Inorg. Chem. **1986**, *25*, 1243–1247

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Structural Characterization of the Solvate Complexes of the Lithium Diorganophosphides $[\{Li(Et_2O)PPh_2\}_\infty]$, $[\{Li(THF)_2PPh_2\}_\infty]$, and $[\{Li(THF)P(C_6H_{11})_2\}_\infty]$

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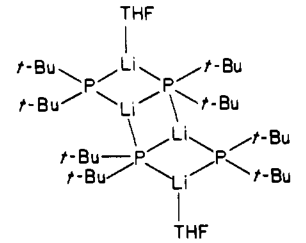
Received September 1, 1985

The complexes $[\{Li(Et_2O)PPh_2\}_\infty]$ (**1**), $[\{Li(THF)_2PPh_2\}_\infty]$ (**2**), and $[\{Li(THF)P(C_6H_{11})_2\}_\infty]$ (**3**) have been synthesized and characterized by X-ray crystallography. Crystal data (140 K) for **1**: $a = 40.868$ (13) Å, $b = 16.050$ (8) Å, $c = 9.616$ (4) Å, $Z = 8$, orthorhombic, space group *Pcab*, $R(F) = 0.055$ for 2180 data with $I > 3\sigma(I)$. Crystal data (140 K) for **2**: $a = 8.662$ (1) Å, $b = 21.438$ (4) Å, $c = 10.389$ (3) Å, $\beta = 95.75$ (2)°, $Z = 4$, monoclinic, space group *Ia*, $R(F) = 0.078$ for 913 data with $I > 3\sigma(I)$. Crystal data (140 K) for **3**: $a = 9.919$ (1) Å, $c = 17.160$ (2) Å, $Z = 4$, tetragonal, space group $P4_1$, $R(F) = 0.052$ for 1408 data with $I > 2\sigma(I)$. The structure, in each case, consists of an alternating sequence of solvated lithium atoms and PPh_2 or $P(C_6H_{11})_2$ units that results in infinite chains of –Li–P–Li–P–. The phosphorus in all three structures has a distorted tetrahedral coordination, and the lithium is either three- (**1** and **3**) or four-coordinate (**2**). These structures differ markedly from those that were previously thought to exist in ether solvents.

Introduction

Lithium diorganophosphides are of importance due to their wide, almost exclusive, use as diorganophosphide transfer agents.[1,2] These lithium compounds are also of significance due to the renewed interest in the properties and structures of organolithium and related lithium complexes.[3,4] Until recently, very little information had been published on the structures of lithium diorganophosphides. On the basis of ^{31}P, ^{7}Li, and ^{13}C NMR studies,[5,6] dimeric or tetrameric structures were reported for $LiPPh_2$ in Et_2O or THF solution. An earlier cryoscopic report[7] for $LiPPh_2$ in 1,4-dioxane seemed to substantiate a dimeric structure although the reported molecular weight also indicated the presence of significant amounts of monomer. The recent publication of the X-ray structures of the ionic compound $[Li(12\text{-crown-}4)_2][PPh_2]$[8] (**4**) and the tetrameric complex $[\{Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu\text{-}t\text{-}Bu_2P)(THF)\}_2]$[9] (**5**) were the first structural characterizations of lithium diorganophosphides. More recently, the crystal structure of $[\{LiP(CH(SiMe_3)_2)_2\}_2]$[10] (**6**) has tended to support the dimeric formulation of $LiPPh_2$ in solution.



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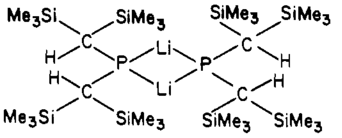

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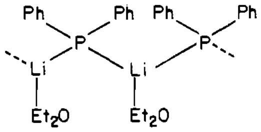
In this paper we describe a new type of structure for the phosphides $LiPR_2$, R = Ph or C_6H_{11}, which has not been previously observed. This consists of infinite chains of alternating diphenylphosphide or dicyclohexylphosphide groups and lithium atoms, with the lithium also coordinated to Et_2O or THF: **1**–**3**.



