such that the O10, O11, and O12 atoms are no longer coplanar, which prevents magnesium from binding to this site as it does with TC. *It is thus likely that in both MLH and ML_2H_2, magnesium binds CTC via its N4–O3 site.* This mode of bonding, which is consistent with CTC adopting conformation B, would also explain the following: (i) The ML_2H_2 complex is much less stable than its TC homologue. Let us indeed recall that, with TC, one ligand is thought to bind magnesium through its N4–O3 atoms whereas the other would coordinate it via its O10–O12 system, which presumably confers a higher stability on the resulting complex. (ii) The formation constant of MLH is about 1 unit lower than that of the same species with TC. It seems effectively logical to assume that, in the MLH complex of TC, the proton lies on the N4 atom, while it is associated with the O12 oxygen in the CTC corresponding species.

Conclusion

The present study confirms the considerable complexity of the coordination chemistry of tetracyclines with calcium and magnesium, with which they predominantly interfere in vivo. In particular, given that the free concentrations of Ca^{2+} and Mg^{2+} ions are several orders of magnitude higher than the therapeutic levels of tetracyclines in blood plasma, their complexes represent almost the totality of the fraction of drug not bound to proteins.[7-9] Thus, the ability of tetracyclines to diffuse into tissues first depends on the physicochemical properties of the main complexes of the above metals.

To impose structural variations on the parent TC molecule so that the resulting derivative could form predominant calcium and magnesium complexes having predetermined specific properties therefore appears a logical way of improving the bioavailability of these antibiotics. Since the minimal equipment represented by DSC is necessary to the antibacterial activity of tetracyclines in vivo,[43] the positions remaining available for such variations are confined to the C5–C9 carbons, which a priori seems to open a limited field of possibilities. On the contrary, the results obtained in the present work definitely show that apparently subtle modifications in the nature and positions of the substituent groups at these positions can entail considerable changes in the chelating properties of these substances. The specific use of substituent effects to improve tetracycline bioavailability through metal chelation thus seems to be a promising field of research.

In a recent article, Martin[19] stated about previous quantitative results of ours on calcium and magnesium complex equilibria with TC, OTC, and DOX[7-9] that "there (did) not seem to be any pattern for the variations among the three closely related antibiotics". Great efforts are probably needed before all subtleties of the metal coordination chemistry of tetracyclines under physiological conditions can be brought to light, but it does seem that part of the hidden profile of the above-mentioned pattern is now being delineated.

Acknowledgment. We thank Dr. Loucheux (INSERM U124, Lille) for the use of the CD spectrometer, and H.K. is grateful to INSERM for the award of a maintenance grant at INSERM U305 in Toulouse.

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(43) Fourtillan, J. B.; Denis, F.; Fabre, J.; Becq-Giraudon, B. *Des Têtracyclines à la Vibramycine*; Pfizer: France, Orsay, 1979.

Contribution from the Departments of Chemistry, Southern Methodist University, Dallas, Texas 75275, University of California, Davis, California 95616, and University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

Isolation and X-ray Crystal Structure of the Lithiated Phosphoranide [Li(THF)cyclenP]$_x$ and the X-ray Crystal and Electron Diffraction Structures of cyclenPH

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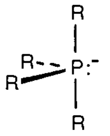
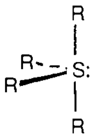
The X-ray crystal structure of the lithiated phosphoranide [Li(THF)cyclenP]$_x$ (**7**) and the X-ray crystal and electron diffraction structures of its precursor, cyclenphosphorane (cyclenPH, **1**), have been determined. Both the gas-phase and solid-state structures of **1** show the geometry to be a distorted trigonal bipyramid (tbp) with the P–N axial bonds longer than the equatorial bonds (the usual case in tbp geometries). However, there is a large difference in the equatorial N–P–N angle: 155° by electron diffraction versus about 138° by X-ray. This difference may reflect the small energy barrier between the tbp and square-pyramidal geometries for pentacoordinate species with crystal packing forces leading to the smaller angle. The structure of **7** is polymeric with each Li(THF) unit bridging two cyclenP units via coordination of the axial nitrogens. The geometry about each lithium is approximately trigonal planar while the phosphorus is a distorted pseudo trigonal bipyramid (ψ-tbp) with a lone pair occupying an equatorial position. The P–N_{ax}–Li angle is only 94°, which may be due to a weak bonding interaction between the phosphorus lone pairs and lithiums throughout the polymeric chain. X-ray data: $C_8H_{17}N_4P$, tetragonal, space group $P4_2/mnm$, a = 6.030 (1) Å, c = 13.740 (3) Å, Z = 2, R = 0.046, R_w = 0.054; $C_{12}H_{24}PON_4Li$, monoclinic, space group $C2$, a = 47.025 (10) Å, b = 10.312 (3) Å, c = 13.802 (3) Å, β = 97.92 (2)°, Z = 18, R = 0.070, R_w = 0.070.

Phosphoranide ions are 10-P-4 phosphorus anions,[1] isoelectronic with the neutral sulfuranes. Structurally, phosphoranides and sulfuranes have similar ψ-trigonal-bipyramidal (tbp) geometries with a lone pair of electrons in the equatorial plane.





However, the presence of a negative charge on the phosphorus

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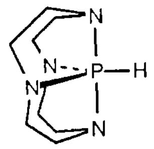
should lead to reactivity differences between the two. A striking example of this is the fact that no complexes have been reported where the sulfurane lone pair has been coordinated whereas several transition-metal adducts of phosphoranides have been synthesized,[2] many of which have come from our laboratory.[3]

Table I. Crystal Data and Data Collection Parameters for cyclenPH (**1**) and [Li(THF)cyclenP]$_x$ (**7**)[a]

