Synthesis and Molecular Structure of a $1,2\lambda^5$-Azaphosphete: A Cyclic 4-π-Electron Ylide

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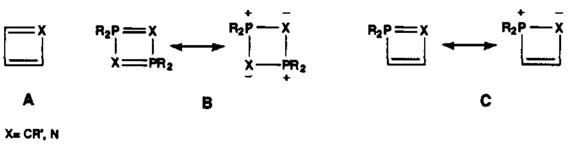
The preparation of stable 4-π-electron 4-membered rings has captured the imaginations of generations of chemists.[1] Nonetheless, only a very few substituted cyclobutadienes[2] **A** (X = CR′) and related azetes[3] **A** (X = N) have been isolable at room temperature. Recently, some $1\lambda^5,3\lambda^5$-diphosphetes[4] **B** (X = CR′) and one $1,3,2\lambda^5,4\lambda^5$-diazadiphosphete[5] (cyclodiphosphazene) **B** (X = N) have been prepared. High-level calculations[6] concluded that the stability of cyclodiphosphazenes is due to their zwitterionic character, although some back bonding from N to P occurs; in other words, the phosphorus–nitrogen bond order is between 1 and 2. The next question was whether the presence of only one second row element would be sufficient to stabilize a 4-π-electron 4-membered ring (**C**) (Scheme I). Here we report the synthesis of the $1,2\lambda^5$-azaphosphete **4** (**C**, X = N), the first example of this new class of compounds.

It is known that vapor flash pyrolysis of 1,2,3-triazines affords azetes by extrusion of dinitrogen.[3d,e,7] On the other hand, although diazo derivatives and nitrile imines are typical 1,3-dipoles,[8] it has been shown that the phosphanyldiazo derivative **D**[9a] and the *N*-phosphanylnitrile imine **E**[9b] can formally act as 1,4-dipoles toward electron-poor alkynes, affording 6-membered rings **F** and **G**, respectively. Thus, it was tempting to extend the formal 1,4-dipolar reactivity of phosphanyl-substituted 1,3-dipoles to phosphanyl azides (Y = Z = N) to prepare a $1,2,3,4\lambda^5$-triazaphosphinine (Scheme II).

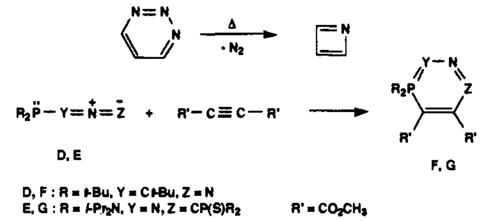
Bis(diisopropylamino)phosphanylazide **1**[10] was chosen since (i) it is one of the very rare stable phosphorus(III)azides[11] and (ii) diisopropylamino groups should stabilize the positively charged phosphorus atom of the desired azaphosphete. A clean reaction occurred when azide **1** was reacted overnight at room temperature with dimethyl acetylenedicarboxylate, affording the desired 6-membered ring **3**, which was obtained as yellow crystals from an ether solution (75% yield, mp 122–123 °C) (Scheme III). The isomeric structure **2** was easily ruled out by NMR spectroscopy.[12,13] Of special interest, CI-mass spectroscopy (NH_3) of **3** gives a $M + 1 - N_2$ peak as the heaviest ion, suggesting the easy elimination of N_2.

Heating **3** in refluxing toluene for 14 h gave rise to the azaphosphete **4**,[13] which was isolated in 80% yield as pale yellow crystals from a cold saturated ether solution (Scheme IV). The deshielding of the ^{31}P chemical shift from **3** to **4** ($\Delta\delta$ = 47) is in good agreement with the 4-membered ring structure, since a similar phenomenon has already been observed going from cyclotriphosphazene to cyclodiphosphazene ($\Delta\delta$ = 20).[5b] In the

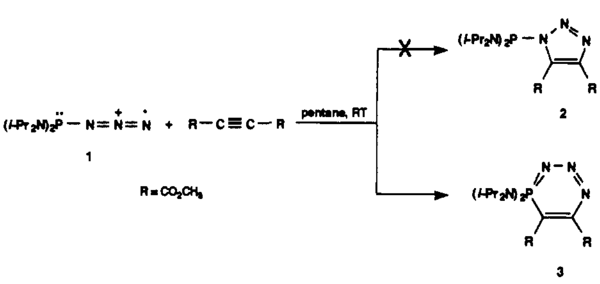
Scheme I



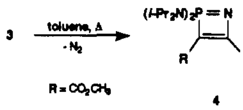
Scheme II



Scheme III



Scheme IV



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[1] Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425. Dewar, M. J. S.; Kohn, M. C.; Trinajstić, M. *J. Am. Chem. Soc.* **1971**, *93*, 3437.