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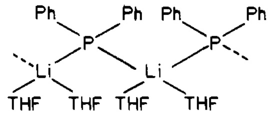

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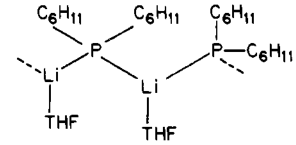

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These structures are in agreement with ^{7}Li and ^{31}P NMR solution data that can also be interpreted on the basis of an infinite chain as well as a dimeric composition. The structures of **1**, **2**, and **4** also underline the often drastic effects on the degree of aggregation obtained by the addition of 12-crown-4 to solutions of lithium salts of organometallic and inorganic anions.

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres H43-2 drybox (under argon). Solvents were freshly distilled from Na/K-alloy/benzophenone and degassed twice immediately before use. Solutions of the phosphide salts are exceptionally air-sensitive and immediately decompose on exposure to moisture or O_2. Solutions of both $LiPPh_2$ and $LiP(C_6H_{11})_2$ were prepared by a modification (*n*-BuLi instead of PhLi) of a procedure described by Issleib.[7]

$[\{Li(Et_2O)PPh_2\}_\infty]$ (1). Crystals of **1** were obtained by treatment of $PHPh_2$ (1.86 g, 10 mmol) in Et_2O (40 mL) with *n*-BuLi in hexane (6 mL of 1.68 M solution). After the mixture was stirred for 1 h, the volume of the solution was reduced in vacuo by 50%. Slow cooling to −20 °C afforded the title compound as yellow crystals.

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0020-1669/86/1325-1243$01.50/0

Table I. Crystal Data and Summary of Data Collection and Refinement

	1	2	3
formula	$C_{16}H_{20}OPLi$	$C_{20}H_{26}O_2PLi$	$C_{16}H_{30}OPLi$
fw	266.2	336.3	276.3
cryst syst	orthorhombic	monoclinic	tetragonal
space group	*Pcab*	*Ia*	$P4_1$
conditions	$0kl$, $l = 2n$ $h0l$, $h = 2n$ $hk0$, $k = 2n$	hkl, $h + k + l = 2n$ $h0l$, $h = 2n$	$00l$, $l = 4n$
cryst dimens, mm	0.2 × 0.3 × 0.45	0.10 × 0.22 × 0.6	0.25 × 0.25 × 1.00
cryst color and habit	yellow needles	yellow needles	colorless needles
temp, K	140	140	140
a, Å	40.868 (13)	8.662 (1)	9.919 (1)
b, Å	10.050 (8)	21.438 (4)	9.919 (1)
c, Å	9.616 (4)	10.389 (3)	17.160 (2)
α, deg	90	90	90
β, deg	90	95.75 (2)	90
γ, deg	90	90	90
Z	8	4	4
V, Å^3	6308	1919	1688.3
d_{calcd}, g/cm^3	1.12	1.16	1.09
radn	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Cu Kα (λ = 1.541 78 Å)
linear abs coeff, cm^{-1}	1.58	1.47	13.4
scan speed, deg min^{-1}	20	30	60
scan width, deg	0.9	1.0	1.0
type of scan	ω	ω	ω
ω offset for bkgd, deg	0.9	1.0	1.0
2θ range, deg	0–45	0–45	0–130
range of abs factors	1.03–1.08	1.01–1.03	1.33–1.50
octants	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,+l$
no. of variables	165	114	171
data/variable ratio	13.2	8.01	8.23
no. of check refl	2, no decay	2, no decay	2, no decay
no. of refl collcd	4693	1186	1633
R(merge)		0.022	0.029
no. of unique data	4127	1095	1427
no. of data used in rfmt	2180 ($I > 3\sigma(I)$)	913 ($I > 3\sigma(I)$)	1408 ($I > 2\sigma(I)$)
$R(F)$	0.055	0.078	0.052
$R_w(F)$	0.060	0.085	0.061
weighting scheme	$[\sigma^2(F_o) + 0.00017F_3{}^2]^{-1}$	$1/(\sigma^2(F_o))$	$1/(\sigma^2(F_o))$
largest Δ/σ	0.007 for *y*/*b* of *P*(2)	0.002 for *x*/*a* of C(17)	0.010 for U_{23} of C(12)
largest feature in final diff map, e Å^{-3}	0.36	0.51	0.43