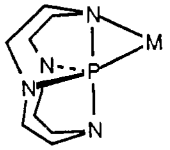
	1	**7**
formula	$C_8H_{17}N_4P$	$C_{12}H_{24}PON_4Li$
fw	200.22	278.27
color and habit	colorless prisms	colorless needles
cryst system	tetragonal	monoclinic
space group	$P4_2/mnm$ (No. 136)	$C2$ (No. 5)
a, Å	6.030 (1)	47.025 (10)
b, Å		10.312 (3)
c, Å	13.740 (3)	13.802 (3)
β, deg		97.92 (2)
V, Å^3	499.6 (2)	6629 (3)
Z	2	18
cryst dimens, mm	0.50 × 0.70 × 0.42	0.25 × 0.32 × 0.30
d_{calcd}, g cm^{-3}	1.33	1.25
μ(Mo Kα), cm^{-1}	2.3	1.8
range of transmn factors	0.88–0.92	0.94–0.96
scan method	ω, 1.0° range, 1.0° offset for bkgd	ω, 0.8° range, 0.8° offset for bkgd
scan speed, deg m^{-1}	15	12
2θ range, deg	0–55	0–50
octants collected	$+h,+k,+l$	$+h,+k,\pm l$
no. of data collcd	645	6284
no. of unique data	338 [R(merge] = 0.010]	6087 [R(merge) = 0.004]
no. data used in refinement	308 [$I > 2\sigma(I)$]	4651 [$I > 2\sigma(I)$]
no. parameters refined	35	343
R^b	0.046	0.070
$R_w{}^c$	0.054[d]	0.070[e]

[a] Conditions: T (K), 130; radiation (Å), Mo Kα (λ = 0.71069); diffractometer, P2$_1$ (graphite monochromator). [b] $R = \sum||F_o| - |F_c||/|F_o|$. [c] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$. [d] $w = 1/\sigma^2(F_o) + 0.00041F_o{}^2$. [e] $w = 1/\sigma^2(F_o)$.

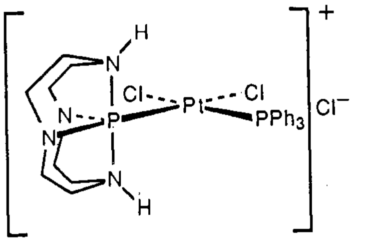
We have found that cyclenphosphorane, cyclenPH[4] (**1**) readily deprotonates at the phosphorus in the presence of transition-metal complexes to yield P–M adducts of the types **2**–**6**.[3] However, isolation and structural characterization of the uncomplexed ion, cyclenP:$^-$, has not been reported. This is important to gain greater insight into the bonding and reactivity of these hypervalent species, particularly for the polycyclic tetraamino phosphorus derivatives where the potential for P–N bond rupture has been demonstrated for the neutral species when two or more trimethylene bridges are present (equilibrium 1).[5]



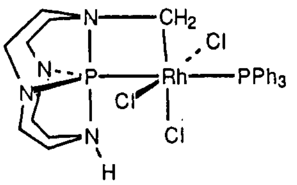
1



M = $Co(CO)_3$ **2**
$MoCp(CO)_2$ **3**
$Pt(Cl)PPh_3$ **4**



5



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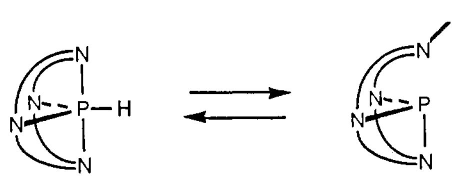

(1)

We herein report the isolation and X-ray crystal structure of THF-solvated lithium cyclenphosphoranide, [Li(THF)cyclenP]$_x$ (**7**), via deprotonation of cyclenPH with butyllithium.[6] Also reported are the (X-ray) solid-state and (electron diffraction) gas-phase structures of cyclenPH.[7] This affords the first direct structural comparison between a P–H phosphorane and deprotonated phosphoranide ion.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen. Solvents were dried, distilled, and purged with nitrogen prior to use. The synthesis of cyclenPH was carried out as previously described,[3a] and a suitable single crystal from the sublimed product was selected for X-ray measurements.

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(4) The cyclic molecule 1,4,7,10-tetraazacyclododecane has been termed "cyclen" (Collman, M. P.; Schneider, P. W. *Inorg. Chem.* **1966**, *5*, 1380). The word "cyclenphosphorane" has been used for **1** (see ref 5). We use the abbreviation cyclenPH to denote **1** and cyclenPX to denote a molecule with a non-hydrogen substituent at phosphorus.

(5) (a) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149. (b) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333.

(6) (a) Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3378. (b) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955.

(7) An X-ray analysis for cyclenPH with an R value of 0.22 has previously been reported: Hamerlinck, J. H. H.; Schipper, P.; Buck, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 385.

All NMR spectra were recorded on an NT-300WB spectrometer, and chemical shifts were measured relative to solvent peaks, referenced to TMS, 85% H_3PO_4, and LiCl for ^1H, ^{31}P, and ^7Li, respectively. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Isolation of [Li(THF)cyclenP]$_x$ (7). In a typical procedure, a stirred solution of cyclenPH (24 mg, 0.12 mmol) in THF (~0.5 mL) was treated dropwise with 1.6 M butyllithium in hexane (90 μL, 0.14 mmol). The mixture was stirred at ambient temperature for 15 min and then placed in a −30 °C freezer for 5 h, yielding clear, colorless crystals. Upon removal of the mother liquor, the crystals turned white and opaque due, most likely, to loss of coordinated solvent. The product was washed with pentane (2 × 1 mL) and pumped dry, yielding 21 mg (85%) of a white, powdery solid. The ^1H NMR spectrum indicated no coordinated THF. Anal. Calcd for Li(cyclenP) ($LiC_8H_{16}N_4P$): C, 46.61; H, 7.82; N, 27.18. Found: C, 46.29; H, 7.85; N, 26.84. NMR (THF-d_8): ^1H, δ 2.62 (br, 8 H), 2.81 (br, 8 H); $^{31}P\{^1H\}$, δ 11 (br); ^7Li, δ 0.09 (br). The unsolvated product Li(cyclenP) is insoluble in pentane and benzene but redissolves readily in THF.

X-ray Structure Determination and Refinement. The crystals were mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. All crystallographic computing was carried out by using SHELXTL, Version 5, installed on a Data General MV/1000 Eclipse Series computer. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[8] Further details are given in Table I.

cyclenPH (1). The structure can be solved by direct methods in either of the two space groups $P4_2/mnm$ (No. 136) or $P4_2nm$ (No. 102). The structure is disordered in both space groups but converges better in $P4_2/mnm$, the centrosymmetric space group. It was therefore selected as the more likely choice. Since $Z = 2$, the molecule is required to possess site symmetry *mmm*. The cyclenPH molecule cannot have this symmetry, but it can be achieved by disorder of phosphorus, its bonded hydrogen, and one of the nitrogens with respect to a mirror plane. In this way there are two half-molecules of cyclenPH at the site, and the periphery of the set of two is essentially fixed. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on phosphorus and C(1) were found on a difference map and allowed to refine freely. The hydrogens on C(2) were subject to disorder, but their positions could be calculated. These latter hydrogens were included at their calculated positions, and only their thermal parameters were refined. The largest feature on a final difference map was of height 0.30 e Å^{-3}, located on the mirror plane that bisects the two hydrogens on C(2).