[2] (a) Lindner, H. J.; von Gross, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 490. (b) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. (c) Kimling, H.; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932. (d) Irngartinger, H.; Nixdorf, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 403. (e) Gompper, R.; Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 824. (f) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.

[3] (a) Vogelbacher, U. J.; Regitz, M.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842. (b) Wagner, H. U. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 848. (c) Ledermann, M.; Regitz, M.; Angermund, K.; Binger, P.; Krüger, C.; Mynott, R.; Gleiter, R.; Hyla-Kryspin, I. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1559. (d) Seybold, G.; Jersak, U.; Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 847. (e) Adger, B. M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Perkin Trans. I* **1975**, 45.

[4] (a) Svara, J.; Fluck, E.; Riffel, H. *Z. Naturforsch.* **1985**, *40B*, 1258. (b) Neumüller, B.; Fluck, E. *Phosphorus Sulfur* **1986**, *29*, 23.

[5] (a) Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088. (b) Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Fatiha, E. A.; Manuel, G. *J. Am. Chem. Soc.* **1985**, *107*, 3945. (c) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Dartiguenave, M.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277.

[6] (a) Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568. (b) Ahlrichs, R.; Schiffer, H. *J. Am. Chem. Soc.* **1985**, *107*, 6494.

[7] Adger, B. M.; Keating, M.; Rees, C. W.; Storr, R. C. *J. Chem. Soc., Chem. Commun.* **1973**, 19.

[8] Padwa, A. *1,3 Dipolar Cycloaddition Chemistry*; J. Wiley and Sons: New York, 1984.

[9] (a) Facklam, T.; Wagner, O.; Heydt, H.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 314. (b) Granier, M.; Baceiredo, A.; Nieger, M.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1123.

[10] Scherer, O. J.; Glabel, W. *Chem. Ztg.* **1975**, *99*, 246.

[11] ***Caution:*** Phosphanyl azides constitute one of the most dangerous classes of azides. For examples, diphenylphosphanyl azide explodes when it is banged or jarred at above −13 °C, and bis(trifluoromethyl)phosphanyl azide is a violent detonator even at the temperature of liquid nitrogen.

[12] The λ^3-phosphorus atom of **2** would give a signal around +100 ppm. For examples: **1**, $\delta(^{31}P)$ + 108; $[(i\text{-}Pr)_2N]_2PNMe_2$, $\delta(^{31}P)$ +98.

[13] **3**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.08 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHN), 1.27 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHN), 3.71 (s, 3 H, CH_3O), 3.85 (sept d, J_{PH} = 16.9 Hz, J_{HH} = 6.9 Hz, 4 H, CH_3CHN), 3.87 (s, 3 H, CH_3O); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.93, 23.62 (s, CH_3CHN), 47.62 (d, J_{PC} = 4.7 Hz, CH_3CHN), 51.70, 52.62 (s, CH_3O), 81.77 (d, J_{PC} = 113.2 Hz, PC), 150.44 (d, J_{PC} = 2.4 Hz, CN), 166.23 (d, J_{PC} = 11.6 Hz, CO), 166.81 (d, J_{PC} = 2.7 Hz, CO); ^{31}P NMR (THF, 32.438 MHz) δ = +5.74; IR (THF) 1748, 1716 cm^{-1} (CO). Anal. Calcd for $C_{18}H_{34}O_4N_5P$: C, 52.04; H, 8.25; N, 16.86. Found: C, 52.34; H, 8.27; N, 17.03. **4**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.24 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 1.26 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 3.52 (s, 3 H, CH_3O), 3.68 (sept d, J_{PH} = 18.4 Hz, J_{HH} = 6.8 Hz, 4 H, CH_3CHN), 3.82 (s, 3 H, CH_3O); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 21.83, 22.12 (s, CH_3CHN), 47.50 (d, J_{PC} = 4.9 Hz, CH_3CHN), 49.63 (d, J_{PC} = 2.1 Hz, CH_3O), 52.16 (s, CH_3O), 91.88 (d, J_{PC} = 81.6 Hz, PC), 158.30 (s, CO), 164.05 (d, J_{PC} = 64.3 Hz, CO), 182.37 (d, J_{PC} = 28.0 Hz, CN); ^{31}P NMR (THF, 32.438 MHz) δ = +52.46; IR (THF) 1743, 1660 cm^{-1} (CO); CIMS ($M^+ + 1$) 388. Anal. Calcd for $C_{18}H_{34}O_4N_3P$: C, 55.80; H, 8.84; N, 10.85. Found: C, 55.79; H, 8.79; N, 10.82.

