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The First N-Only-Bonded Metal Derivatives of Cyclenphosphorane. Formation of cyclenPH·MCl$_2$ and cyclenPH·HMCl$_3$ (M = Zn, Cd)

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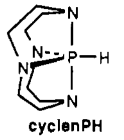
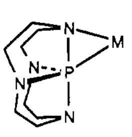
The reactions of cyclenphosphorane (cyclenPH) with group 12 metal halides MCl$_2$ (M = Zn, Cd) yield the 1:1 complexes cyclenPH·MCl$_2$ [M = Zn (**1**), Cd (**2**)], in which coordination to the metal most likely occurs through the axial nitrogen atom on cyclenPH. A mixture of cyclenPH and MCl$_2$ in a 1:0.5 molar ratio gives one peak in the ^{31}P NMR spectrum at a chemical shift between the resonances for cyclenPH and the 1:1 complexes, indicating that **1** (or **2**) readily exchanges MCl$_2$ with free cyclenPH. Treatment of these 1:1 complexes with HCl yields the adducts cyclenPH·HMCl$_3$ [M = Zn (**3**), Cd (**4**)]. The X-ray crystal structure of **3** was obtained and shows the phosphorus to form a distorted trigonal bipyramid with a hydrogen and two nitrogens occupying the equatorial positions and two nitrogens at the axial positions. One axial nitrogen is attached to a ZnCl$_3$ unit and the other to a proton. The compound crystallizes as "head-to-toe" dimers linked by N-H---Cl hydrogen bonds. X-ray data: $C_8H_{18}N_4PCl_3Zn$, monoclinic, space group $P2_1/c$, $a = 10.5788$ (14) Å, $b = 9.611$ (2) Å, $c = 14.604$ (2) Å, $\beta = 103.6$ (1)°, $Z = 4$, $R = 0.027$, $R_w = 0.031$.

We have found that cyclenphosphorane (cyclenPH) exhibits novel ligand behavior with metals for several reasons: the presence of highly nucleophilic lone pairs of electrons on the axial nitrogens,

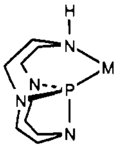


cyclenPH

the labile P-N and P-H bonds, and the constraint of the 12-membered tetraaza ring. Most reactions of cyclenPH yielding metal complexes have proceeded via P-H bond cleavage, thus leading to P-M (M = metal) bond formation.[1] Structures A-D



A



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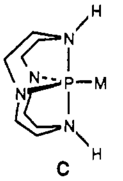

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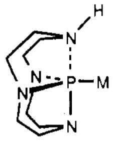
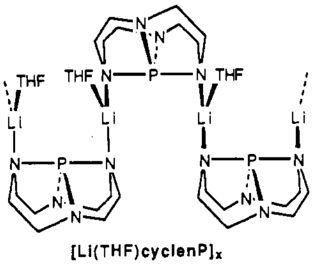


D

are representative of the types of bonding modes usually found in these complexes where M = Pt^{2+}, Rh$^+$, and metal carbonyl derivatives. (Note that, in addition to the P-M bond, there is N-M and/or N-H bond formation which incorporates only the "axial" nitrogens of the cyclenP unit.) The only apparent exception to P-M bond formation was found in the deprotonation reaction of cyclenPH with butyllithium; this led to the polymeric phosphoranide (R_4P:$^-$) species [Li(THF)cyclenP]$_x$, a species where



[Li(THF)cyclenP]$_x$

the lithium atom bridges cyclenP units at the axial nitrogens, yielding a chain.[2] This structure emphasizes the highly nucleophilic character of the axial nitrogens in the cyclenP unit. However, what determined the preference of lithium for the nitrogen compared to the phosphorus? Might it simply be the hardness of the lithium, since the metals previously used are much softer?