The disorder in the structure of cyclenPH is unusual but appears to be real. There is no evidence for axial doubling from an examination of axial photos. Furthermore, the average atomic volume (19 Å^3) is normal, and there are no short intermolecular contacts. Since the disorder constrains atoms to be located in one or two of three mirror planes, there is a loss in the precision of the calculated bond distances and angles. The thermal parameters, in fact, are approximately twice as large as they should be for a structure determined at 130 K, and this is a reflection of the actual physical situation. That is, for normal atoms at 130 K, typical values of U are between 0.018 and 0.022 Å^2, or 0.13–0.15-Å rms displacements. For cyclenPH, the U's range from 0.033 for P to 0.060 Å^2 for C(1), or 0.18–0.24-Å displacements. For a given disordered atom, its true position can be to either the one side or the other side of the mirror plane in which it resides, but it is difficult to assign a model for the disorder when every atom is involved. A reasonable estimate of the actual esd's on the bond distances is in the range 0.02–0.05 Å and for the bond angles, 4 to 7°. Of particular interest is the N(1)–P–N(1′) angle, which differs by 17.4° from the electron diffraction value. Is it possible that the disorder can cause such a large difference? Several different calculations indicate that the answer is *no*. For example, if 0.18-Å displacement of the N(1) and N(1′) atoms to the phosphorus side of their mirror plane is allowed, the N(1)–P–N(1′) angle is increased by 13.8° from 137.9 to 151.7°, but at the same time the P–N distance is decreased to 1.634 Å, a value that is unreasonably short. If the P–N distance is constrained to the electron diffraction value, an angle of 139.9° results. If we take into account the natural thermal motion of the atoms at 130 K, it seems likely that the angle is no more than 5° larger than the reported angle.

[Li(THF)cyclenP]$_x$ (7). The structure was solved by direct methods in the space group $C2$ (No. 5). It could not be solved in the other two possible space groups (based on the condition hkl, $h + k = 2n$) Cm (No. 8) and $C2/m$ (No. 12). Final refinement was carried out with isotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included by using a riding model, with C–H of 0.96 Å, and $U_H = 1.2U_C$.

Table II. Atomic Coordinates (×10^4; ×10^3 for H) and Isotropic Thermal Parameters (Å^2 × 10^3) for cyclenPH (1)

	x	y	z	U
P	715 (2)	715 (2)	0	33 (1)[a]
N(1)	−1858 (3)	1858 (3)	0	44 (1)[a]
N(2)	537 (4)	537 (4)	1281 (3)	47 (1)[a]
C(1)	−2693 (4)	2693 (4)	908 (2)	60 (1)[a]
C(2)	−1418 (4)	1418 (4)	1680 (2)	56 (1)[a]
H	241 (8)	241 (8)	0	33 (16)
H(1)	−431 (4)	263 (3)	92 (2)	71 (7)
H(2A)	−232	22	192	95 (18)
H(2B)	−105	240	221	83 (15)

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

The largest feature on a final difference map was of height 0.63 e Å^{-3}.

Atomic coordinates and isotropic thermal parameters for 1 and 7 are given in Tables II and III, respectively.

Electron Diffraction. Electron diffraction scattering intensities were recorded photographically on Kodak Electron Image plates by using the Edinburgh diffraction apparatus.[9] Nozzle-to-plate distances of 96 and 256 mm were used, with two plates being obtained at each distance. The sample was maintained at 380 K for the long-distance exposures and at 410 K for the short distance, and the nozzle temperatures were 400 and 420 K, respectively. The accelerating voltage was ca. 44 kV, and the electron wavelength was determined from scattering patterns for benzene, recorded consecutively with those for the compound. Data were obtained in digital form by using a Joyce-Loebl MDM6 densitometer[10] at the SERC Daresbury Laboratory. All data analysis was performed by using standard data reduction[10] and least-squares refinement[11] programs and the scattering factors of Schäfer et al.[12]

For the purposes of least-squares refinements, it was assumed that the molecules of cyclenPH have C_{2v} symmetry. In principle, it is possible that distortions of the structure could lead to lower symmetry than this, for example by lengthening of one of the P–N(axial) bonds or by twisting of the rings to give overall C_{2v} symmetry. However, the fit to the experimental data using the C_{2v} model was very good (final R factors were $R_G = 0.060$ and $R_D = 0.046$), and we believe that the true structure is close to this. The structure of the N_4PH fragment was defined by the P–H bond length, the mean P–N length, the difference between axial and equatorial P–N distances, and the angles $N_{eq}PN_{eq}$ and $N_{ax}PN_{ax}$. The coordination at phosphorus was thus assumed to be trigonal bipyramidal with hydrogen in an equatorial position, although the model would allow distortion to a square pyramid. So that no unnecessary constraints would be applied to the five-membered rings, the positions of the carbon atoms were simply defined by their x, y, and z coordinates. These parameters are inevitably correlated with each other, but provided all the parameters are refined, this does not cause any problems. The bond lengths, bond angles, and dihedral angles in the rings were all calculated as dependent parameters. The placing of the hydrogen atoms involved several assumptions. All the C–H distances were taken to be equal, as were the two HCH angles. The bisectors of these angles were assumed to coincide with the bisectors of the NCC angles. Just two parameters were therefore required to define the hydrogen atoms positions, making a total of 13 geometrical parameters.

Of the 13 independent geometrical parameters, 12 could be refined without great difficulty. The P–H bond length refined to 1.46 ± 0.06 Å, and it was subsequently fixed at 1.42 Å, and the HCH angle was excluded from the final refinement to keep the total number of refining parameters within the limit of the refinement program. In addition, eight amplitudes of vibration or groups of amplitudes were refined. Those that were not refined were fixed at reasonable values, as observed or calculated from spectroscopic data for related molecules. The only vibrational parameters that did not refine satisfactorily were those for the bonded distances P–N and for the group of N–C and C–C bonded distances. In each case the refined value was rather small and poorly determined (0.038 ± 0.009 and 0.031 ± 0.012 Å, respectively), so they were fixed at more reasonable values, so that the best possible estimates of bond lengths could be obtained. The electron diffraction data were tested for

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

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(12) Schäfer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.

