Further studies to elucidate the electronic and steric effects of fluorination on the physicochemical properties of allyl and heteroallyl anions (and their corresponding free radicals) are in progress.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (5 pages). Ordering information is given on any current masthead page.

Synthesis of Skeletally Stabilized Acyclic Triphosphazanes

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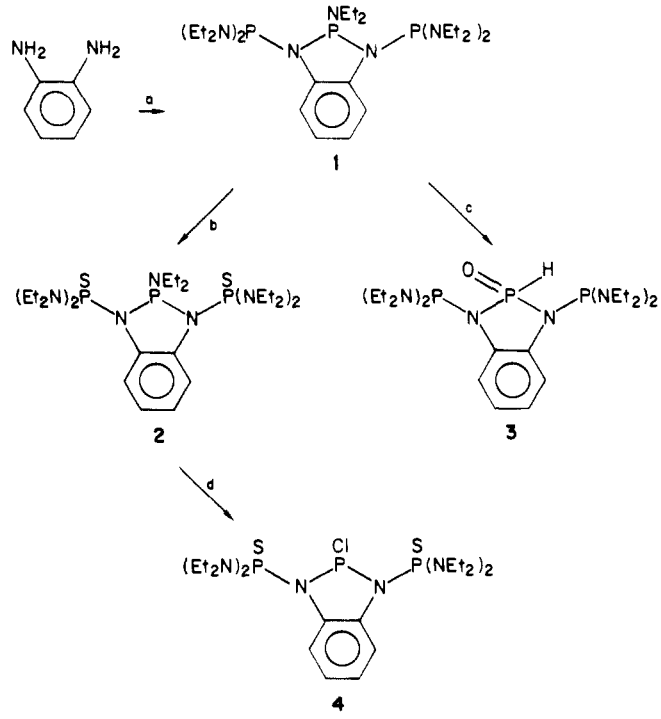
In contrast to the many studies of linear phosphazenes reported,[1] relatively few dealing with analogous phosphazanes $-(PRNR'-)_n$ containing more than two phosphorus atoms have appeared. The absence of acyclic phosphazanes (where $n > 2$) apparently results from the tendency, in their formation reactions, to form low molecular weight four-, six-, or eight-membered rings.[2] We now wish to report the preparation of a new class of skeletally stabilized triphosphazanes, which, because of their high stability, allow first studies of acyclic phosphazane chemistry and offer potential as novel synthons in higher oligomer/polymer formation reactions.

Reaction of 1,2-diaminobenzene with excess $P(NEt_2)_3$ for 10 h at 85 °C results in near quantitative formation of triphosphazane **1** (Scheme I). Excess $P(NEt_2)_3$ is removed in vacuo. Passage of **1** in toluene through a 5-cm silica gel column, followed by removal of toluene in vacuo, yields pure **1**. **1** has not been obtained crystalline. However, in 4 h with 2 equiv of S_8 at 25 °C in toluene it under goes oxidation selectively and quantitatively at the exo phosphorus atoms [P(1) and P(3)] to form **2**. **2** is obtained crystalline from CH_2Cl_2 (mp 115-118 °C) (figure 1).

Triphosphazane **1**[3,4] and the bis(sulfide) **2**[3,5] have been characterized by a combination of ^1H and ^{31}P NMR, IR, and mass spectral data. Both **1** and **2** contain symmetrically oriented triphosphazane units in solution, since both exhibit symmetrical AX_2 ^{31}P NMR spectral patterns. The $^2J_{PP}$ coupling constant in trans P-N-P diphosphazane conformations are known to be relatively small, 18-25 Hz, whereas for cis conformations they are larger, typically 200-732 Hz.[6] Since $^2J_{PP}$ for **1** varies only from 29.4 to 53.0 Hz over the temperature range -90 to +104 °C, it appears to be in or close to a trans-trans conformation in solution and is primarily in this conformation to 104 °C.

The structure of **2**, and by inference **1**, has been confirmed by a single-crystal X-ray analysis.[7] Crystals of **2** contain eight

Scheme I[a]



[a] Conditions: (a) $3P(NEt_2)_3$, $-4Et_2NH$; (b) 1/4 S_8/toluene; (c) H_2O/CH_2Cl_2; (d) 2HCl (anhydrous), $-Et_2NH_2Cl$/toluene.

