(3) (a) Holmes, R. R.; Forstner, J. A. *Inorg. Chem.* **1963**, *2*, 380. (b) Hill, T. G.; Haltiwanger, R. C.; Thompson, M. L.; Katz, S. A.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1770. (c) Scherer, O. J.; Schnabel, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 772. (d) Kumaravel, S. S.; Krishnamurthy, S. S.; Cameron, T. S.; Linden, A. *Inorg. Chem.* **1988**, *27*, 4546. (e) Davies, A. R.; Dronsfield, A. T.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 379. (f) Zeiss, W.; Schwarz, W.; Hess, H. *Z. Naturforsch.* **1980**, *35b*, 959. (g) Dou, D.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1999**, *38*, 788.

(4) (a) Keat, R. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 2, p 467. (b) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S. *Phosphorus Sulfur* **1990**, *49/50*, 409−412. (c) Payne, D. S.; Mokuolu, J.; Speakman, J. C. *J. Chem. Soc., Chem. Commun.* **1965**, 599. (d) Johnson, T. R.; Nixon, J. F. *J. Chem. Soc. A.* **1969**, 2518. (e) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243. (f) Scherer, O. J.; Anselmann, R.; Sheldrick, W. S. *J. Organomet. Chem.* **1984**, *263*, C26. (g) Dubois, D. A.; Duesler, E. N.; Paine, R. T. *Organometallics* **1983**, *2*, 1903.

(5) (a) Grocholl, L.; Stahl, L.; Staples, R. J. *Chem. Commun. (Cambridge)* **1997**, 1465. (b) Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1493.

(6) Moser, D. F.; Schranz, I.; Gerrety, M. C.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **1999**, 751.

10.1021/ic991405r CCC: $19.00

lines. The hydrocarbon or ethereal solvents were predried over molecular sieves or CaH_2 and distilled under a nitrogen atmosphere from sodium or potassium benzophenone ketyl immediately before use. Sodium azide, PCl_3, and $AsCl_3$ were obtained from Aldrich and used as received. Lithium bis(trimethylsilyl)amide was provided by United Chemical Technologies, Bristol, PA, as a 15% w/w hexane solution and diluted to 0.10 M before use. *cis*-[(^{t}BuNP)$_2$(^{t}BuNLi•THF)$_2$] was synthesized according to a published procedure.[5b]

Mass spectra were recorded on a VG Micromass 7070E-HF double-focusing spectrometer in the FAB mode, using an MNBA (meta nitrobenzyl alcohol) matrix, or in the chemical ionization mode, using methane as the reacting gas. NMR spectra were recorded on a Varian VXR-300 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced relative to C_6D_5H (7.15 ppm), C_6H_6 (128.0 ppm), and external P(OEt)$_3$ (137.0 ppm), respectively, with shifts to higher frequency (lower field) given a more positive value. Melting points were recorded on a Mel-Temp melting point apparatus; they are uncorrected. E&R Microanalytical Laboratory, Parsippany, NJ, performed the elemental analyses. Mass spectral data were recorded at the Mass Spectral Service Laboratory of the University of Minnesota, Minneapolis, MN.

Syntheses. {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]PCl}, 1. To a cooled (0 °C) solution of PCl_3 (1.24 g, 9.03 mmol) in 20 mL of toluene was added dropwise 4.56 g (9.05 mmol) of *cis*-[(^{t}BuNP)$_2$(^{t}BuNLi•THF)$_2$], dissolved in 30 mL of toluene. Upon addition of the cyclodiphosphazane solution, a white precipitate formed. The cloudy reaction mixture was allowed to warm to room temperature, stirred at 50 °C overnight, and then filtered through a medium-porosity frit. The ensuing light-yellow solution was concentrated to 10 mL in vacuo and stored at −14 °C. After several days, 3.18 g (85.3%) of **1** was isolated.

