Inorg. Chem. **1995,** *34,* 1638−1641

Articles

Isolation of the “Open Form” of Cyclenphosphorane by Deprotonation and Reaction with Electrophilic Reagents†

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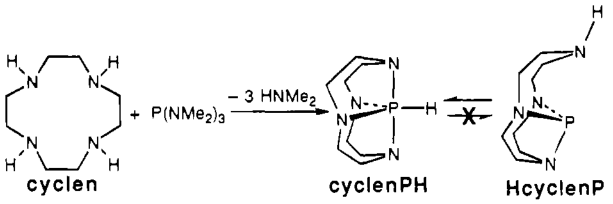
Received October 13, 1994⊗

Depending on the electrophilic reagent RX, the substitution reactions of Li(cyclen)P afford both the “open” N−R bonded species R(cyclen)P as well as the “closed” P−R bonded species (cyclen)PR. With Mes$_2$BF or Ph$_2$PCl, the open products Mes$_2$B(cyclen)P and Ph$_2$P(cyclen)P are formed. With MeCl, a mixture of both (cyclen)PMe and Me(cyclen)P are produced, with the former being the primary product. The X-ray crystal structure of Mes$_2$B(cyclen)P was obtained and reveals that there is no interaction between the (boron-bound) nitrogen and the phosphorus, while the B−N bond length of 1.407(5) Å indicates significant π-bonding. These data suggest that larger substituents capable of π-bonding favor the open isomer. Crystal data: *Pbca*, orthorhombic, $a = 12.083$ (3) Å, $b = 13.447$ (3) Å, $c = 30.533$ (7) Å, $Z = 8$.

The chemistry of cyclenphosphorane ((cyclen)PH) is usually controlled by the constraint of the macrocyclic tetraamine around the phosphorus. This constraint favors pentacoordinate trigonal bipyramidal (tbp) geometries. Richman and Atkins[2] first demonstrated this in 1978 in the initial synthesis of (cyclen)PH (eq 1) in which no tricoordinate phosphine tautomer, the so-called “open form”, was observed. Results from our laboratories,[3] as well as several others,[4] confirmed that the tendency to form tbp geometries persists in derivatives of (cyclen)PH. For example, deprotonation with butyllithium leads to the phosphoranide species Li(cyclen)P,[5] while many pentacoordinate η^2-cyclenPML$_n$ transition-metal complexes have been isolated.[3]



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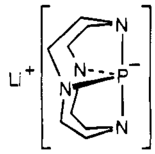
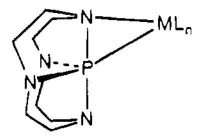
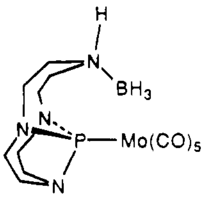
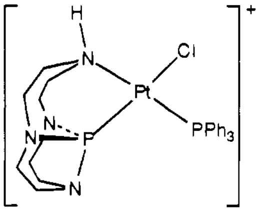




To date, the open form has been isolated only in certain metal complexes such as (BH$_3$)H(cyclen)PMo(CO)$_5$ and [η^2-H(cyclen)PPt(Cl)PPh$_3$]$^+$.[6]





Might it be possible to observe the open form without complexation to metals? For example, would non-hydrogen substituents R lead to closed geometries ((cyclen)PR) or, perhaps, to open structures (R(cyclen)P)? The availability of the lithiated species Li(cyclen)P should allow access to these derivatives, and we herein report our efforts in this direction.

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 using standard Schlenk techniques, unless otherwise indicated. Solvents

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† Dedicated to Dr. Dilip Vishwanath Khasnis (1955−1995), my co-worker and my friend.—M.L.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1995.