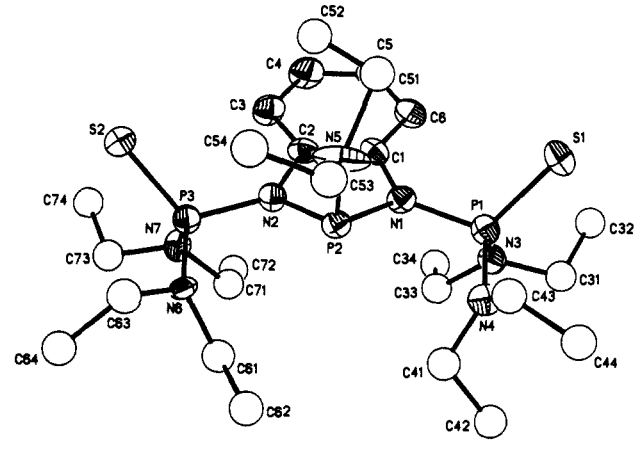


Figure 1. Structure and numbering scheme for $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**2**) showing 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)-N(1), 1.672 (5); P(2)-N(1), 1.744 (5); P(2)-N(2), 1.762 (5); P(3)-N(2), 1.664 (5); P(1)-N(3), 1.645 (5); P(1)-N(4), 1.647 (5); P(1)-S(1), 1.940 (2); P(2)-N(5), 1.633 (6); P(3)-N(6), 1.649 (5); P(3)-N(7), 1.639 (5); P(3)-S(2), 1.936 (2); C(1)-N(1), 1.427 (7); C(2)-N(2), 1.426 (7); P(2)-N(1)-C(1), 112.6 (4); N(1)-P(2)-N(2), 87.5 (2); P(2)-N(2)-C(2), 111.5 (4); N(1)-C(1)-C(2), 110.9 (5); N(2)-C(2)-C(1), 112.0 (5); C(2)-N(2)-P(3), 125.3 (4); P(2)-N(2)-P(3), 123.0 (3); P(1)-N(1)-C(1), 125.8 (4); P(1)-N(1)-P(2), 121.6 (3); N(2)-P(2)-N(5), 107.8 (3); N(1)-P(2)-N(5), 103.8 (3); S(1)-P(1)-N(1), 114.8 (2); S(2)-P(3)-N(2), 114.7 (2).

(1) (a) Allcock, H. R.; Tollefson, N. M.; Arcus, R. A.; Whittle, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5166. (b) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22. (c) Allcock, H. R. In *Rings, Clusters, and Polymers of the Main Group Elements*; Cowley, A. H., Ed.; ACS Symposium Series 232; American Chemical Society: Washington, DC, 1982; p 49.

(2) (a) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101. (b) Keat, R. *Top. Curr. Chem.* **1983**, *102*, 89. (c) Thompson, M. L.; Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1981**, *103*, 6770. (d) Niecke, E.; Ruger, R.; Schoeller, W. W. *Angew Chem., Int. Ed. Engl.* **1981**, *20*, 1034. (e) Zeiss, W.; Barlos, K. *Z. Naturforsch., B* **1979**, *34B*, 423. (f) Chen, H.-J.; Hartiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.*, in press. (g) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D. *J. Chem. Soc., Chem. Commun.* **1979**, 647. (h) Zeiss, W.; Schwarz, W.; Hess, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 407.

(3) Satisfactory elemental analyses were obtained for all compounds except **3**, which was thermally unstable and persistently contaminated by traces of thermolysis products.

(4) **1**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 106.5 (d, $^2J_{PP}$ = 43.5 Hz, area 2), 100.5 (t, area 1); ^1H NMR (C_6D_6) δ 7.11-6.66 (complex, area 4, C_6H_4), 3.14-2.71 (complex, area 20, CH_2CH_3). 1.02 (complex, area 30, CH_2CH_3); MS, parent at m/e 557, $C_{26}H_{54}N_7P_3^+$.

(5) **2**; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 98.3 (t, $^2J_{PP}$ = 63.9 Hz, area 1), 65.1 (d, area 2); ^1H NMR (C_6D_6) δ 7.91 and 6.90 (multiplets, area, 4, C_6H_4), 3.62-2.75 (m, area 20, CH_2CH_3), 1.03 (m, area 30, CH_2CH_3); MS, parent at *m/e* 621, $C_{26}H_{54}N_7P_3S_2^+$; IR (KBr), characteristic absorption at 606 cm^{-1} (P=S).

(6) Keat, R.; Manojlovic-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192.