In an effort to synthesize other N-only-bound metal derivatives of cyclenPH, possibly leading to other polymeric species via N-M-N bridges, we studied the reactions of cyclenPH with MCl$_2$ (M = Zn, Cd)[3] and the subsequent reactions of these species with HCl. We herein report the results of this study as well as the X-ray crystal structure of the HCl derivative of the zinc complex.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents ZnCl$_2$ and CdCl$_2$ were obtained commercially and sublimed before use, while HCl (anhydrous, 1.0 M in ether, Aldrich) was used without further purification. cyclenPH was prepared by a literature method.[1d] All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.132 (^{1}H), 81.026 (^{31}P), and 50.327 MHz (^{13}C). ^{31}P spectra are proton-decoupled unless otherwise indicated. ^{1}H resonances were measured relative to residual proton solvent peaks, while ^{13}C resonances were measured relative to solvent peaks (both referenced to Me$_4$Si). ^{31}P resonances were measured relative to external 85% H$_3$PO$_4$. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained either on a Carlo Erba Strumentazione Model 1106 elemental analyzer or from Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of cyclenPH·ZnCl$_2$ (1). A mixture of cyclenPH (0.200 g, 1.00 mmol) and ZnCl$_2$ (0.136 g, 1.00 mmol) in THF (10 mL) was stirred for 12 h. The mixture was filtered to separate the product, and the precipitate was washed with THF and pumped dry to yield **1** as a white, microcrystalline, air-stable solid (0.320 g, 95%), soluble only in Me$_2$SO. Dec pt: 180-182 °C. Anal. Calcd for $C_8H_{17}Cl_2N_4PZn$: C, 28.55; H, 5.09; N, 16.65. Found: C, 27.96; H, 5.20; N, 16.20.

Synthesis of cyclenPH·CdCl$_2$ (2). A procedure indentical with that for **1**, using CdCl$_2$ (0.183 g, 1.00 mmol), yielded **2** as a white, microcrystalline, air-stable solid (0.372 g, 97%), soluble only in Me$_2$SO. Dec pt: 200-202 °C. Anal. Calcd for $C_8H_{17}CdCl_2N_4P$: C, 25.05; H, 4.47; N, 14.61. Found: C, 24.93; H, 4.47; N, 14.64.

Synthesis of cyclenPH·HZnCl$_3$ (3). A stirred solution of **1** (0.168 g, 0.500 mmol) in Me$_2$SO-d_6 (1 mL) was treated dropwise with a 1.0 M HCl solution in ether (0.50 mL, 0.50 mmol). After 8 h of stirring, the volatiles were pumped off and THF was layered on top of the Me$_2$SO-d_6

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(1) (a) Lattman, M.; Chopra, S. K.; Burns, E. G. *Phosphorus Sulfur* **1987**, *30*, 185. (b) Lattman, M.; Burns, E. G.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Inorg. Chem.* **1987**, *26*, 1926. (c) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 681. (d) Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M.; *Organometallics* **1986**, *5*, 2383. (e) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (f) de Meester, P.; Lattman, M.; Chu, S. S. C. *Acta Crystallogr., Sect. C* **1987**, *C43*, 162. (g) Khasnis, D. V.; Lattman, M.; Siriwardane, U.; Chopra, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 3103.

(2) Lattman, M.; Olmstead, M. M.; Power, P. P.; Rankin, D. W.; Robertson, H. E. *Inorg. Chem.* **1988**, *27*, 3012.

(3) Zn^{2+} is usually considered a borderline acid, while Cd^{2+} is usually considered to be soft. However, Zn^{2+} and Cd^{2+} have similar chemical behavior. See: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984; p 1401.