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0020-1669/95/1334-1638$09.00/0

were dried using standard procedures 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 chlorodiphenylphosphine (distilled before use), butyllithium (1.6 M in hexanes), and chloromethane (1.0 M in ether) were purchased commercially. The starting materials (cyclen)PH,[2,3a] and Mes_2BF[7] (Mes = mesityl = 2,4,6-trimethylphenyl) were synthesized and purified according to literature procedures. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 (^1H), 50.327 (^{13}C), and 81.026 (^{31}P) MHz. ^1H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. ^{13}C resonances were measured relative to solvent peaks and referenced to Me_4Si. ^{31}P resonances were measured relative to external 85% H_3PO_4. ^{13}C NMR spectra are proton-decoupled unless otherwise indicated. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from E + R Microanalytical Laboratories, Inc., Corona, NY, or on a Carlo Erba Strumentazione Model 1106 elemental analyzer.

Synthesis of Mes_2B(cyclen)P. A stirred solution of (cyclen)PH (100 mg, 0.500 mmol) in THF (3 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 340 μL, 0.55 mmol). After 2 h, a solution of Mes_2BF (135 mg, 0.503 mmol) in THF (3 mL) was added dropwise, and stirring was continued for another 4 h. The dark orange solution was then filtered, and the volatiles pumped off from the filtrate to yield Mes_2B(cyclen)P as a light orange solid (225 mg, 100%). The crude product can be further purified by recrystallization from THF/hexane to obtain an analytically pure sample. Mp: 199−201 °C. Anal. Calcd for $C_{26}H_{38}BN_4P$: C, 69.64; H, 8.54; N, 12.49. Found: C, 69.71; H, 8.54; N, 12.45. NMR (C_6D_6): ^1H δ 2.17 (s, 6 H), 2.33 (s, 6 H), 2.58 (s, 6 H), 2.0−3.9 (m, 16 H), 6.87 (s, 2H), 6.89 (s, 2H); ^{13}C (cyclen ring) δ 50.1 (J_{PC} = 17 Hz), 51.1 (J_{PC} = 4 Hz), 52.5 (J_{PC} = 4 Hz), 56.6 (J_{PC} = 9 Hz); ^{31}P δ 100.

Synthesis of Ph_2P(cyclen)P. A stirred slurry of (cyclen)PH (100 mg, 0.500 mmol) in ether (5 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 344 μL, 0.55 mmol). After 1 h, chlorodiphenylphosphine (104 μL, 0.579 mmol) was added dropwise, and stirring was continued overnight. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate, yielding 159 mg of the crude product. The crude product was washed with small amounts of hexane several times to remove impurities (the product being slightly soluble in hexane) and pumped dry to yield Ph_2P(cyclen)P as a white, moisture-sensitive solid (80 mg, 42%). Mp: 90−92 °C. Anal. Calcd for $C_{20}H_{26}N_4P_2$: C, 62.49; H, 6.82; N, 14.57. Found: C, 62.04; H, 7.03; N, 13.77. NMR (C_6D_6): ^1H δ 2.0−2.1 (m, 2 H), 2.5−2.7 (m, 8 H), 3.1−3.3 (m, 6 H), 7.1−7.2 (m, 6 H), 7.5−7.6 (m, 4 H); ^{13}C (cyclen ring) δ 51.3 (J_{PC} = 13 Hz), 51.4 (J_{PC} = 5 Hz), 55.7 (J_{PC} = 11 Hz), 56.1 (J_{PC} = 5 Hz); ^{31}P δ 62 (PC), 94 (PN).

Reaction of Li(cyclen)P with Chloromethane. In a typical reaction, a stirred solution of (cyclen)PH (100 mg, 0.500 mmol) in THF (10 mL) was treated dropwise with butyllithium (1.6 M in hexanes, 370 μL, 0.60 mmol). After 4 h, chloromethane (1.0 M in ether, 500 μL, 0.50 mmol) was added dropwise, and stirring was continued for another 4 h. The volatiles were then pumped off. The residue was dissolved in ether and filtered, and the filtrate pumped to dryness to yield a colorless, air-sensitive oil (192 mg, 90%). Analysis of the NMR spectra showed this to be a mixture of (cyclen)PMe and Me(cyclen)P. The ratio of (cyclen)PMe/Me(cyclen)P varies from about 70/30 to 85/15. Further separation could not be accomplished. NMR (C_6D_6): ^1H δ 1.31 (d, J_{PH} = 14.1 Hz, PCH_3), 2.12 (s, NCH_3), 2.2−2.4 (m), 2.5−2.9 (m), 3.1−3.3 (m); ^{13}C (cyclen ring, closed) δ 45.0 (J_{PC} = 18 Hz); ^{13}C (cyclen ring, open) δ 47.7, 49.4 (J_{PC} = 3 Hz), 52.2 (J_{PC} = 9 Hz), 55.3; ^{31}P δ −43 (closed), 103 (open).