(7) Crystal data for **2**: $C_{26}H_{54}N_7P_3S_2$, formula weight 621.81, orthorhombic, *Pbca*, a = 14.652 (5) Å, b = 18.911 (9) Å, c = 24.324 (9) Å, V = 6739 (4) Å^3, Z = 8, D_{obsd} = 1.25 g/cm, D_{calcd} = 1.23 g/cm. Intensity data: Nicolet P3/F autodiffractometer equipped with low-temperature apparatus, data collected at -80 °C, Mo K_α (λ = 0.71069 Å), Wycoff ω scan mode, 3.0 < 2θ < 45.0, 5029 reflections collected, of which 2754 were observed [$(F_o) > 6\sigma(F_o)$]. The structure was solved by direct methods and refined by block cascade least-squares calculations; R = 0.060, R_w = 0.075. Hydrogen atoms were included in idealized geometries, riding on the atoms to which they are attached, with a single refined thermal parameter.

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molecules per unit cell. **2** is a $(Et_2N)_2P$-substituted 4,5-benzo-1,3,2-diazaphosphole[12] in which a P_3N_2 triphosphazane unit is stabilized by bonding of the ortho-C_6H_4 ring to nitrogen atoms N(1) and N(2). **2** has approximate C_s point group symmetry, with a symmetry plane passing through P(2) perpendicular to and bisecting the $C_6H_4N_2$ ring, consistent with that observed for **1** in solution. The $(Et_2N)_2P(S)$ units are oriented around the P(1)-N(1) and P(3)-N(2) bonds such that the P=S bond vectors are approximately perpendicular to the $C_6H_4N_2$ plane and trans to the P(2) lone pair electrons. The N(1)-P(2)-N(2) and $C_6H_4N_2$ planes are close to coplanar; the interplane dihedral angle (bend along the N···N axis) of the PN_2C_2 ring is 21.4°. Phosphorus atoms P(1) and P(3) are displaced out of the $C_6H_4N_2$ plane by 0.28 Å. P(2) is displaced in the opposite direction by 0.46 Å. P(2) is in a protected "cleft" in the molecule and consequently is relatively inaccessible to attack by external reagents. The mean ring P(2)-N(1,2) distance [1.753 (5) Å] is considerably longer than the exo ring P(1)-N(1), P(3)-N(2) distance [1.668 (6) Å], although both are in the range of P-N distances observed for other phosphazane[2] and 1,3,2-diazaphosphole[8,9] systems.

Triphosphazanes **1** and **2** display high thermal and chemical stability and phosphorus atom reaction selectivity. Thermolysis of **1** or **2** for 1 day in vacuo at 100 °C produced no decomposition. In contrast to the selective exo phosphorus atom [P(2) and P(3)] reaction of **1** with S_8 which yields **2**, **1** with H_2O in CH_2Cl_2 reacts at the central phosphorus [P(2)] to form phosphine oxide **3**[10] in 80-85% yield. Cleavage of the P(2)-N(5) bond occurs without significant cleavage of other P-N bonds in the system. Reaction of **2** with anhydrous gaseous HCl yields chlorophosphine **4**,[11] again with barely detectable cleavage of skeletal or exo P-N bonds. It appears the nucleophilicity of P atoms in **1** and **2** is generally reduced, but more so for P(2) than for P(1) and P(3). Conversely, the H_2O-**1** reaction suggests that P(2) is activated electrophilically relative to P(1) and P(3). This difference in P(1,3) vs. P(2) reactivity might be a function both of the specific conformation assumed by **1** and the protected nature of P(2), a premise that can be tested only after other conformationally characterized acyclic phosphazanes become available.

Since the new triphosphazanes **1-4** contain a functional phosphorus atom [P(2)] in an unusually protected position, given the novel phosphorus atom selective reactivity these molecules display, and they contain functionally useful groups on the terminal [P(1) and P(3)] phosphorus atoms, it is expected that further derivative chemistry will be developed. Related studies, including efforts to incorporate these phosphazanes into new phosphazane macromolecules, are in progress currently.

Acknowledgment. Support for this work by National Science Foundation Grant CHE-8312856 is gratefully acknowledged. The assistance of Dr. C. Campana and the Nicolet Instrument Co., Madison, WI, in obtaining low-temperature X-ray diffraction data is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, positional, isotropic, and anisotropic thermal parameters, hydrogen coordinates, temperature factors, and bond distances and angles for **2** (6 pages). Ordering information is given on any current masthead page.

(8) Malavaud, C.; Boisdon, M. T.; Charbonnel, Y.; Barrans, J. *Tetrahedron Lett.* **1979**, *20*, 447.