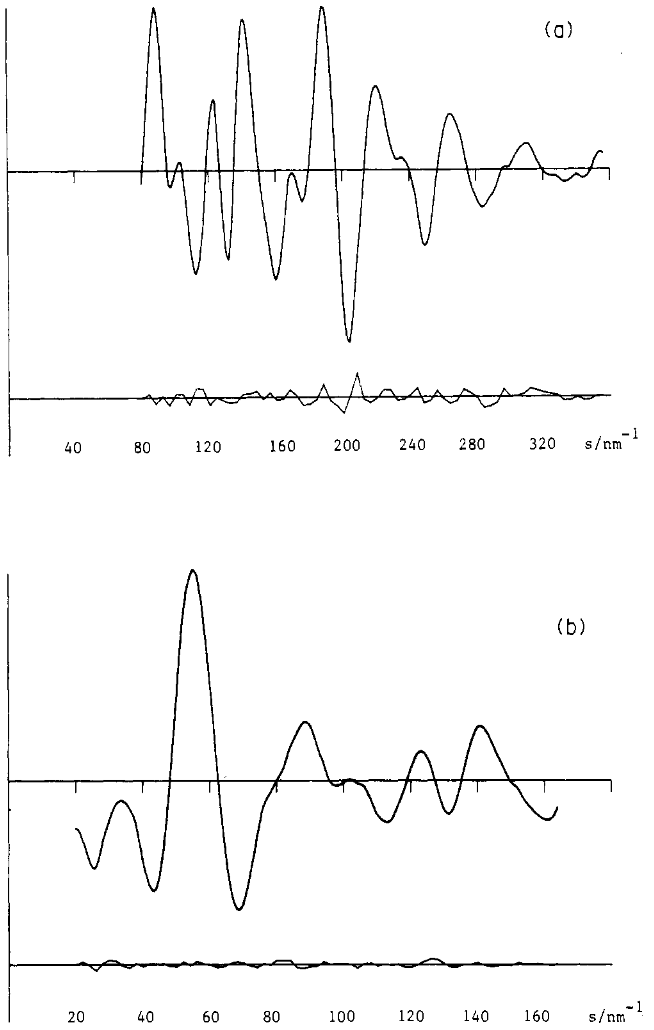

Figure 1. Observed and final weighted difference molecular electron scattering intensity curves at nozzle-to-plate distances of (a) 96 and (b) 256 mm.

smaller equatorial angles by constraining the equatorial N–P–N angle to 145 and 135°. The R_G values rose to 0.078 and 0.114, respectively. The N–P–N axial angle varied by about 2°, and the main changes were in the angles at N and C and in the associated dihedral angles. Thus, the data do not fit a model with an equatorial angle significantly below 155°.

The final parameters are given in Table IV. Errors (in parentheses) are standard deviations obtained in the least-squares analysis and include allowances for systematic errors in the electron wavelength etc. They cannot take account of correlations between refining and nonrefining parameters, such as some amplitudes of vibration, but the effects of correlations between refining parameters are of course included automatically.

Observed and final weighted difference molecular electron scattering intensity curves and observed and final difference radial distribution curves are shown in Figures 1 and 2, respectively.

Structural Description

cyclenPH (1). Selected atomic distances and angles obtained by both X-ray and electron diffraction methods are listed in Table V,[13] and the X-ray crystal structure of cyclenPH is illustrated in Figure 3. Both methods show the same overall geometry, that of a distorted tbp with the P–N axial bonds longer than the equatorial bonds (the usual case in tbp geometries). However, there is a large difference in the equatorial N–P–N angle: 155.3 (18)° by electron diffraction versus 138 (5)° by X-ray. This difference may reflect the small energy barrier between the tbp and square-pyramidal (sp) geometries for pentacoordinate species,[14] with crystal packing forces leading to the smaller angle. [The large (X-ray) bond angle error is due to the disorder in the X-ray structure; see Experimental Section.]

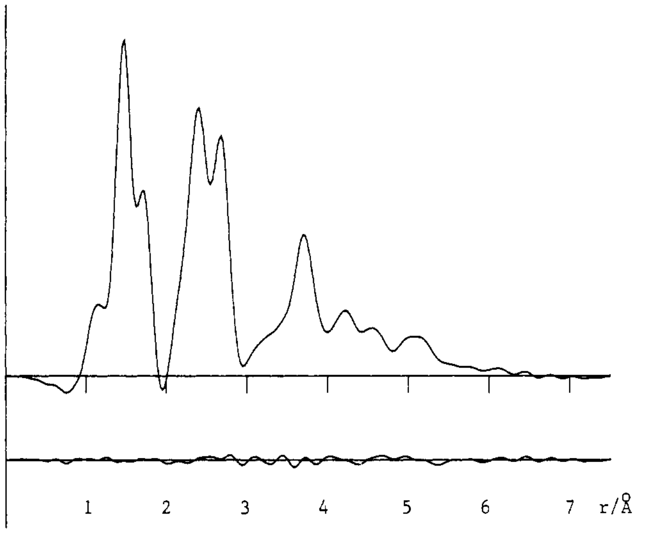

Figure 2. Observed and final difference radial distribution curves, $P(r)/r$. before Fourier inversion the data were multiplied by s exp[$-0.00002s^2/(Z_P - f_P)(Z_N - f_N)$].

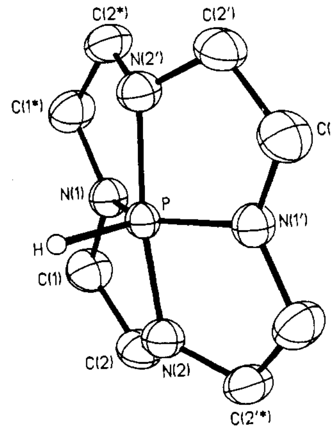

Figure 3. Computer-generated drawing of cyclenPH (1). Symmetry positions: ′ = $y, x, -z$; * = $-y, -x, -z$; ′* = $-x, -y, z$.