[{Li(THF)$_2$PPh$_2$}$_\infty$] (2). Similarly, by replacement of Et_2O with THF, a solution of **2** was obtained. The volume was then reduced almost to dryness, and the orange yellow paste redissolved in a minimum volume of Et_2O. Slow cooling to −20 °C gave the product as yellow crystals.

[{Li(THF)P(C$_6$H$_{11}$)$_2$}$_\infty$] (3). A solution of **3** was prepared in a manner identical with the case of **2**. The volume was reduced in vacuo to ca. 15 mL, and *n*-hexane added until incipient crystallization. Slow cooling to −20 °C gave the product as colorless needles.

Each of the above crystalline materials can be isolated in ca. 50% yield after one crystallization. However, if they are dried in vacuo, the crystals deteriorate rapidly, giving amorphous solids. This behavior has been noted already for LiP(*t*-Bu)$_2$.[9]

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 device, Mo Kα radiation, and a graphite monochromator. Calculations were carried out on a Data General Eclipse using SHELXTL, version 4, programs. Scattering factors and corrections for anomalous scattering were from ref 11.

Yellow needles of **1** were obtained as described and protected from air contamination by a layer of hydrocarbon oil. A crystal was selected, attached to a glass fiber on a mounting pin, and immediately placed in the low-temperature N_2 stream. Orthorhombic lattice constants were determined by least-squares fit of 18 accurately centered reflections with 25° < 2θ < 44°. The space group was uniquely determined to be *Pcab*, the *c̄ba* setting of *Pbca*, No. 61, by the conditions listed in Table I. The structure was solved by direct methods. Disorder was not observed in the ether groups. Further details are given in Table I.

In a similar manner, data were collected for **2** by assuming monoclinic *C* symmetry with *a* = 12.842 (4) Å, *b* = 21.438 (4) Å, *c* = 10.389 (3) Å, and β = 137.85 (2)°. The cell and data were then transformed to monoclinic *I* with *a* = 8.662 (1) Å, *b* = 21.438 (4) Å, *c* = 10.389 (3) Å, and β = 95.75 (2)° to reduce the β angle before refinement. *Ia* and *I*2/*a* were in agreement with the systematic absences, but the values of $|E^2 - 1|$ indicated the noncentrosymmetric space group, *Ia*, was probably correct. The successful solution and refinement in this space group confirms its choice. Direct methods were used to solve the structure. One THF ring is disordered at two carbon atoms with an occupancy of 62% at sites C(19) and C(20) and a 38% occupancy at sites C(19b) and C(20b). Cell handedness was not determined. Further details are given in Table I.

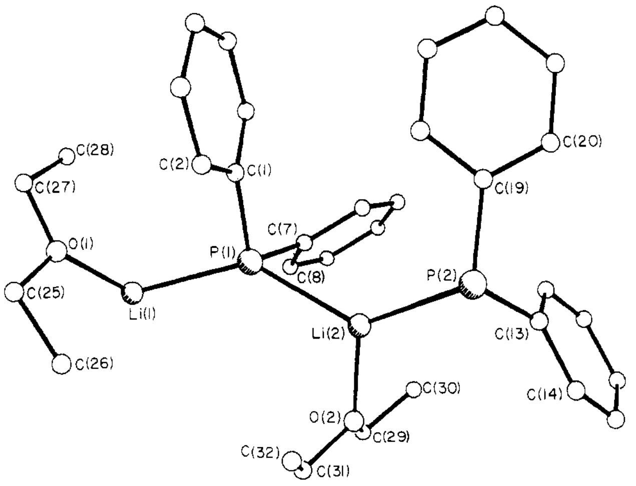

Figure 1. Computer-generated drawing illustrating **1**.