(9) Malavaud, C.; N'Gando M'Pondo, T.; Lopez, L.; Barrans, J.; Legros, J.-P. *Can. J. Chem.* **1984**, *62*, 43.

(10) **3**: ^{31}P NMR (C_6D_6) δ 111.9 (d, $^2J_{PP}$ = 22.4 Hz, area 2), 8.8 (d of t, $^1J_{PH}$ = 664.0 Hz, area 1); MS, parent at *m/e* 502, $C_{22}H_{45}N_6OP_3^+$; ^1H NMR (C_6D_6) δ 7.16-6.84 (m, area 4, C_6H_4), 3.66-2.63 (m, area 16, CH_2CH_3), 1.10 (m, area 24, CH_2CH_3); IR (NaCl), characteristic absorption at 2418 cm^{-1} (P-H).

(11) **4**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 143.9 (t, $^2J_{PP}$ = 66.7 Hz, area 1), 64.5 (d, area 2); ^1H NMR δ 7.65 and 6.93 (multiplets, area 4, C_6H_4), 3.20 (m, area 16, CH_2CH_3), 0.96 (m, area 24, CH_2CH_3); MS, parent ion at *m/e* 684, $C_{22}H_{44}N_6P_3S_2Cl^+$; IR (KBr), characteristic absorption at 604 cm^{-1} (P=S).

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Lewis Acid Mediated Version of the Nicholas Reaction: Synthesis of Syn-Alkylated Products and Cobalt-Complexed Cycloalkynes

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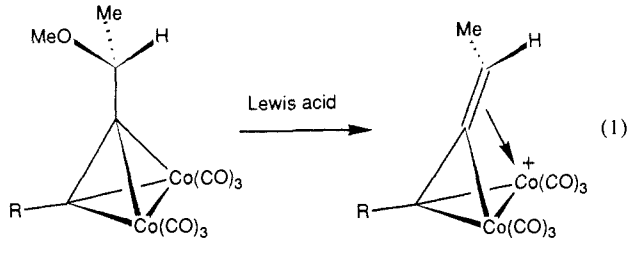
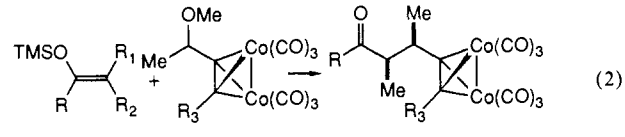
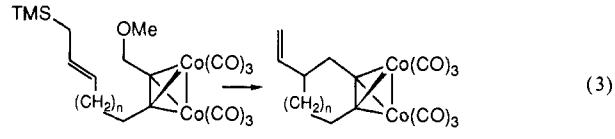
The reaction of cobalt complexed propargylic alcohols with HBF_4 provides a cobalt-stabilized carbocation that can be treated with a variety of carbon nucleophiles to provide alkylated products (Nicholas reaction).[1] The application of this reaction to systems with acid-sensitive functionality or where the nucleophile is part of the cobalt cluster (intramolecular reaction) is complicated by the action of the tetrafluoroboric acid on these groups in preference to the propargylic alcohol.[2] We have investigated a Lewis acid mediated version of this reaction on cobalt-complexed propargylic *ethers* that can be carried out by adding a Lewis acid to a 1:1 mixture of the carbon nucleophile and cobalt cluster (eq 1-3).



(1)



(2)



(3)

The intermolecular version of this reaction provides high levels of diastereoselection for syn-alkylated products provided certain stereocontrol elements are maintained. The intramolecular alkylation reaction with allylic silanes affords either intra- or extraannular cobalt alkyne complexes. This reaction process, in combination with the Pauson-Khand annelation protocol, provides a method for the construction of polycycles containing a medium-sized ring.

The attempted alkylation of 1-(trimethylsiloxy)cyclohexene by treatment of 1:1 mixture of the enol ether and the propargylic alcohol dicobalt hexacarbonyl complex with tetrafluoroboric acid or various Lewis acids was unsuccessful. The alkylation of this silyl enol ether with the cobalt complex of the corresponding

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(2) Unpublished results from these laboratories. For a BF_3·OEt_2-promoted alkylation of cobalt-complexed propargylic alcohols with several carbon nucleophiles, see: (a) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1982**, *25*, 2555. For the alkylation and alkynylation of cobalt-complexed propargylic acetates with aluminum reagents, see: (b) Padmanabhan, S.; Nicholas, K. M.; *J. Organomet. Chem.* **1981**, *212*, 115. (c) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1983**, *24*, 2239.

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