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Table I. Crystal Data and Data Collection Parameters for **3**

chem formula	$C_8H_{18}N_4PCl_3Zn$	space group	$P2_1/c$
formula mass	373.0 u	T	299 K
a	10.5788 (14) Å	λ	0.71073 Å
b	9.611 (2) Å	ρ_{calcd}	1.717 g cm^{-3}
c	14.604 (2) Å	μ	2.398 mm^{-1}
β	103.6 (1)°	transm coeff	0.6881–0.5640
V	1443.1 (4) Å^3	R^a	0.027
Z	4	R_w	0.031

[a] $R = \sum||F_o| - |F_c||/\sum w|F_o|$, $R_w = [w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$, and $w = 1/\sigma^2(F_o) + k(F_o)^2$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **3**

	x	y	z	U(eq)^a
Zn	7372 (1)	1856 (1)	4675 (1)	32 (1)
Cl(1)	7770 (1)	605 (1)	6010 (1)	52 (1)
Cl(2)	5693 (1)	3330 (1)	4422 (1)	51 (1)
Cl(3)	9252 (1)	2931 (1)	4590 (1)	52 (1)
P	7887 (1)	−889 (1)	3449 (1)	28 (1)
N(1)	6864 (2)	593 (3)	3458 (2)	31 (1)
N(2)	7944 (3)	−591 (3)	2348 (2)	40 (1)
N(3)	8849 (3)	−2581 (4)	3357 (2)	57 (1)
N(4)	6853 (3)	−1877 (3)	3827 (2)	44 (1)
C(1)	6933 (4)	1480 (4)	2638 (2)	50 (1)
C(2)	7122 (4)	521 (4)	1855 (2)	49 (1)
C(3)	8409 (4)	−1665 (5)	1799 (3)	56 (1)
C(4)	9381 (4)	−2488 (6)	2506 (3)	69 (2)
C(5)	7956 (5)	−3767 (4)	3382 (3)	73 (2)
C(6)	7130 (5)	−3342 (4)	4029 (3)	66 (2)
C(7)	5709 (3)	−1209 (4)	4008 (3)	52 (1)
C(8)	5523 (3)	29 (4)	3373 (3)	50 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

solution to induce crystallization. The resulting crystals were separated by filtration, washed with THF, and pumped dry to yield white, hygroscopic crystals of **3** (0.160 g, 86%), soluble only in Me_2SO. Dec pt: 195–197 °C. Anal. Calcd for $C_8H_{18}Cl_3N_4PZn$: C, 25.76; H, 4.86; N, 15.02. Found: C, 26.32; H, 4.87; N, 14.51.

Synthesis of cyclenPH·HCdCl$_3$ (4). A procedure identical with that for **3**, using **2** (0.192 g, 0.457 mmol), yielded white, hygroscopic crystals of **4** (0.188 g, 90%), soluble only in Me_2SO. Dec pt: 256–258 °C. Anal. Calcd for $C_8H_{18}CdCl_3N_4P$: C, 22.88; H, 4.32; N, 13.34. Found: C, 22.41; H, 4.15; N, 13.17.

X-ray Structure Determination and Refinement. Off-white crystals of **3** were grown from a solution of Me_2SO and CH_2Cl_2. The crystals were mounted on an automatic Nicolet R3m/V diffractometer for data collection. The pertinent crystallographic data are summarized in Table I. The unit cell parameters were determined by a least-squares fit of 25 reflections in the range $15 \leq 2\theta \leq 25°$. The space group assignment was consistent with systematic absences. Three standard reflections were remeasured during the data collection after every 100 reflections; no significant decay was observed. All data were corrected for decay and Lorentz-polarization effects. Data were corrected for absorption based on ψ-scans. The structure was solved by direct methods using SHELXTL-PLUS[4] and subsequent difference Fourier methods. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[5] Full-matrix least-squares refinements were carried out by using only the observed reflections $F > 6.0\sigma(F)$, the function minimized being $\sum w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were refined anisotropically. Hydrogens on carbon atoms were included in calculated positions by using a riding model and fixed isotropic thermal parameters. Hydrogens attached to P and N(3) were included with fixed isotropic thermal parameters. Atomic coordinates and equivalent isotropic thermal parameters are given in Table II.