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

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times$ 10^3) for **1**

atom	x	y	z	U
P(1)	1143 (1)	6780 (1)	6814 (2)	24 (1)
P(2)	1365 (1)	9416 (1)	5511 (2)	23 (1)
O(1)	612 (1)	5628 (2)	9111 (4)	28 (1)
O(2)	1871 (1)	7940 (2)	7871 (4)	34 (1)
Li(1)	1059 (2)	5610 (6)	8486 (10)	27 (2)
Li(2)	1480 (2)	8068 (6)	6699 (11)	34 (3)
C(1)	734 (1)	6885 (3)	6069 (6)	20 (1)
C(2)	492 (1)	7278 (3)	6870 (6)	25 (2)
C(3)	170 (1)	7326 (4)	6409 (6)	28 (2)
C(4)	79 (1)	6980 (4)	5153 (6)	32 (2)
C(5)	314 (1)	6579 (4)	4366 (7)	29 (2)
C(6)	636 (1)	6536 (3)	4804 (6)	22 (2)
C(7)	1398 (1)	6525 (3)	5300 (6)	21 (1)
C(8)	1624 (1)	5876 (3)	5362 (6)	22 (1)
C(9)	1838 (1)	5714 (4)	4275 (6)	30 (2)
C(10)	1836 (1)	6200 (3)	3093 (6)	27 (2)
C(11)	1616 (1)	6850 (4)	3001 (6)	29 (2)
C(12)	1400 (1)	7009 (3)	4087 (6)	25 (2)
C(13)	1772 (1)	9623 (3)	4788 (6)	19 (1)
C(14)	1983 (1)	10168 (4)	5490 (6)	28 (2)
C(15)	2307 (1)	10289 (4)	5061 (6)	30 (2)
C(16)	2424 (2)	9873 (4)	3909 (6)	34 (2)
C(17)	2220 (1)	9332 (4)	3197 (7)	32 (2)
C(18)	1903 (1)	9205 (3)	3639 (6)	26 (2)
C(19)	1101 (1)	9272 (3)	3992 (6)	21 (1)
C(20)	1153 (1)	9640 (3)	2683 (6)	24 (1)
C(21)	925 (1)	9557 (4)	1636 (6)	30 (2)
C(22)	639 (1)	9117 (4)	1840 (7)	35 (2)
C(23)	582 (1)	8756 (4)	3100 (6)	31 (2)
C(24)	809 (1)	8817 (3)	4167 (6)	25 (2)
C(25)	519 (2)	6033 (4)	10373 (7)	42 (2)
C(26)	793 (2)	6600 (4)	10826 (7)	43 (2)
C(27)	354 (2)	5135 (4)	8510 (7)	40 (2)
C(28)	483 (2)	4709 (4)	7233 (7)	48 (2)
C(29)	2162 (2)	7480 (4)	7515 (7)	45 (2)
C(30)	2232 (2)	7629 (4)	6019 (7)	46 (2)
C(31)	1806 (2)	7913 (5)	9348 (8)	59 (2)
C(32)	1511 (2)	8418 (4)	9684 (7)	45 (2)

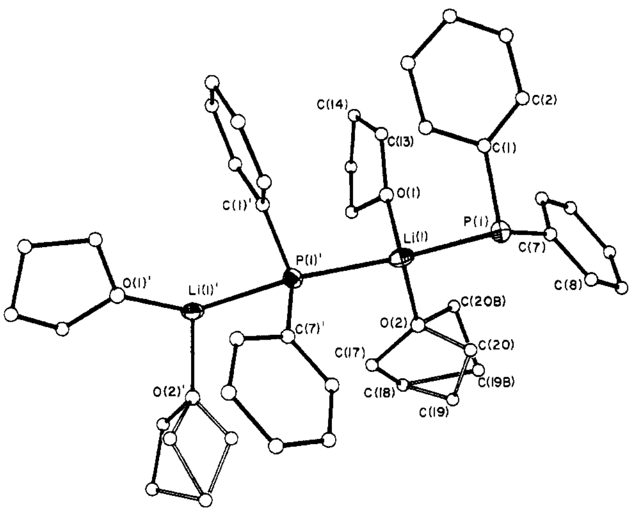

Figure 2. Computer-generated drawing illustrating **2**.