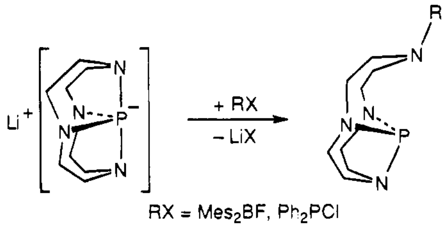
X-ray Structure Determination and Refinement. Crystals of Mes_2B(cyclen)P were grown from a solution of THF/hexane. Crystal data and data collection parameters are collected in Table 1. The structure was solved by direct methods in the space group *Pbca* which was unambiguously determined by the conditions 0*kl*, *k* = 2*n*; *h*0*l*, *l* = 2*n*; *hk*0, *h* = 2*n*. One reflection (0, 0, 2) appeared to be affected by extinction and was omitted from the final set of reflections. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included using a riding model, with C−H distances of 0.96 Å and $U_H = 1.2U_C*$. The largest feature on a final difference map was of height 0.27 Å^{-3}. The computer programs used were from SHELXTL, Version 5, installed on a Data General Eclipse computer. An absorption correction was applied using the program XABS by Hope and Moezzi which obtains an absorption tensor from $F_o - F_c$ differences. Neutral atom scattering factors and corrections for anomalous dispersion were taken from common sources.[8] Agreement indices are $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$.

Table 1. Crystal Data and Data Collection Parameters for Mes_2B(cyclen)P

formula	$C_{26}H_{38}PN_4B$
fw	448.40
color and habit	colorless parallelepipeds
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a, Å	12.083(3)
b, Å	13.447(3)
c, Å	30.533(7)
V, Å^3	4961(2)
T, K	130
Z	8
cryst dimens, mm	0.92 × 0.42 × 0.125
D_{calcd}, g cm^{-3}	1.20
radiation, Å	Mo Kα (λ = 0.710 69)
μ(Mo Kα), cm^{-1}	1.3
range of transm factors	0.95−0.99
diffractometer	P2$_1$, graphite monochromator
scan method	ω, 0.9° range, 0.9° offset for bkgd
scan speed, deg min^{-1}	30
2θ range, deg	0−50
octants collcd	*h,k,l*
no. of data collcd	4897
no. of unique data	4357 [*R*(merge) = 0.005]
no. of data used in refinement	2732 [$I > 2\sigma(I)$]
no. of params refined	307
R	0.057
R_w	0.060 [$w = 1/\sigma^2(F_o)$]

Results and Discussion

When Li(cyclen)P is treated with Mes_2BF (eq 2), a product is formed which has a signal in the ^{31}P NMR spectrum at δ 100. This is 154 ppm downfield of (cyclen)PH and suggests a lower coordination number for phosphorus. In addition, four resonances are observed for the cyclen ring in the ^{13}C NMR spectrum for this product compared to the single resonance found in (cyclen)PH. These results strongly suggest that the product formed is Mes_2B(cyclen)P, which contains a boron−nitrogen bond and the open tricoordinate phosphine geometry. This was confirmed by X-ray analysis (see below). If chlorodiphenylphosphine is substituted for Mes_2BF in this reaction, a similar product is isolated, Ph_2P(cyclen)P. Here again, the ^{31}P NMR signal (for the cyclen phosphorus) at δ 94 and four resonances for the cyclen ring in the ^{13}C NMR spectrum are consistent with the open form.