Mp: 157 °C. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.528$ (d, 18H, $J = 1.2$ Hz, amido), 1.474 (s, 9H, ^{t}Bu, imido, N1), 1.192 (s, 9H, ^{t}Bu, imido, N2). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 58.97$ (dd, $J_{PC} = 22$, 18 Hz, C_q, amido), 53.95 (t, $J_{PC} = 13$ Hz, C_q, imido, N1), 52.10 (t, $J_{PC} = 2$ Hz, C_q, imido, N2), 31.13 (dt, $J_{PC} = 16$, 5 Hz, CH_3, amido), 29.25 (dt, $J_{PC} = 16$, 6 Hz, CH_3, imido). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 21 °C): $\delta = 202.6$ (d, $J_{PP} = 26$ Hz), 139.6 (t, $J_{PP} = 25$ Hz). MS (PCI, methane): *m/z* (%), 412.1842(34.5) = M$^+$. Anal. Calcd for $C_{16}H_{36}ClN_4P_3$: C, 46.56; H, 8.79; N, 13.57. Found: C, 46.18; H, 8.91; N, 13.57.

Variable-Temperature NMR Analysis for 1. The signals for the diastereotopic N^{t}Bu groups at 1.474 and 1.192 ppm did not broaden up to 373 K. By substituting these data into the formula $\Delta G_c^{\ddagger} = 4.575 \bullet 10^{-3}\, T_c[9.972 + \log(T_c/\delta\nu)]$, a minimal $\Delta G^{\ddagger}$ value of 18.1(4) kcal/mol was obtained.[8]

{[(^{t}BuNP)$_2$(^{t}BuN)$_2$]PN$_3$}, 2. In a 100-mL, two-necked flask, 0.874 g (2.12 mmol) of **1** and 0.146 g (2.25 mmol) of NaN_3 were mixed in 10 mL of THF and then stirred at room temperature. The water-clear suspension slowly turned yellow with the formation of a white precipitate. After 1 d the THF was removed in vacuo and the crystalline residue was extracted with 15 mL of toluene. This solution was filtered through a medium-porosity frit, concentrated to 3 mL, and stored at −15 °C. After 3 days, colorless plates, 0.767 g (83.5%), of **2** were isolated.

Mp: 104 °C dec ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.422$ (s, 9H, imido, N1), 1.414 (d, 18H, amido), 1.201 (s, 9H, imido, N2). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 57.59$ (dd, $J = 22$, 19 Hz, C_q, amido), 53.34 (t, $J_{PC} = 13$ Hz, C_q, imido, N1), 52.02 (t, $J_{PC} = 3$ Hz, C_q, imido, N2), 32.16 (dt, $J_{PC} = 15$, 8 Hz, 1 °C, amido), 29.47 (t, $J_{PC} = 7$ Hz, CH_3, imido). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 21 °C): $\delta = 197.9$ (d, 2P, $J_{PP} = 17$ Hz), 117.7 (t, 1P, $J_{PP} = 17$ Hz). MS (FAB, MNBA): *m/z* (%), 419.(20.2) = M$^+$. Anal. Calcd for $C_{16}H_{36}N_7P_3$: C, 45.82; H, 8.65; N, 23.38. Found: C, 45.69; H, 8.80; N, 23.35.

{[(^{t}BuNP)$_2$(^{t}BuN)$_2$]P[N(SiMe$_3$)$_2$]}, 3. A sample (0.285 g, 0.690 mmol) of **1** was dissolved in 15 mL of toluene in a 100-mL, two-necked flask. To this cooled (0 °C) solution was added, via syringe, 7.0 mL of a 0.10 M hexane solution of lithium bis(trimethylsilyl)amide. The reaction mixture, which turned light orange with the formation of a lithium chloride precipitate, was stirred at room temperature for 1 d and then filtered through a fine frit and concentrated to 3 mL. This furnished, upon cooling to 0 °C, 0.267 g (71.9%) of **3**.