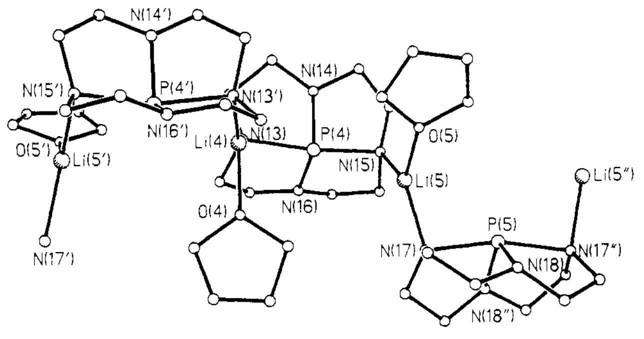

Figure 4. Computer-generated drawing of [Li(THF)cyclenP]$_x$ (7) showing a portion of one of the polymeric chains. Symmetry positions: ′ = $-x, y, -z$; ″ = $-x, y, -z - 1$.

[Li(THF)cyclenP]$_x$ (7). The asymmetric unit contains 4.5 [Li(THF)cyclenP] units. By a combination of the 2-fold axis and translation along c, they form two parallel, spiral, noninteracting chains propagating in the c direction. One chain comprises three

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(13) Due to difficulties in assigning correlations, X-ray esd values for the bond lengths and angles were calculated by assigning average isotropic positional parameters (Å) as follows: P, 0.001; N(1), 0.0015; N(2), 0.003; C(1) and C(2), 0.0025. We thank a reviewer for bringing this to our attention.

(14) Holmes, R. R. *Pentacoordinated Phosphorus*; American Chemical Society: Washington, DC, 1980; Vols. 1 and 2.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Li(THF)cyclenP]_x$ (**7**)

	x	*y*	*z*	*U*
P(1)	1564 (1)	4083 (2)	3910 (1)	17 (1)
P(2)	2114 (1)	6600 (2)	7236 (1)	21 (1)
P(3)	1386 (1)	7070 (2)	10308 (1)	21 (1)
O(1)	1995 (1)	5988 (5)	2117 (4)	30 (1)
O(2)	1479 (1)	6955 (5)	5297 (3)	26 (1)
O(3)	1769 (1)	4540 (5)	8854 (3)	28 (1)
N(1)	1475 (1)	4052 (6)	2479 (4)	21 (1)
N(2)	1196 (1)	3930 (6)	3918 (4)	25 (1)
N(3)	1592 (1)	3757 (6)	5358 (4)	23 (1)
N(4)	1725 (1)	2566 (6)	3830 (4)	21 (1)
N(5)	2152 (1)	6393 (6)	5839 (4)	22 (1)
N(6)	2439 (1)	5766 (6)	7507 (4)	26 (1)
N(7)	2155 (1)	7083 (7)	8663 (4)	23 (1)
N(8)	2174 (1)	8253 (6)	7056 (4)	26 (1)
N(9)	1354 (1)	7122 (7)	8894 (4)	24 (1)
N(10)	1028 (1)	6674 (7)	10156 (4)	31 (2)
N(11)	1331 (1)	7426 (6)	11663 (4)	24 (1)
N(12)	1461 (1)	8708 (7)	10233 (5)	32 (2)
C(1)	1164 (2)	3837 (8)	2208 (5)	27 (2)
C(2)	1028 (2)	4424 (8)	3029 (5)	28 (2)
C(3)	1093 (2)	4203 (9)	4824 (5)	32 (2)
C(4)	1298 (2)	3504 (9)	5599 (6)	33 (2)
C(5)	1776 (2)	2641 (8)	5565 (5)	25 (2)
C(6)	1730 (2)	1735 (8)	4685 (5)	29 (2)
C(7)	1646 (2)	1911 (8)	2903 (5)	25 (2)
C(8)	1639 (2)	2956 (7)	2136 (5)	21 (2)
C(9)	2205 (2)	5724 (8)	2942 (5)	29 (2)
C(10)	2417 (2)	6851 (8)	2972 (5)	30 (2)
C(11)	2405 (2)	7247 (9)	1904 (5)	33 (2)
C(12)	2157 (2)	6471 (10)	1387 (6)	46 (2)
C(13)	2388 (2)	5465 (8)	5807 (5)	30 (2)
C(14)	2608 (2)	5681 (8)	6698 (5)	23 (2)
C(15)	2607 (2)	6100 (8)	8433 (5)	29 (2)
C(16)	2393 (2)	6293 (8)	9150 (5)	32 (2)
C(17)	2219 (2)	8464 (8)	8765 (6)	34 (2)
C(18)	2090 (2)	9073 (8)	7812 (5)	30 (2)
C(19)	2099 (2)	8679 (8)	6060 (5)	27 (2)
C(20)	2214 (2)	7646 (8)	5438 (5)	31 (2)
C(21)	1419 (2)	7702 (8)	4409 (5)	29 (2)
C(22)	1166 (2)	8529 (9)	4536 (6)	35 (2)
C(23)	1205 (2)	8765 (9)	5623 (6)	37 (2)
C(24)	1322 (2)	7499 (9)	6034 (6)	37 (2)
C(25)	1136 (2)	6149 (8)	8577 (5)	28 (2)
C(26)	891 (2)	6272 (8)	9210 (5)	31 (2)
C(27)	857 (2)	6871 (8)	10928 (5)	28 (2)
C(28)	1029 (2)	7771 (8)	11665 (5)	28 (2)
C(29)	1517 (2)	8525 (8)	11965 (5)	29 (2)
C(30)	1503 (2)	9480 (8)	11104 (5)	27 (2)
C(31)	1427 (2)	9354 (8)	9304 (5)	26 (2)
C(32)	1253 (2)	8428 (8)	8595 (5)	29 (2)
C(33)	1808 (2)	3671 (8)	8077 (5)	29 (2)
C(34)	1757 (2)	2331 (9)	8436 (6)	37 (2)
C(35)	1789 (3)	2478 (12)	9494 (8)	67 (3)
C(36)	1776 (2)	3821 (10)	9743 (7)	49 (3)
Li(1)	1578 (3)	5795 (13)	1958 (9)	27 (3)
Li(2)	1757 (3)	5570 (14)	5486 (10)	31 (3)
Li(3)	1751 (3)	6417 (14)	8736 (9)	32 (3)
P(4)	381 (1)	1954 (2)	−1571 (1)	21 (1)
P(5)	0	4748 (3)	−5000	27 (1)
O(4)	0	4201 (8)	0	37 (2)
O(5)	−260 (1)	2125 (6)	−3383 (4)	39 (1)
N(13)	402 (1)	1701 (6)	−141 (4)	22 (1)
N(14)	400 (1)	285 (7)	−1613 (5)	32 (2)
N(15)	444 (1)	1865 (7)	−2966 (4)	29 (2)
N(16)	722 (1)	2679 (6)	−1339 (4)	26 (1)
N(17)	29 (2)	4977 (7)	−3558 (5)	36 (2)
N(18)	−313 (2)	5706 (7)	−5096 (5)	36 (2)
C(37)	479 (2)	356 (8)	86 (6)	39 (2)
C(38)	334 (2)	−423 (9)	−765 (5)	36 (2)
C(39)	333 (2)	−287 (9)	−2553 (5)	37 (2)
C(40)	486 (2)	536 (9)	−3225 (7)	44 (2)
C(41)	704 (2)	2660 (10)	−3049 (6)	41 (2)
C(42)	899 (2)	2554 (9)	−2108 (5)	32 (2)
C(43)	865 (2)	2605 (9)	−351 (6)	35 (2)
C(44)	629 (2)	2601 (9)	297 (6)	35 (2)
C(45)	46 (2)	5010 (10)	871 (7)	52 (3)
C(46)	−22 (2)	6332 (10)	528 (6)	47 (2)
C(47)	−271 (2)	5337 (10)	−3414 (7)	46 (2)
C(48)	−386 (2)	6204 (9)	−4209 (6)	40 (2)
C(49)	238 (2)	5917 (11)	−3226 (7)	53 (3)
C(50)	352 (2)	6551 (12)	−4069 (7)	67 (3)
C(51)	−372 (2)	1562 (11)	−4301 (7)	52 (3)
C(52)	−640 (3)	886 (14)	−4136 (8)	80 (4)
C(53)	−639 (3)	769 (13)	−3114 (8)	72 (3)
C(54)	−401 (2)	1576 (9)	−2626 (6)	40 (2)
Li(4)	0	2344 (19)	0	33 (5)
Li(5)	99 (3)	3060 (15)	−3259 (10)	37 (3)