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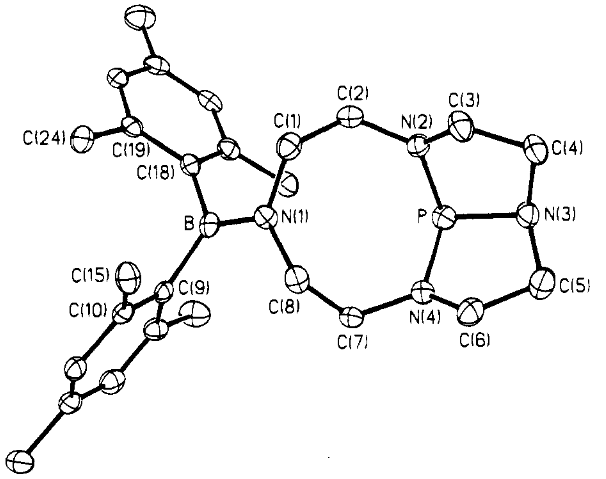


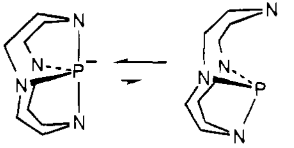
Figure 1. Computer-generated drawing of Mes_2(cyclen)P. All hydrogen atoms omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for Mes_2B(cyclen)P

P−N(2)	1.692 (3)	P−N(3)	1.755 (3)
P−N(4)	1.712 (3)	N(1)−C(1)	1.478 (5)
N(1)−C(8)	1.480 (4)	N(1)−B	1.407 (5)
N(2)−C(2)	1.449 (4)	N(2)−C(3)	1.455 (5)
N(3)−C(4)	1.482 (5)	N(3)−C(5)	1.475 (5)
N(4)−C(6)	1.485 (5)	N(4)−C(7)	1.456 (4)
C(9)−B	1.592 (6)	C(18)−B	1.600 (5)
N(2)−P−N(3)	92.0 (1)	N(2)−P−N(4)	111.8 (2)
N(3)−P−N(4)	91.6 (1)	C(1)−N(1)−C(8)	117.1 (3)
C(1)−N(1)−B	120.7 (3)	C(8)−N(1)−B	121.1 (3)
P−N(2)−C(2)	122.8 (2)	P−N(2)−C(3)	114.0 (2)
C(2)−N(2)−C(3)	120.3 (3)	P−N(3)−C(4)	109.0 (2)
P−N(3)−C(5)	109.1 (2)	C(4)−N(3)−C(5)	114.7 (3)
P−N(4)−C(6)	114.0 (2)	P−N(4)−C(7)	121.2 (2)
C(6)−N(4)−C(7)	118.6 (3)	N(1)−B−C(9)	121.2 (3)
N(1)−B−C(18)	118.6 (3)	C(9)−B−C(18)	120.0 (3)

The X-ray crystal structure of Mes_2B(cyclen)P is illustrated in Figure 1 with selected bond distances and angles listed in Table 2. The structure clearly indicates that the phosphorus is three-coordinate: the P---N(1) nonbonded distance of 3.61 Å is larger than the sum of the van der Waals radii. The geometry around the phosphorus is distorted pyramidal, but the constraint of the two five-membered rings is evident since the two N(2)−P−N(3) and N(3)−P−N(4) angles are close to 90° each. Both N(1) and B have essentially planar geometries [sums of bond angles around N(1) and B are 359.8(5) and 358.9(5)°, respectively]. The torsion angle between the C(9)−B−C(18) and C(1)−N(1)−C(8) planes of 24° is rather large for a strong π-bond; however, the B−N(1) bond length of 1.407(5) Å is toward the short end of aminoborane bond lengths which range from 1.38 Å (in Cl_2BNMe_2) to 1.49 Å [in $F_2BN(SiH_3)_2$], and indicates appreciable double bond character.[9] The eight-membered ring containing P and N(1) adopts an approximate crown conformation.