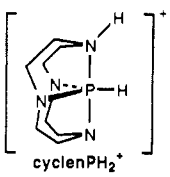
Results and Discussion

Reactions. Stirring an equimolar mixture of cyclenPH and MCl_2 (M = Zn, Cd) in THF led to the formation of a precipitate after a few hours that analyzed as the 1:1 complexes cyclenPH·MCl$_2$ [M = Zn (**1**), Cd (**2**)]. The products are insoluble in most common solvents such as hexane, THF, dichloromethane, acetonitrile, and methanol. They are very slightly soluble in DMF and reasonably soluble in Me_2SO. (Note that cyclenPH is soluble in all of these solvents.) The NMR spectral data for these complexes are reported in Table III, along with data from cyclenPH. The spectra of **1** and **2** are very similar to that of cyclenPH except that the ^1H chemical shift of the P–H hydrogen has moved downfield and there is an increase in the P–H coupling constant. This large $^1J_{PH}$ value and the upfield (negative) ^{31}P chemical shift indicate that the P–H bond is still intact and that the phosphorus is still pentacoordinate. Of particular note is the presence of only one ^{13}C resonance since any reasonable structures of the complexes should have inequivalent carbon atoms.[1] A similar ^{13}C NMR spectrum was observed for the cyclenPH$_2^+$ cation in solution at room temperature;[1e] however, at −76 °C, four resonances were found. This was attributed to N–H exchange at room temperature (accompanied by either pseudorotation and/or P–N bond cleavage). A similar experiment in the present case was precluded by the freezing point (18 °C) of Me_2SO. From the preceding discussion, species **1** and **2** most likely contain cyclenPH bound to the metals via axial N–M bonds that are labile and undergo exchange similar to those of cyclenPH$_2^+$.[6] All attempts to grow crystals suitable for X-ray crystallography for either **1** or **2** were unsuccessful.

Table III. NMR Data in Me_2SO (ppm)

compd	^{31}P ($^1J_{PH}$, Hz)	^1H	^{13}C
cyclenPH	−52.8 (615)	2.6–2.9 (comp m, CH_2, 16 H) 6.66 (d, PH, 1 H, $^1J_{PH}$ = 615 Hz	43.9 (d, $^2J_{PC}$ = 8 Hz)
cyclenPH·ZnCl$_2$ (**1**)	−50.2 (681)	2.7–3.6 (comp m, CH_2, 16 H) 7.08 (d, PH, 1 H, $^1J_{PH}$ = 682 Hz)	42.9 (d, $^2J_{PC}$ = 7 Hz)^a
cyclenPH·CdCl$_2$ (**2**)	−51.6 (642)	2.7–3.0 (comp m, CH_2, 16 H) 6.85 (d, PH, 1 H, $^1J_{PH}$ = 643 Hz)	42.8 (d, $^2J_{PC}$ = 9 Hz)
cyclenPH·HZnCl$_3$ (**3**)	−44.0 (726)	2.9–3.2 (comp m, CH_2, 16 H) 7.14 (d, PH, 1 H, $^1J_{PH}$ = 726 Hz) 7.03 (s, NH, 1 H)	41.0 (d, $^2J_{PC}$ = 12 Hz)^a 43.0 (d, $^2J_{PC}$ = 4 Hz)^a
cyclenPH·HCdCl$_3$ (**4**)	−44.6 (732)	2.9–3.1 (comp m, CH_2, 16 H) 7.16 (d, PH, 1 H, $^1J_{PH}$ = 732 Hz) 7.16 (s, NH, 1 H)	41.1 (d, $^2J_{PC}$ = 13 Hz) 43.1 (d, $^2J_{PC}$ = 4 Hz)

[a] Coupling constants confirmed by comparison with 125.8-MHz ^{13}C data.



cyclenPH$_2^+$

There is no change in the ^{31}P chemical shift of **1** (nor of pure cyclenPH) upon dilution, suggesting that equilibrium 1 lies far to the right. However, a solution of cyclenPH and $ZnCl_2$ in a

$$\text{cyclenPH} + \text{MCl}_2 \rightleftharpoons \text{cyclenPH·ZnCl}_2 \qquad (1)$$

1:0.5 molar ratio shows only *one* ^{31}P resonance at −51.2 ppm with $^1J_{PH}$ equal to 653 Hz, values intermediate between cyclenPH and **1**, rather than two peaks for free cyclenPH and **1**. This observation also supports the lability of the N–Zn bond whereby **1** readily

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(4) Sheldrick, G. M. *SHELXTL-PLUS88, Structure Determination Software Programs*; Nicolet Instrument Corp.: 5225-5 Veronad., Madison, WI 53711, 1988.