Mp: 132 °C. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.581$ (d, 18H, amido) 1.445 (s, 9H, imido, N1), 1.297 (s, 9H, imido, N2), 0.546 (s, 9H, TMS), 0.500 (d, 9H, $J_{PH} = 3$ Hz, TMS). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 58.72$ (dd, $J_{PC} = 24$, 23 Hz, C_q, amido), 54.89 (t, $J_{PC} = 15$ Hz, C_q, imido, N1), 52.32 (t, $J_{PC} = 4$ Hz, C_q, imido, N2), 34.19 (dd, $J_{PC} = 15$, 9 Hz, CH_3, amido), 30.41 (t, $J_{PC} = 5$ Hz, CH_3, imido), 29.72 (t, $J_{PC} = 10$ Hz, CH_3, imido), 7.91 (s, TMS), 6.38 (d, $J_{PC} = 15$ Hz, TMS). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 21 °C): $\delta = 198.8$ (br s, 2P), 110.2 (br t, 1P). MS (FAB, MNBA): *m/z* (%), 538.(21.1) = M$^+$. Anal. Calcd for $C_{22}H_{54}N_5P_3Si_2$: C, 49.13; H, 10.12; N, 13.02. Found: C, 49.24; H, 9.93; N, 12.86.

{[(^{t}BuNP)$_2$(^{t}BuN)$_2$]AsCl}, 4. In a 100-mL two-necked flask, 12 mL of a 0.237 M $AsCl_3$ solution in toluene was added dropwise to 1.37 g (2.71 mmol) of *cis*-[(^{t}BuNP)$_2$(^{t}BuNLi•THF)$_2$] dissolved in 40 mL of toluene. The light-yellow reaction mixture was stirred at room temperature for 12 h, filtered, and then cooled (−15 °C), producing 0.97 g (78%) of colorless, rod-shaped crystals.

Mp: 137 °C. ^{1}H NMR (300 MHz, benzene-d_6, 21 °C): $\delta = 1.514$ (s, 9H, imido, N1), 1.468 (s, 18H, amido), 1.224 (s, 9H, imido, N2). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, 21 °C): $\delta = 59.20$ (d, $J_{PC} = 17.6$ Hz, C_q, amido), 53.73 (t, $J_{PC} = 13.7$ Hz, C_q, imido, N1), 51.96 (t, $J_{PC} = 3.6$ Hz, C_q, imido, N2), 31.93 (t, $J_{PC} = 5.3$ Hz, CH_3, amido), 29.54 (t, $J_{PC} = 6.0$ Hz, 1 °C, imido). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 21 °C): 189.5 (s). MS (FAB, MNBA): *m/z* (%), 456.(2.) = M$^+$. Anal. Calcd for $C_{16}H_{36}AsClN_4P_2$: C, 42.07; H, 7.94; N, 12.26. Found: C, 42.23; H, 7.78; N, 12.02.

X-ray Diffraction Studies. {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]PCl}, 1. A colorless block of the approximate dimensions 0.3 × 0.5 × 0.5 mm was sealed inside an argon-filled capillary and then optically aligned on an Enraf-Nonius CAD 4 diffractometer. The intensities of the unique quadrant− $-11 \le h \le 11$, $0 \le k \le 13$, $0 \le l \le 11$ ($3.0 < 2\Theta < 50.0°$) of the reciprocal lattice were collected with ω-2Θ scans. Of the 2102 unique data collected, 1551 with $F > 2.5\sigma(F)$ were used in the structure refinement. The probable centrosymmetric space group $P2_1/m$ was corroborated by the successful refinement of the structure. The data were corrected for Lp effects, decay, and absorption (ψ-scans). Data reduction, structure solution, and refinement were performed using the NRCVAX program suite.[9]