Data for **3** were obtained as described for **1** and **2**. In contrast, the data collection was made by using Cu Kα radiation. Lattice constants were determined from centered reflections between 91 and 130° in 2θ. The space group $P4_1$ (or its enantiomorph) was uniquely determined by systematic absences. The structure was solved by direct methods. Trial refinement in $P4_3$ resulted in a 0.3% increase in R, which indicates it is probably not possible to discriminate between the two hands. Further details are given in Table I.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times$ 10^3) for **2**

atom	x	y	z	U
P(1)	3613	380 (1)	2438	29 (1)[a]
O(1)	−141 (10)	1221 (4)	3052 (9)	38 (2)
O(2)	57 (13)	774 (5)	253 (10)	67 (3)
Li(1)	586 (26)	515 (9)	2028 (19)	36 (8)[a]
C(1)	3744 (13)	533 (5)	4190 (12)	24 (3)
C(2)	4667 (15)	964 (5)	4865 (13)	33 (3)
C(3)	4671 (16)	1039 (5)	6167 (13)	40 (3)
C(4)	3799 (17)	671 (6)	6887 (14)	43 (4)
C(5)	2857 (16)	216 (5)	6263 (13)	42 (4)
C(6)	2824 (14)	161 (5)	4927 (12)	30 (3)
C(7)	4086 (14)	1153 (5)	1759 (11)	25 (3)
C(8)	4791 (17)	1152 (6)	642 (15)	45 (4)
C(9)	5037 (18)	1702 (7)	−25 (15)	52 (4)
C(10)	4512 (18)	2261 (6)	447 (15)	50 (4)
C(11)	3808 (17)	2255 (6)	1605 (14)	45 (4)
C(12)	3618 (18)	1710 (5)	2232 (14)	33 (3)
C(13)	129 (19)	1357 (7)	4385 (15)	57 (4)
C(14)	−1058 (24)	1826 (9)	4700 (19)	84 (6)
C(15)	−1911 (19)	1996 (7)	3415 (16)	57 (4)
C(16)	−1678 (23)	1479 (8)	2622 (19)	81 (5)
C(17)	−1483 (28)	618 (10)	−481 (23)	105 (7)
C(18)	−1542 (29)	1174 (10)	−1506 (23)	106 (7)
C(19)	−117 (26)	1116 (9)	−1900 (22)	37 (6)
C(20)	1090 (37)	960 (13)	−593 (30)	80 (10)
C(20b)	350 (44)	1539 (17)	35 (36)	50 (11)
C(19b)	523 (39)	1455 (14)	−1514 (30)	33 (9)