(5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

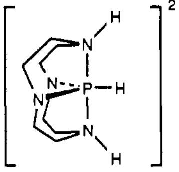
(6) Attempts were made to isolate 1:2 complexes by addition of more MCl_2. The only spectral differences that were observed were small changes in the ^{31}P chemical shift and P–H coupling constant. No species could be isolated that analyzed as the 1:2 complexes.

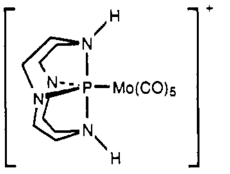
Table IV. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3**

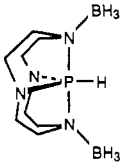
Distances (Å) for **3**			
Zn–Cl(1)	2.245 (1)	Zn–Cl(2)	2.233 (1)
Zn–Cl(3)	2.270 (1)	Zn–N(1)	2.115 (2)
P–N(1)	1.790 (3)	P–N(2)	1.649 (3)
P–N(3)	1.940 (4)	P–N(4)	1.639 (3)
N(3)···Cl(2b)	3.210 (3)	P–H(1p)	1.274 (30)
Bond Angles (deg) for **3**			
Cl(1)–Zn–Cl(2)	117.6 (1)	Cl(1)–Zn–Cl(3)	107.6 (1)
Cl(2)–Zn–Cl(3)	112.0 (1)	Cl(1)–Zn–N(1)	112.4 (1)
Cl(2)–Zn–N(1)	100.9 (1)	Cl(3)–Zn–N(1)	105.6 (1)
N(1)–P–N(2)	91.7 (1)	N(1)–P–N(3)	174.3 (1)
N(2)–P–N(3)	86.4 (1)	N(1)–P–N(4)	90.3 (1)
N(2)–P–N(4)	127.5 (1)	N(3)–P–N(4)	86.6 (2)
N(1)–P–H(1p)	94.1 (16)	N(2)–P–H(1p)	115.7 (17)
N(3)–P–H(1p)	91.5 (16)	N(4)–P–H(1p)	116.5 (17)
Zn–N(1)–P	115.3 (1)	Zn–N(1)–C(1)	107.3 (2)
P–N(1)–C(1)	107.9 (2)	Zn–N(1)–C(8)	109.0 (2)
P–N(1)–C(8)	105.9 (2)	C(1)–N(1)–C(8)	111.5 (2)
P–N(2)–C(2)	117.0 (2)	P–N(2)–C(3)	120.5 (2)
C(2)–N(2)–C(3)	119.1 (3)	P–N(3)–C(4)	108.4 (3)
P–N(3)–C(5)	107.2 (3)	C(4)–N(3)–C(5)	115.8 (3)
P–N(4)–C(6)	120.7 (3)	P–N(4)–C(7)	117.2 (2)
C(6)–N(4)–C(7)	122.0 (3)		

exchanges $ZnCl_2$ with free cyclenPH. The cadmium complex exhibits similar behavior.

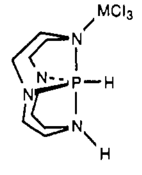
Both complexes form derivatives with strong acids. Treatment of **1** or **2** with one equiv of HCl immediately led to the formation of cyclenPH·$HMCl_3$ [M = Zn (**3**), Cd (**4**)]. The NMR spectra of these species (Table III) still show large P–H couplings and the ^{31}P chemical shifts are again in the pentacoordinate region. The (P–H) ^1H chemical shifts of **3** and **4** have moved even more downfield, accompanied by a further increase in the P–H coupling constant. A new resonance has appeared in the ^1H NMR spectrum at about δ 7, which integrates to one proton, suggesting that one of the axial nitrogens is protonated.[7] In addition, there are now two resonances in the ^{13}C NMR spectrum, each split by two-bond phosphorus coupling. The observation of only two resonances would be consistent with a symmetrical structure in which both axial nitrogens are attached to identical groups such as in cyclenPH_3^{2+},[8] $H_2\text{cyclenPMo(CO)}_5^+$,[1g] and cyclenPH·$2BH_3$.[9]