Table IV. Electron Diffraction Molecular Parameters (Distances, Å; Angles, deg)

(a) Independent Parameters

p_1	r(P–H)	1.420 (fixed)
p_2	r(P–N) mean	1.731 (1)
p_3	r(P–N) ax–eq	0.087 (3)
p_4	C(1*)[a] x coord	−2.297 (14)
p_5	C(1*) y coord	1.261 (7)
p_6	C(1*) z coord	0.466 (15)
p_7	C(2*) x coord	−1.220 (11)
p_8	C(2*) y coord	2.276 (18)
p_9	C(2*) z coord	0.825 (24)
p_{10}	$\angle N_{ax}PN_{ax}$	169.0 (15)
p_{11}	$\angle N_{eq}PN_{eq}$	155.3 (18)
p_{12}	r(C–H)	1.133 (3)
p_{13}	∠HCH	108.8 (18[b])

(b) Dependent Parameters

$\angle PN_{eq}C$	117.5 (5)	ϕNCCN	31.9 (10)
$\angle PN_{ax}C$	112.7 (5)	$\phi PN_{eq}CC$	24.7 (15)
$\angle N_{eq}CC$	106.7 (11)	$\phi PN_{ax}CC$	28.8 (8)
$\angle N_{ax}CC$	104.5 (8)		

[a] Electron diffraction atom numbering changed to be consistent with X-ray atom numbering. [b] Refined earlier but fixed in final refinement.

[Li(THF)cyclenP] units that simply propagate by translation along *c*. A portion of the chain containing the remaining 1.5 units is illustrated in Figure 4. One 2-fold axis passes through Li(4) and O(4), and another, through P(5). The distance from Li(5′) to Li(5″) is the repeat distance along *c*. Selected bond distances and angles are presented in Table VI as both ranges and mean values. The overall geometry about the phosphorus atom in the cyclenP moiety is ψ-tbp with nitrogen atoms at both axial and two equatorial positions. The third equatorial position is occupied by a lone pair of electrons. As in cyclenPH, the P–N axial bonds are longer than the equatorial bonds, though in this case by about 0.25 Å. Each lithium is bonded to an axial nitrogen from two different cyclenP units, leading to the polymeric chain structure. In addition, one molecule of THF is coordinated to each lithium. The geometry around each lithium is approximately trigonal planar [the sum of the lithium bond angles is about 360° (see Table VI)]. However, a further weak interaction with the phosphorus may also be present (see below). The sum of the axial nitrogen bond angles (within the cyclenP unit) has decreased to about 326° and reflects the distorted tetrahedral geometry.

Discussion

Both **1** and **7** exhibit the "closed" form of cyclenP, where all four nitrogens remain bonded to the phosphorus atom. In fact, this is the usual geometry for cyclenPX derivatives and is found in the related species $(HcyclenP)(CH_2)RhCl_3(PPh_3)$ (**6**),[3b] $(cyclenP)_2$ (**8**),[6] $cyclenPH{\cdot}2BH_3$ (**9**),[15] and cyclenPF (**10**).[16] Com-

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

(16) A very crude description of the X-ray crystal structure of cyclenPF stating that the molecule is distorted midway between tbp and sp and giving the values listed in Table VII has appeared: Richman, J. E. *Tetrahedron Lett.* **1977**, 559.