{[(^{t}BuNP)$_2$(^{t}BuN)$_2$]PN$_3$}, 2, and {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]AsCl}, 4. With a Bruker SMART CCD diffractometer, 6087 (6978) reflections were collected between 4.0 and 49.4° in 2Θ. Of these data, with indices of $-11 \le h \le 11$, $-7 \le k \le 14$, $-11 \le l \le 11$ ($-12 \le h \le 12$, $-15 \le k \le 11$, $-12 \le l \le 13$), 2111 (2895) were considered unique, $R_{int} = 0.0433$ (0.0232), and observed ($I > 2\sigma(I)$) and used in the refinement. Cell parameters were retrieved with SMART[10] software and refined with SAINT[11] on all observed reflections. An empirical absorption correction was applied using SADABS.[12] The structures were solved with the direct-methods option of the SHELXS-90 program[13] and refined by least-squares methods on F^2 with SHELXL-97,[14] incorporated in SHELXTL-PC version 5.03.[15] Hydrogen atom positions were

---

(7) (a) Bertrand, G.; Majoral, J.-P.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17. (b) Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088. (c) Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 459. (d) Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 271.

(8) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(9) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(10) *SMART Software for the CCD Detector System*, version 4.043; Siemens Analytical Instruments Division: Madison, WI, 1995.

(11) *SAINT Software for the CCD Detector System*, version 4.035; Siemens Analytical Instruments Division: Madison, WI, 1995.

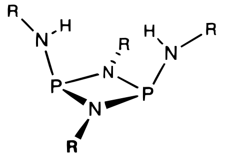
(12) *SADABS Program for Absorption Corrections Using the Bruker CCD Detector System*. Based on: Blessing, R. *Acta Crystallogr.* **1995**, *A 51*, 33.

(13) Sheldrick, G. M. *SHELXS-90, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany, 1990.

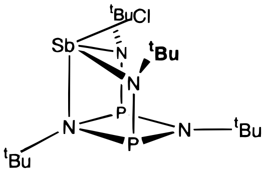
calculated by geometrical methods and refined using a riding model. Difference maps showed no electron peaks outside the range ± 0.362 (0.947) e Å^{-3}.

Results and Discussion

Phosphorus−nitrogen bonds are commonly formed by transamination or the aminolysis of P−Cl bonds.[16] Because these reactions are not always predictable, we chose a selective salt-elimination (eq 1) for the introduction of phosphorus (and arsenic) into **A**. The synthesis of **1** had been attempted previously, but the interaction of $PhPCl_2$ with $\{[(^tBuNP)_2(^tBuN)_2]SnMe_2\}$ yielded the diphosphine **6** instead.[17]

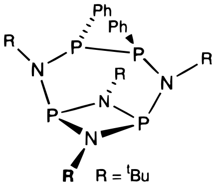


A



5

Treatment of **1** with sodium azide (eq 2) and lithium bis(trimethylsilyl)amide (eq 3) yielded compounds **2** and **3**, respectively (Scheme 1). These derivatives were synthesized because the small and reactive azide group allows further functionalization of the molecule, while the bulky bis(trimethylsilyl)amide affords a robust cage with three sterically shielded phosphorus atoms. All compounds are thermally stable, air-sensitive, colorless solids.



6

The ^{1}H NMR spectra of **1**−**4** are similar and easily interpreted from the expected structures of the molecules. The signals for the bis(*tert*-butylamido)cyclodiphosphazane ligand appear as three singlets in a 2:1:1 ratio, proving that these molecules, unlike their antimony and bismuth counterparts,[6] are stereorigid in solution. Variable-temperature studies suggest activation energies of at least 18.1(4) kcal/mol,[8] and thus more than 5 kcal/mol higher than those of the bismuth analogue.[6]

The crystal and bond parameters for **1**, **2**, and **4** are collected in Tables 1 and 2, and their solid-state structures appear in Figures 1, 2, and 3, respectively. These molecules are isomorphous; **1** and **4** strictly so, and **2** to a slightly lesser extent. The crystallographic mirror plane, which contains the central group 15 atom and the monodentate ligand, bisects the molecules and their puckered $(P-N)_2$ rings. Three of the nitrogen atoms are almost perfectly trigonal planar, but N2 is pyramidal because of the steric interaction of its *tert*-butyl group with the monodentate ligand. The three unique P−N bonds in the ligand portion of these compounds range from 1.713(2) to 1.740(4) Å and are shorter than P−N single bonds, 1.79 Å.[1a] The shortness of the E−N3 bonds, together with the planarity of their nitrogen atoms, may reflect partial double-bond character. In contrast to the planar nitrogen atoms, the bridgehead phosphorus atoms are highly pyramidalized (282.4°) compared to those in PCl_3 (300.3°).[18]