Indeed, this has been observed for these species. However, such a symmetrical geometry would be unlikely for **3** and **4**. In these species, most likely one axial nitrogen is protonated, while the other is coordinated to the metal, viz.



cyclenPH·HMCl₃
M = Zn(3), Cd(4)

and the observation of only two resonances is due to the fact that protonation and metal coordination have similar effects on the carbon atoms of the ring.[10] This structure for **3** was confirmed by single-crystal X-ray diffraction (see below).

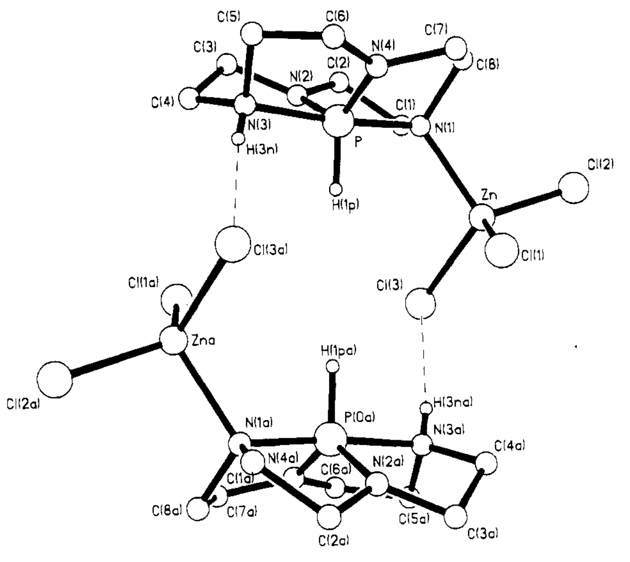


Figure 1. Computer-generated drawing of the hydrogen-bonded dimer of **3**. All hydrogen atoms, except for those attached to phosphorus and nitrogen, are omitted for clarity.

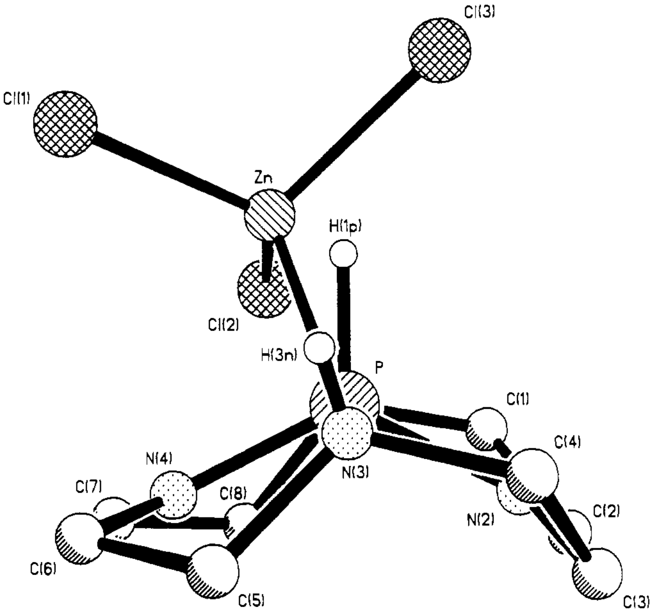


Figure 2. View of **3** down the plane containing N(3), P, and N(1).