Table V. Selected Internuclear Distances (Å) and Angles (Deg) for cyclenPH (**1**)[a]

	X-ray (130 K)[b] dist	electron diffraction (380–410 K) dist	electron diffraction (380–410 K) amplitude
P–H	1.45 (7)	1.46 (6)[c]	0.085
P–N(1)	1.698 (2)	1.687 (2)	0.045
P–N(2)	1.767 (3)	1.775 (2)	0.045
N(1)–C(1)	1.436 (3)	1.421 (3)	0.042
N(2)–C(2)	1.404 (4)	1.476 (4)	0.042
C(1)–C(2)	1.519 (4)	1.523 (4)	0.042

	X-ray[b] angle	electron diffraction angle
N(1)–P–N(2)	88.2 (2)	88.8
N(1)–P–H	111 (1)	102.3
N(1)–P–N(1′)	137.9 (2)	155.3 (18)
N(2)–P–N(2′)	170.1 (4)	169.0 (15)
N(2)–P–H	95 (1)	95.5
C(1)–C(2)–N(2)	110.1 (2)	104.5
P–N(1)–C(1)	117.6 (1)	117.5 (5)
C(1)–N(1)–C(1*)	120.5 (2)	125.0
P–N(2)–C(2)	114.6 (2)	112.7 (5)
C(2)–N(2)–C(2′*)	118.9 (5)	111.5
N(1)–C(1)–C(2)	104.6 (2)	106.7 (11)
∑N(1)[d]	355.7	360.0
∑N(2)[d]	348.1	336.9

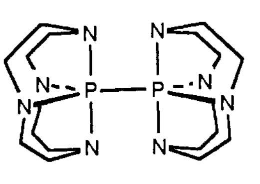
[a] Symmetry codes: ′ = *y*, *x*, −*z*; * = −*y*, −*x*, −*z*; ′* = −x, −y, z. [b] The esd values listed do not take into account the disorder; see Experimental Section. Also, see ref 13. [c] The P–H bond length refined to this value but was subsequently fixed at 1.42 Å to reduce the number of parameters in the final refinement. [d] The sum of the nitrogen bond angles defined as the sum of the C–N–C and twice the P–N–C angle.

Table VI. Selected Internuclear Distances (Å) and Angles (deg) for [Li(THF)cyclenP]$_x$ (**7**)

	range	mean
P–N$_{eq}$	1.717 (7)–1.761 (7)	1.74
P–N$_{ax}$	1.937 (6)–2.014 (6)	1.98
Li–N	2.02 (2)–2.05 (2)	2.03
Li–O	1.92 (2)–1.95 (1)	1.94
Li–P	2.67 (1)–3.23 (1)	2.92
N$_{eq}$–P–N$_{eq}$	110.7 (3)–115.4 (3)	112
N$_{ax}$–P–N$_{ax}$	162.6 (3)–166.6 (3)	165
N$_{ax}$–P–N$_{eq}$	84.3 (3)–87.7 (3)	86
N–Li–N	130.0 (7)–142.0 (11)	137
O–Li–N	107.6 (7)–118.1 (7)	111
P–Li–P	159.4 (4)–164.7 (4)	162
P–N–Li	83.6 (4)–108.4 (4)	94
∑N(eq)[a]	344–360	350
∑N(ax)[a]	322–328	326
∑Li[b]	358–360	359

[a] The sum of the nitrogen bond angles defined as the sum of the one C–N–C and two P–N–C angles. [b] The sum of the lithium bond angles defined as the sum of the one N–Li–N and two O–Li–N angles.

parative structural data for these compounds are presented in Table VII.



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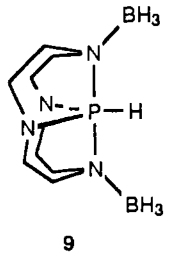

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Table VII. Selected Internuclear Distances (Å) and Angles (deg) for (HcyclenP)(CH$_2$)RhCl$_3$(PPh$_3$) (**6**), (cyclenP)$_2$ (**8**), cyclenPH·2BH$_3$ (**9**), and cyclenPF (**10**)[a]

	6	**8**	**9**	**10**
P–N$_{eq}$	1.67 (1)[b]	1.694 (2)	1.65 (1)[b]	
P–N$_{ax}$	1.937 (7) [P–N(H)] 1.911 (8) [P–N(C)]	1.782 (2)	1.87 (1)[b]	
N$_{eq}$–P–N$_{eq}$	112.4 (3)	131.1 (1)	125.6 (3)	
N$_{ax}$–P–N$_{ax}$	170.6 (3)	169.6 (1)	176.8 (3)	
N$_{ax}$–P–N$_{eq}$	86.7 (3)–88.7 (3)	87.8 (1)	88.5 (2)–90.0 (2)	
∑N$_{eq}$[c]	357, 360	351	359[b]	352
∑N$_{ax}$[c]	323, 331	343	323[b]	347

[a] Data from the following references: **6**, ref 3b; **8**, ref 6; **9**, ref 15; **10**, ref 16. [b] Average value. [c] The sum of the nitrogen bond angles defined as the sum of the one C–N–C and two P–N–C angles (within the cyclenP unit).

The only unusual feature of the structure of cyclenPH is the extremely large equatorial N–P–N angle, which reflects the small steric effects of the hydrogen atom; the corresponding angle in **8** is 131.1°. The equatorial nitrogen atoms are more planar than the axial nitrogens (Table V), a trend that has been observed before in **8** and **10**. This is in line with the more general trend of P–N bond lengths vs hybridization at the nitrogen atom: as the hybridization of nitrogen changes from sp^3 to sp^2, the P–N bond length decreases.[15,17] Two other factors may contribute to the bond length difference. One is that axial bonds are usually longer than equatorial bonds in a tbp. Another is the fact that P–N π-bonding is more efficient in the equatorial plane of a tbp, which should lead to a shorter P–N equatorial bond.[18]

Turning now to **7**, the overall geometry of the cyclenP group is preserved in the phosphoranide ion. The most prominent features of the structure of **7** are that (1) no P–N bonds are cleaved although the axial P–N bonds are extremely long, (2) the equatorial N–P–N angle is considerably smaller than that in cyclenPH, (3) the lithium atoms are bonded to nitrogen rather than phosphorus, and (4) the lithium atoms bridge cyclenP units leading to the polymeric chains.

Although phosphoranides have a formal negative charge on the phosphorus atom, the fact that the lithiums are directly bonded to nitrogen suggests that the axial nitrogens in cyclenphosphoranide are more nucleophilic than phosphorus. This is consistent with the experimental observation of the high nucleophilicity of the axial nitrogens in other cyclenPX derivatives (see **2**–**6**, above).