Scheme 1

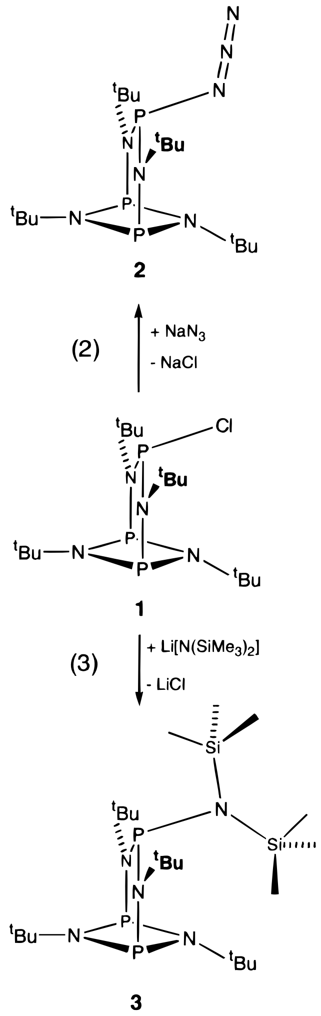


Table 1. Crystallographic Data for **1**, **2** and **4**

	1	2	4
empirical formula	$C_{16}H_{36}ClN_4P_3$	$C_{16}H_{36}N_7P_3$	$C_{16}H_{36}AsClN_4P_2$
fw	412.81	419.43	456.80
space group	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)
T (°C)	20	−60	−60
a, Å	9.777(1)	9.496(7)	9.688(3)
b, Å	11.745(1)	12.455(7)	11.873(3)
c, Å	9.986(2)	10.043(6)	9.975(3)
β, deg	97.44(1)	97.23(4)	97.80(3)
V, Å^3	1137.0(3)	1178(1)	1136.8(6)
Z	2	2	2
ρ_{calc}, g cm^{-3}	1.206	1.182	1.334
λ, Å	0.710 73	0.710 73	0.710 73
μ, cm^{-1}	3.8	2.67	17.60
$R(F)^a$	0.061	0.0499	0.0326
$R_w(F^2)^b$	0.052	0.1073	0.0813

For **1**: $^a R = \sum|F_o - F_c|/\sum|F_o|$. $^b R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$ For **2** and **4**: $^a R = \sum|F_o - F_c|/\sum|F_o|$. $^b R_w(F^2) = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

---

(14) Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(15) *SHELXTL 5.03 (PC version), Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(16) Lappert, M. F.; Sanger, A. R.; Srivastava, R. C.; Power, P. P. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U. K., 1981.

(17) Linti, G.; Nöth, H.; Schneider, E.; Storch, W. *Chem. Ber.* **1993**, *126*, 619.

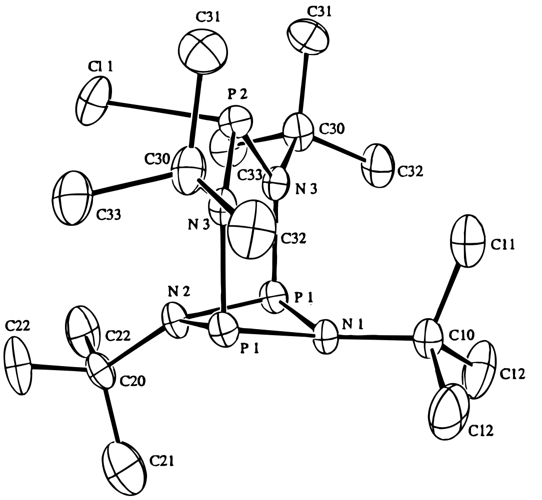


Figure 1. Perspective view of the solid-state structure of {[(^{t}BuNP)$_2$-(^{t}BuN)$_2$]PCl}, **1**.