Structural Description. Selected internuclear distances and angles for **3** are listed in Table IV, and its structure is illustrated in Figure 1. The compound crystallizes as "head-to-toe" hydrogen-bonded dimers, with the N–H hydrogen interacting with one of the chlorines of the $ZnCl_3$ unit. Each molecule of the dimer is related by a crystallographic center of symmetry with the a-labeled atoms generated by this center. The N(3)---Cl(3b) distance is 3.210 (3) Å, in excellent agreement with similar N---Cl hydrogen-bonding distances in a related $LZnCl_3$ (L = adeninium) complex.[11] The phosphorus atom is pentacoordinate, with both axial nitrogens four-coordinate. N(1), Zn, and N(3) all exhibit distorted tetrahedral geometries, while N(2) and N(4) are close to trigonal planar [sum of bond angles: around N(2), 356.6 (4)°; around N(4), 359.9 (5)°]. The phosphorus is a distorted trigonal bipyramid with N(2), N(4), and H(1p) at the equatorial positions and N(1) and N(3) at the axial positions. The N(2)–P–N(4) angle is 127.5 (1)°, while the N(1)–P–N(3) angle is 174.3 (1)°.

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[7] Several previous cyclenP derivatives having protonated axial nitrogens show ^1H NMR chemical shifts around δ 7. See ref 1b,c,e.

[8] Bouvier, F.; Dupart, J.-M.; Riess, J. G. *Inorg. Chem.* **1988**, *27*, 427.

[9] (a) Dupart, J.-M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051. (b) Dupart, J.-M.; Le Borgne, G.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 1202.

[10] As an alternative explanation of the observation of only two ^{13}C resonances, exchange of H and $ZnCl_3$ could occur involving *only* the axial positions of the cyclenP moiety.

[11] Taylor, M. R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 884.

As usual, the axial P–N bonds are longer than the equatorial bonds; however, the P–N(3) axial bond is 1.940 (4) Å, 0.15 Å longer than the P–N(1) axial bond. This significant difference may be due to the greater polarizing effect of the proton, relative to $ZnCl_3$. Interestingly, both of the P–N axial bonds in cyclenPH$_3^{2+}$ are only about 1.87 Å.[8] The $NZnCl_3$ geometry is comparable to that in other derivatives.[11,12] Species **3** and **4** can be viewed as zwitterionic molecules with positive charges on the two quaternized nitrogens and a 2− charge on the zinc.

The conformations of the rings show some asymmetry when viewed down the plane containing the N(1), P, and N(3) atoms (Figure 2): C(5) and C(8) lie "below" the P–C(6)–C(7) plane, while C(1) and C(4) lie "above" the P–C(2)–C(3) plane. This conformation has been observed before in cyclenPH$_3^{2+}$ and referred to as an "S" pattern. Such a geometry should lead to similarly directionalized lone pairs on the axial nitrogens, which is apparent from the similar torsion angles the N(1)–Zn and N(3)–H(3n) bonds make with the P–H(1p) bond [19.9 (1.7) and 17.6 (3.9)°, respectively] (see Figure 2). Similar torsion angles were not found for the two N–H hydrogens in cyclenPH$_3^{2+}$. This was attributed to the fact that hydrogen bonding only occurred between one of the hydrogens and one of the counterions, CF_3COO^-. The other N–H hydrogen was not involved in such an interaction.

The structure of **3** and [Li(THF)cyclenP]$_x$ (above) demonstrate the tendency for cyclenPH (or cyclenP) to bind primarily through both axial nitrogens under suitable conditions, i.e., with harder metallic Lewis acids such as Li^+ and Zn^{2+}.[3] The fact that [Li(THF)cyclenP]$_x$ polymerizes rather than dimerizes may be due to the steric repulsion of the two phosphoranide lone pairs that would face each other in a dimer similar to **3** (where the cyclenP units would only be separated by a lithium atom). This suggests that the structures of **1** and **2** may also be polymeric (to avoid P–H repulsions) via N–M–N linkages. However, this conjecture needs to be substantiated by structural data on related metal complexes of cyclenPH.[13]

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, torsion angles, hydrogen atom coordinates, and full crystallographic data and a crystal packing diagram for **3** (6 pages); a table of observed and calculated structure factors for **3** (9 pages). Ordering information is given on any current masthead page.