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

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times$ 10^3) for **3**

atom	x	y	z	U
P	−356 (1)	9547 (1)	1000	26 (1)[a]
O	1616 (4)	10396 (5)	−344 (3)	70 (2)[a]
C(1)	−2112 (4)	7916 (4)	1214 (2)	23 (1)[a]
C(2)	−3075 (4)	9131 (4)	1254 (3)	28 (1)[a]
C(3)	−4542 (4)	9646 (4)	1385 (3)	35 (1)[a]
C(4)	−4662 (4)	7814 (5)	2115 (3)	40 (1)[a]
C(5)	−3696 (4)	6618 (5)	2093 (3)	41 (1)[a]
C(6)	−2247 (4)	7097 (4)	1963 (3)	32 (1)[a]
C(7)	591 (3)	6915 (4)	880 (3)	29 (1)[a]
C(8)	1296 (5)	6840 (5)	85 (3)	45 (2)[a]
C(9)	2074 (5)	5518 (6)	−33 (4)	53 (2)[a]
C(10)	3092 (4)	5296 (5)	611 (4)	45 (2)[a]
C(11)	2418 (5)	5336 (5)	1408 (4)	48 (2)[a]
C(12)	1615 (5)	6641 (5)	1515 (3)	42 (1)[a]
C(13)	2273 (4)	10901 (5)	−1017 (3)	39 (1)[a]
C(14)	3253 (7)	11921 (7)	−706 (4)	61 (2)[a]
C(15)	3596 (8)	11329 (8)	98 (4)	86 (3)[a]
C(16)	2449 (7)	10667 (11)	336 (5)	104 (4)[a]
Li	−195 (7)	9681 (7)	−269 (5)	38 (2)[a]

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

Crystallographic Results. The crystal structure of $[\{Li(Et_2O)PPh_2\}_\infty]$ (**1**) consists of a chain of alternating $Li(Et_2O)^+$ and PPh_2^- groups propagated along the 2_1 axis parallel to b. There are two formula units in the asymmetric unit, illustrated in Figure 1. Rather wide angles join the chain-propagating atoms. Thus, for the sequence P(2)′–Li(1)–P(1)–Li(2)–P(2)–Li(1)′ the consecutive angles are 139.6 (4), 136.9 (3), 129.6 (4), and 126.0 (3)°. The geometry at phosphorus is highly distorted tetrahedral while that at lithium is planar. There are no close intermolecular contacts between adjacent chains. Table II gives the positional parameters for **1**. Important bond distances and angles are compiled in Table V for comparison to other structures.

A similar, alternating arrangement of $Li(THF)_2^+$ and PPh_2^- units is found for $[\{Li(THF)_2PPh_2\}_\infty]$ (**2**) with wide angles along the chain: Li–P–Li′ = 135.0 (5)° and P–Li–P′ = 123.1 (8)°. In this structure the lithium is solvated by two THF's and achieves four-coordination. Both lithium and phosphorus exhibit a distorted tetrahedral geometry. Figure 2 shows a portion of the chain, the atom-numbering scheme, and the disorder in one of the THF's. The chain is propagated by an a glide. The positional parameters are given in Table III; important bond distances and angles are in Table V.

The crystal structure of $[\{Li(THF)P(C_6H_{11})_2\}_\infty]$ (**3**) consists of a helical chain of alternating $Li(THF)^+$ and $P(C_6H_{11})_2^-$ groups propagated along c, the 4_1 axis. The three-coordinate, planar, lithium takes up much of the steric strain in this structure by having an extremely wide P–Li–P′ angle of 145.6 (3)°. The Li–P–Li angle is only 119.7 (2)°. A portion of this chain and the atom-numbering scheme are shown in Figure 3.

Table V. Summary of Important Bond Distances (Å) and Angles (deg) in Lithium Diorganophosphides