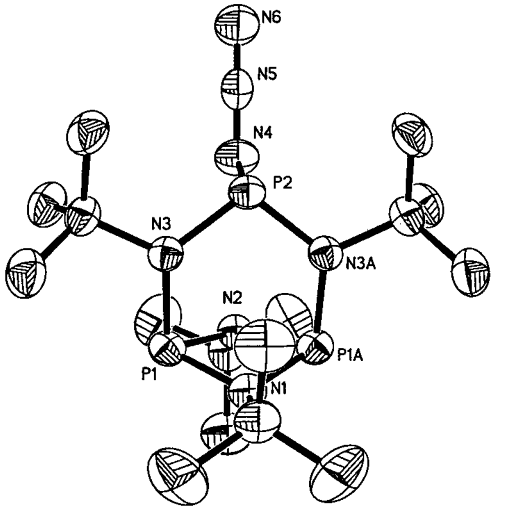


Figure 2. Perspective view of the solid-state structure of {[(^{t}BuNP)$_2$-(^{t}BuN)$_2$]PN$_3$}, **2**.

Ring puckering is greatest in **1**, where the relatively small phosphorus atom causes sufficient strain in the molecule to distort the normally planar (P−N)$_2$ ring. Compared to the P−Cl bonds in the structurally related heterocycle *cis*-1,3-di-*tert*-butyl-2,4-dichlorocyclodiphosphazane (2.105(9) Å),[19] the phosphorus−chloride bond in **1** is very long, 2.244(3) Å.

With the exception of the azide moiety, all structural parameters of **2** are identical to those of **1**. The azide ligand is almost linear (177.8(5)°) and has the typical long−short bond pattern of covalent azides, but the phosphorus−azide bond (1.852(4) Å) is much longer than those in conventional phosphine azides (ca. 1.74 Å).[20]

The arsenic derivative **4** (Figure 3) is isostructural with the phosphorus, rather than the antimony, analogue,[6,17] and although this may reflect the greater similarity in size of phosphorus and arsenic, other factors probably play a role as well (vide infra). As in **1**, the element−chloride bond is elongated, 2.3325(11) Å, compared to those in [ClAs(μ-N^{t}Bu)$_2$AsCl] (2.250(3) Å).[21]

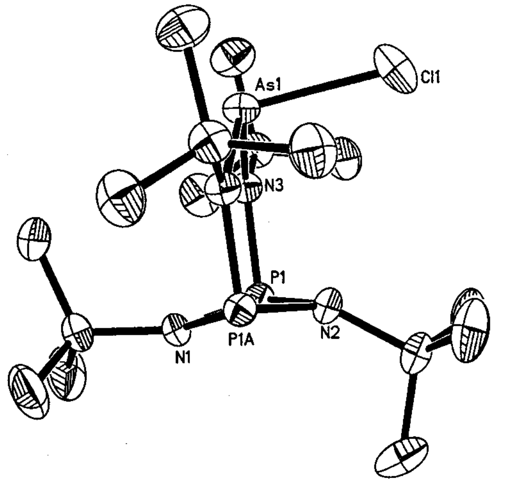


Figure 3. Perspective view of the solid-state structure of {[(^{t}BuNP)$_2$-(^{t}BuN)$_2$]AsCl}, **4**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, **4** and **5**