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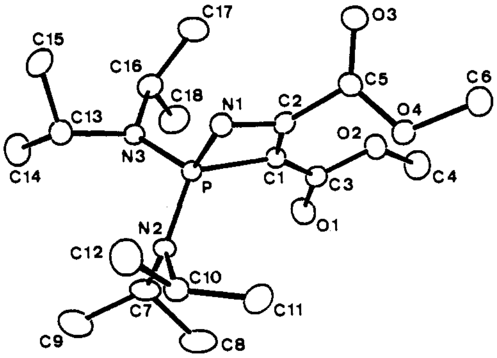
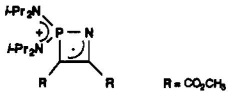


Figure 1. ORTEP plot of **4** showing the numbering scheme used. Ellipsoids are scaled to enclose 35% of the electronic density. Hydrogen atoms are omitted. Pertinent bond lengths (Å) and bond angles (deg) are as follows: C1–C2 1.406(6), C2–N1 1.352(5), N1–P 1.702(3), P–C1 1.764(4), P–N2 1.626(3), P–N3 1.629(3), C1–C3 1.419(6), C3–O1 1.214(5), C2–C5 1.497(6), C5–O3 1.199(6), C1–C2–N1 109.7(3), C2–N1–P 86.5(2), N1–P–C1 81.2(2), P–C1–C2 82.6(3), P–N3–C13 117.7(3), P–N3–C16 123.9(3), C13–N3–C16 114.7(3), P–N2–C7 117.5(3), P–N2–C10 124.5(3), C7–N2–C10 115.8(3).

same way, the deshielding of the CN ^{13}C chemical shift from **3** (150.44 ppm) to **4** (182.37 ppm) is comparable to that observed going from triazines (~160 ppm)[14] to azete (~200 ppm).[3]

The structure of **4** has been clearly established by a single crystal X-ray diffraction study.[15] The thermal ellipsoid plot of the molecule is shown in Figure 1, with pertinent structural parameters listed in the legend. As expected for a cyclobutadiene derivative, the four-membered ring has a planar structure (maximum deviation 0.003(4) Å). Although the C1–P–N1 angle [81.2(2)°] is small, the large N1–C2–C1 angle [109.7(3)°] induces a short diagonal P···C2 distance [2.109(4) Å]. This short distance between 1,3-centers seems to be a characteristic feature of polarized 4-π-electron 4-membered rings such as 1,3-push–2,4-pull cyclobutadienes,[2a] azete,[3c] diphosphete,[4a] and cyclodiphosphazene.[5] The exocyclic phosphorus–nitrogen bond lengths [1.629(3), 1.626(3) Å] are shorter than the endocyclic P–N1 bond length [1.702(3) Å] and are comparable to those observed in bis(diisopropylamino)phosphenium salts (1.61 Å).[16] This is an indication of a positive charge delocalization on the N2–P–N3 fragment, which is confirmed by the planarity of N2 and N3. The N1–C2 [1.352(5) Å] and C2–C1 [1.406(6) Å] bond lengths are half-way between those of single and double bonds, indicating that the N1–C2–C1 part of the ring can be regarded as an anionic allylic system. Thus, the 4-π-electron 4-membered ring **4** is best described by the "non-antiaromatic" structure **4'**.



4'

The surprising stability of **4** (air-stable crystals, mp 109–110 °C without decomposition) is due not only to its non-antiaromatic structure but also to both the high thermodynamic energy of the corresponding phosphorus fragments (>P≡C— or >P≡N), preventing dissociation, and the steric factors which hinder polymerization.

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Supplementary Material Available: Crystal data and methods of data collection; tables of atomic coordinates, positional and thermal parameters, bond lengths and angles, and torsion angles (7 pages). Ordering information is given on any current masthead page.

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(14) Katritzky, A. R.; Rees, C. W. *Comprehensive Heterocyclic Chemistry*; Pergamon Press: Oxford, 1984.

(15) Crystal data for **4**: $C_{18}H_{34}N_3O_4P$, mol wt = 387.5, monoclinic, space group $P2_1/c$, $a = 10.586(1)$ Å, $b = 12.354(1)$ Å, $c = 17.019(2)$ Å, $\beta = 92.32(1)°$, $V = 2223.9(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.157$ g cm^{-3}, λ(Mo Kα) = 0.710 73 Å (graphite monochromated), $\mu = 1.43$ cm^{-1}. An Enraf-Nonius CAD4 diffractometer was used to collect 3094 independent reflections ($3 < 2\theta < 46°$) on a crystal of 0.50- × 0.15- × 0.125-mm dimension. Data were corrected for Lorentz and polarization effects but not for absorption. A linear decay correction of 5% was applied. 1772 reflections were considered observed [$F_o^2 > 2\sigma(F_o^2)$]. All non-hydrogen atoms were located by direct methods, and they were refined anisotropically. The hydrogen atoms were included as idealized contributions. $R = 0.042$, $R_w = 0.042$, 235 variables, $S = 1.16$, maximum residual peak of 0.17 e Å^{-3}.

(16) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.