Several factors could account for the formation of open derivatives in the above reactions. First of all, π-bonding between the nitrogen lone pair and R might stabilize the open form, and this is definitely a factor in Mes_2B(cyclen)P. Secondly, the steric requirements of R may be too great at the axial position of a tbp, particularly for the mesityl groups. Thirdly, the kinetics of the reaction may be important. For example, although the formal negative charge on (cyclen)P^- is on phosphorus, the nitrogens at the axial positions of (cyclen)PH have been shown to be quite nucleophilic.[3] Moreover, an equilibrium could exist between the closed and open forms of (cyclen)P^- in solution (eq 3) in which the open form may be the more reactive. Finally, the inherent P−R and N−R bond strengths will play a role.



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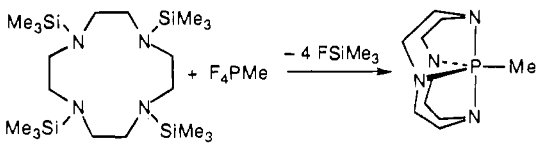
To partially address these possibilities, we attempted to synthesize the known compound (cyclen)PMe by the same procedure used above. The reported synthesis[10] (82% yield) involved the use of a reagent already containing the P−Me bond (eq 4). Under our reaction conditions, treatment of Li(cyclen)P with chloromethane yields an oil which shows two signals in the ^{31}P NMR spectrum at δ −43 and 103. In addition, the ^{13}C NMR spectrum shows one intense resonance and four smaller signals in the cyclen region. These data are consistent with the formation of both the closed and open forms, (cyclen)PMe and Me(cyclen)P (eq 5).



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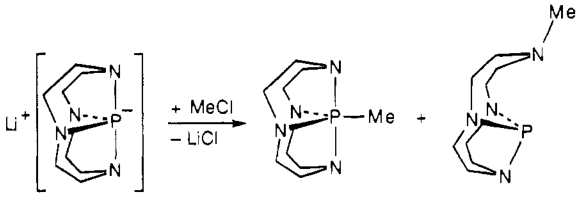
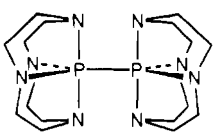


(5)

The ratio of these products (by ^1H NMR integration) varies from about 70/30 to 85/15 (cyclen)PMe/Me(cyclen)P. Thus, the closed form is the primary product, consistent with the usual constraint of the macrocycle. However, the fact that some open form is observed demonstrates that both the nitrogen and phosphorus are accessible nucleophilic sites under these reaction conditions, and the preference for the N−B and N−P linkages in Mes_2B(cyclen)P and Ph_2P(cyclen)P must be due to factors other than the greater reactivity of the nitrogen in (cyclen)P^-.

Two previous reactions of (cyclen)P^- have been reported to give P-bonded pentacoordinate products. One is the reaction of (cyclen)P^- with (cyclenP)F to give the P−P-bonded bisphosphorane $(cyclenP)_2$.[11] However, $(cyclenP)_2$ was isolated in low yield (27%) and other products were not reported. The other reaction is the high-yield synthesis of the phosphorane alcohol, (cyclen)PC(OH)CF_3Ph, via the treatment of (cyclen)P^- with trifluoroacetophenone, followed by hydrolysis. In this case, the exclusive formation of the phosphorane



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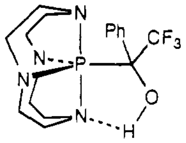
product may be due to the added stability introduced by



intramolecular hydrogen-bonding, viz.[12]

The results of this investigation reveal that the previously unknown open R(cyclen)P derivatives can be accessed via treatment of (cyclen)P$^-$ with electrophilic reagents. In these reactions, both the nitrogen and phosphorus atoms can act as nucleophilic sites. With small electrophiles having no π-bonding capability, the preference is for pentacoordinate P−R bond formation; with larger electrophiles capable of π-bonding, the preference is for open N−R bonded products.

Acknowledgment. M.L. acknowledges the National Science Foundation (Grant CHE-0123811), the Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement coordinates, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates (6 pages). Ordering information is given on any current masthead page.

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