As expected, substitution of a lone pair of electrons for hydrogen causes a decrease in all of the N–P–N angles, with the equatorial angle showing the greatest dimution. This angle is comparable to the corresponding angle in **6** and reflects the large steric bulk of the lone pair in **7** and the trans chlorine atoms in **6**. Accompanying the bond angle lowering is an increase in both P–N bond lengths, particularly the axial distances. The increase in the equatorial distances is probably due to repulsion between the lone-pair electrons on the phosphorus and nitrogens. (Note that the P–N equatorial bonds in **6** and **9** are slightly shorter than those in cyclenPH.) However, the axial P–N bonds have increased by an average of about 0.21 Å and are now more than 0.1 Å longer than the sum of their covalent radii! A definite trend is apparent in the compounds where the axial nitrogen lone pairs are coordinated; the axial bond lengths increase in the order **9** < **6** < **7**, and this sequence corresponds to the expected electron-withdrawing abilities of BH$_3$ < CH$_2$R$^+$ ≈ H$^+$ < Li$^+$. As more electron density is removed from the three-center/four-electron hypervalent bond, the bond lengths increase.

It has previously been suggested that the three-coordinate phosphine resonance form may be an important consideration in R$_4$P:$^-$ systems. In fact, phosphoranide/phosphine equilibria have been postulated in certain systems containing spirocyclic oxygen ligands attached to the phosphorus.[1d,f,k] The elongated P–N axial bonds in **7** imply that this structure more closely resembles a

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(17) (a) Rømming, C.; Songstad, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 187. (b) Rømming, C.; Songstad, J. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 689.

(18) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

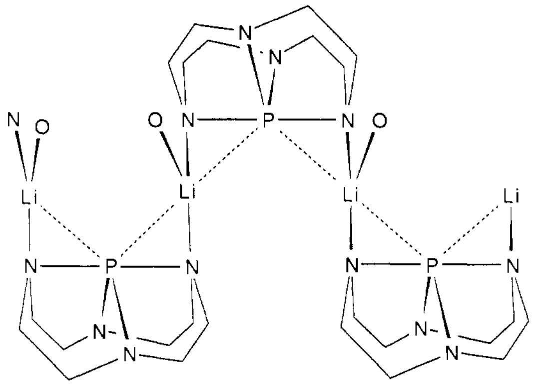
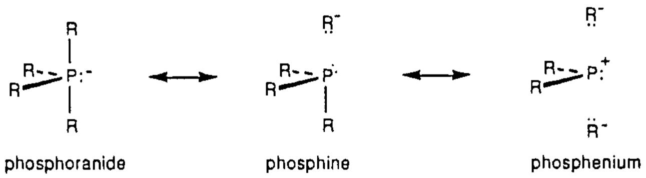


Figure 5. Illustration of $[\mathrm{Li(THF)cyclenP}]_x$ (**7**) showing the Li- - -P interaction. Methylene groups of THF are omitted for clarity.

stabilized transition state involving cleavage of both axial bonds resulting in a phosphenium ion, not a phosphine.



In light of the geometry of **7**, it appears that all three resonance forms are important in describing the electronics of phosphoranides, with the dominant form being dictated by the specific ligand set around the phosphorus atom.

The lithium geometry is approximately trigonal planar, considering the bonds to oxygen and nitrogen. The Li–O bond lengths are typical for Li–THF bonds, while the Li–N bonds are about 0.1 Å shorter than in usual $R_3N \rightarrow Li$ linkages.[19,20] The Li–N bond lengths are closer to amide–Li bond lengths (ca. 2.0 Å),[20,21] again reflecting the strong nucleophilic character of the axial nitrogens. Although the axial nitrogens are four-coordinate, the average P–N–Li angle is only 94°. This value can be compared to the close to tetrahedral P–N–B angle of 111° in **9**. The small angle may be due to a secondary interaction of the lithium with the lone pairs on the phosphorus atoms. The average Li–P distance in **7** of 2.92 Å is outside the usual range of directly bonded Li–P atoms in lithium diorganophosphides (about 2.4–2.7 Å)[22] but well within the range for a weak bonding interaction extended over the chain as depicted in Figure 5. In this way, each lithium bonds to two phosphorus atoms and each phosphorus to two lithiums. The P–M–N (M = metal) triangular bonding arrangement that results is quite common in cyclenPX derivatives (see **2**–**4**, above). This interaction may be primarily covalent, involving overlap of the empty 2p orbital on lithium with the phosphorus lone pair, or ionic, where electrostatic factors predominate.[20]

Acknowledgment. We thank the Robert A. Welch Foundation (M.L.) and National Science Foundation (P.P.P.) for generous financial support. M.L. thanks Fred Davidson for obtaining the NMR spectra.

Supplementary Material Available: Tables of anisotropic thermal parameters for **1** (X-ray), bond distances, bond angles, and hydrogen atom coordinates for **7**, a stereoview of **7** showing the packing, tables of camera distances and weighting functions, interatomic distances and amplitudes of vibration, a least-squares correlation matrix, and atomic coordinates, and molecular structure figures for **1** (electron diffraction) (12 pages); tables of observed and calculated structure factors for **1** and **7** (30 pages). Ordering information is given on any current masthead page.

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(19) For example, N–Li bond lengths range from about 2.1 to 2.2 Å in Li(TMEDA) (TMEDA = tetramethylethylenediamine) complexes (see ref 20).

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EPR, ENDOR, and Optical Absorption Studies on the Electrochemically Produced Cycloheptatrienylcyclopentadienyltitanium $[(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_7)]$ Anion Radical

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Cycloheptatrienylcyclopentadienyltitanium $[(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_7)]$ exhibits by cyclic voltammetry in THF a one-electron reversible reduction wave at −2.0 V (vs Ag/AgCl/KCl). The 17-electron paramagnetic radical anion produced, $[(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_7)]^-$, was fully characterized by EPR, and the magnetic parameters were determined by studies on liquid and frozen solutions. The optical spectra of both the neutral compound and the anion were measured and interpreted according to a molecular orbital scheme. The structure of the radical anion was determined by proton ENDOR at 30 and 100 K whereby it is shown that the geometry of the parent neutral molecule is preserved upon this one-electron reduction.

Introduction

Electron transfer in sandwich π complexes is a subject of continuing investigations, and of particular interest are simple systems such as the widely studied ferrocene/ferrocenium couple, in which this process occurs reversibly.

In the case of group 4 transition metals, the mixed-sandwich compounds are structural analogues of ferrocene and are therefore expected to undergo similar electron-transfer reactions. Nonetheless, this aspect of their chemistry seems to be very poorly documented. For this reason we undertook the following study on the diamagnetic 16-electron cyclopentadienylcycloheptatrienyltitanium compound, $[(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_7)]$, and the

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