	1	**2**	**4**	**5**
		Bond Lengths		
E−Cl	2.244(3)		2.3325(11)	2.492(3)
E−N(3)	1.689(4)	1.696(3)	1.843(2)	2.095(5)
P(1)−N(1)	1.718(4)	1.713(2)	1.718(2)	1.772(5)
P(1)−N(2)	1.721(4)	1.718(2)	1.717(2)	1.719(5)
P(1)−N(3)	1.733(4)	1.740(4)	1.727(2)	1.680(6)
P(2)−N(4)		1.852(4)		
N(4)−N(5)		1.218(5)		
N(5)−N(6)		1.144(5)		
		Bond Angles		
N(3)−E−N(3a)	103.8(2)	104.3(2)	102.06(10)	103.5(2)
N(3)−E−Cl	101.8(1)		101.24(6)	94.8(2)
N(3)−P(2)−N(4)		100.35(12)		
N(3)−P(1)−N(1)	101.2(2)	98.52(14)	102.04(10)	91.6(20
N(3)−P(1)−N(2)	98.1(2)	101.28(14)	100.14(10)	108.0(3)
P(1)−N(1)−P(1a)	94.8(3)	95.3(3)	95.98(12)	
P(1)−N(2)−P(1a)	94.6(3)	94.(2)	95.64(12)	
P(1)−N(3)−E	124.9(3)	123.792)	122.68(9)	92.2(2)
N(4)−N(5)−N(6)	83.1(2)	82.61(13)	82.62(9)	
P(2)−N(4)−N(5)		112.3(3)		
N(4)−N(5)−N(6)		177.8 (5)		

With the completed characterization of **1** and **4**, a homologous series of group 15 compounds of formula {[(^{t}BuNP)$_2$(^{t}BuN)$_2$]-ECl} now exists. Important bond parameters for the X-ray structurally characterized P, As, and Sb analogues are compared in Table 2. These molecules adopt either a configuration in which the unique group 15 atom resides in a central position (**1** and **4**), or one in which it interacts with the cyclodiphosphazane ring (**5**). The E−X bonds are elongated in all compounds, making it improbable that van der Waals strain alone is responsible for the dissimilar structures. It is more likely that the central atom's size and bond energies determine the molecular structures. In **1** and **4** the central phosphorus and arsenic atoms are barely big enough to form bonds to both amido nitrogens, and they would likely suffer excessive bond strain if they adopted the structure of **5**. Multiple bonding should also favor the central disposition of phosphorus and arsenic, as indicated by the short E−N bonds and the planarity of the nitrogen atoms. The larger antimony does not engage in π-bonding, but forms an additional σ-bond with one of the ring-nitrogen atoms instead.[17]

Heterocycles are common inorganic molecules, but heterobicycles are rare by comparison and limited mainly to compounds with group 14 and 15 bridgehead atoms.[4a] The structural

---

(18) Kislink, P.; Townes, C. H. *J. Chem. Phys.* **1950**, *18*, 1109.

(19) Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259.

(20) Cowley, A. H.; Gabbaï, F.; Schluter, R.; Atwood, D. *J. Am. Chem. Soc.* **1992**, *114*, 3144.

(21) Bohra, R.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *Acta Crystallogr.* **1984**, *C40*, 1150.

similarity of the title compounds to bicyclo[3.1.1]heptanes[22] can be rationalized in terms of the valence−isoelectronic nature of N−R and P−X with CH_2, although inorganic heterocycles have more polar bonds and smaller interior angles.

Just like their organic counterparts, however, inorganic bicycles exhibit substitution- and reactivity patterns that have no acyclic analogues. In the title compounds, the bridgehead moieties can be considered the structural equivalents of the unknown $P(NH^tBu)_3$. Because of their unusual geometries, these compounds should lend themselves to reactivity studies. The phosphine−azide derivative, for example, may yield a phosphino nitrene on photolysis.[7] These short-lived species normally dimerize to cyclodiphosphazenes, but in **2** this fate might be avoided because of the steric protection of the terminal P−N bond.

Acknowledgment. We thank the Phillips Petroleum Company for financial support.

Supporting Information Available: Tables of crystal data, atomic positional and displacement parameters, and complete tables of interatomic distances and angles for **1**. Two X-ray crystallographic files for structures **2** and **4**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991405R

---

(22) (a) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, 35, 489. (b) Szeimies, G.; Schlosser, A.; Philipp, F.; Dietz, P.; Mickler, W. *Chem. Ber.* **1978**, *111*, 1922.