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(12) See, for example: (a) Purnell, L. G.; Hodgson, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 3651. (b) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1978**, *17*, 1338. (c) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308.

(13) Attempts at obtaining reliable molecular weight data for these complexes in Me_2SO, from either commercial or our laboratories, proved unsuccessful.

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$[Fe_6S_6(PEt_3)_6]^+$: Extension of Stabilization of the Basket Core Topology to the $[Fe_6S_6]^+$ Oxidation Level

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The influence of terminal ligands on Fe–S cluster structures formed in self-assembly systems is evident. In recent work it has been shown that systems containing Fe(II), Et_3P, and L = halide or thiolate assemble the clusters $Fe_6S_6(PEt_3)_4L_2$ (**1**, **2**), whose $[Fe_6S_6]^{2+}$ cores possess a C_{2v} basket-type stereochemistry with the bridging modalities $Fe_6(\mu_2\text{-}S)(\mu_3\text{-}S)_4(\mu_4\text{-}S)$. In order to determine the nature of the cluster formed when the only possible terminal ligand is a tertiary phosphine, the assembly system 1:4:1 $[Fe(OH_2)_6](BF_4)/Et_3P/Li_2S$ in THF was investigated. The compound $[Fe_6S_6(PEt_3)_6](BF_4)$ was isolated in 14% purified yield. It crystallizes in monoclinic space group $P2_1/m$ with a = 12.370 (5) Å, b = 16.745 (6) Å, c = 15.151 (4) Å, β = 93.76 (3)°, and Z = 2. The crystal structure contains the cluster $[Fe_6S_6(PEt_3)_6]^+$ (**4**), which has imposed C_s symmetry but closely approaches C_{2v} symmetry. Cluster **4** has the basket stereochemistry of **1** and **2** with only relatively minor dimensional differences. As in the latter two clusters, the six Fe sites of **4** divide into two that have tetrahedral stereochemistry and four that exhibit distorted trigonal-planar coordination. The tetrahedral sites are those that bind halide and thiolate in **1** and **2**. Retention of this geometry in **4** indicates that it is intrinsic to the basket core topology, which has now been shown to stabilize the (reduced) $[Fe_6S_6]^+$ oxidation level. Thus far, the basket structure has been observed only in the oxidation levels $[Fe_6S_6]^{2+,+}$ and only with four or six Et_3P ligands. Cluster **4** does not show clean electrochemical reactions but does react with chloride or chlorinated solvents to give $Fe_6S_6(PEt_3)_4Cl_2$, and with dioxygen and elemental sulfur to afford the known species $[Fe_6S_8(PEt_3)_6]^{2+}$ and $[Fe_6S_8(PEt_3)_6]^+$, respectively. The two oxidation reactions are further examples of core conversions of basket clusters, in this case affording a stellated octahedral cluster product. The characterization of **4** raises to 5 the number of characterized *hexa*nuclear Fe–S clusters. Those of the type $[Fe_6S_6L_6]^{2-,3-}$ (L = RO^-, RS^-, halide), with more oxidized cores than in **1**, **2**, and **4**, have been shown earlier to have the prismane stereochemistry.

Introduction

In addition to the usual variables of solvent and stoichiometry, it is now evident that the products generated in iron–sulfur cluster self-assembly systems are influenced by the terminal ligand reactant(s) present. With systems containing an Fe(II,III) salt, a sulfide source, and thiolate as the sole terminal ligand, the principal or exclusive product is $[Fe_2S_2(SR)_4]^{2-}$, $[Fe_4S_4(SR)_4]^{2-}$, or $[Fe_6S_9(SR)_2]^{4-}$, depending on the particular experimental conditions.[1-4] When the terminal ligand is chloride or bromide, the product is $[Fe_nS_nX_4]^{2-}$ (n = 2, 4).[5-7] The system Fe(0), S, and I_2 affords the clusters $[Fe_nS_nI_4]^{2-}$ (n = 2, 4) or $[Fe_6S_6I_6]^{2-}$.[8-10]

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