	$[\{Li(Et_2O)PPh_2\}_\infty]$[a] (**1**)	$[\{Li(THF)_2PPh_2\}_\infty]$[a] (**2**)	$[\{(Li(THF)$-$P(C_6H_{11})_2\}_\infty]$[a] (**3**)	$[Li(12\text{-crown-}4)_2][PPh_2]$[b] (**4**)	$[\{Li_2(\mu_3\text{-}t\text{-}Bu_2P)$-$(\mu\text{-}t\text{-}Bu_2P)THF\}_2]$[c] (**5**)	$[\{LiP(CH(SiMe_3)_2)_2\}_2]$[d] (**6**)
C–P–C	103.3 (3) 104.7 (2)	102.8 (5)	101.3 (2)	105.2 (2)	112.3 (3) 113.1 (4)	102.0 (5)
Li–P–Li	136.9 (3) 126.0 (3)	135.0 (5)	119.7 (2)	...		72.0 (3) 72.4 (3)
P–Li–P	139.6 (4) 129.6 (4)	123.1 (8)	145.6 (3)	...		108.1 (3) 107.5 (3)
dihedral between Ph's	59.8 52.8	50.6	...	43.4	...	...
P–C	1.828 (5) 1.829 (5) 1.838 (6) 1.836 (5)	1.842 (12) 1.862 (11)	1.886 (4) 1.883 (4)	1.811 (4) 1.804 (4)	1.898 (6) 1.893 (6) 1.919 (7) 1.897 (7)	1.888 (7) 1.894 (5) 1.898 (5) 1.887 (7)
P–Li	2.496 (10) 2.486 (10) 2.492 (10) 2.483 (10)	2.629 (22) 2.634 (21)	2.455 (9) 2.543 (9)	...	2.476 (10) 2.498 (9) 2.595 (10) 2.669 (9)	2.481 (10) 2.473 (9) 2.456 (9) 2.481 (10)
Li–O	1.925 (10) 1.966 (1)	1.937 (22) 1.988 (22)	1.936 (8)	2.487 (6) 2.361 (7) 2.361 (7) 2.323 (8) 2.315 (7) 2.323 (8) 2.308 (7) 2.430 (5) 2.467 (7)	1.923 (10)	...

[a] This work. [b] Reference 8. [c] Reference 9. [d] Reference 10.

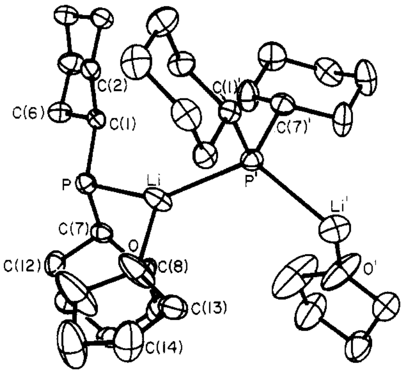

Figure 3. Computer-generated drawing of a portion of the chain of **3**.

Table IV contains positional parameters; Table V contains important bond distances and angles.

Discussion

The crystal structures of **1**–**3** consist of an alternating sequence of solvated lithium atoms and PPh_2 or $P(C_6H_{11})_2$ moieties, which results in infinite zigzag chains of –Li–P–Li–P–Li. There are no close interactions between the chains. A major difference in the structures involves the degree of solvation at lithium. The lithium is coordinated to one solvent molecule and two phosphido groups in **1** and **3**, resulting in a distorted three-coordinate planar geometry. In **2** a further solvent molecule is coordinated, resulting in an irregular tetrahedral configuration at Li.

In all three compounds the phosphorus is in a distorted tetrahedral environment, being surrounded by two lithiums and two organic groups. The P–C distances in all compounds are normal[12] and fairly uniform. They are slightly (0.05 Å) larger for the bulkier complexes **3**, **4**, and **6**. Other bond distances and angles at both Li and P show wide variations, presumably due to differences in coordination number and in steric effects.

Table V compares the structural results for dialkyl- and diarylphosphides. Other disubstituted phosphido (PX_2^-) complexes of some relevance involve those with X = CN,[13] CN/Ph,[13] P(O-*i*-Pr)$_2$O,[14] PPh_2O,[15] or CPhO[16] groups. However, only the first two mentioned have P–C bonds and may be classified only marginally as diorganophosphides.

A significant feature of Table V is the relatively small variation in P–C bond lengths despite the large differences in ligand size. The P–Li distances appear to be closely related to the coordination number at lithium. This is seen in **1** and **3** and in one of the lithiums in **5** that has three-coordination. These P–Li bond lengths are about 2.49 Å, whereas in the case of four-coordinate lithium atoms in **2** and **5** the distance is ca. 2.63 Å. On this basis the distances for the two-coordinate Li in **6** should be a little less than 2.4 Å. The larger than expected distances in **6**, ca. 2.47 Å, are probably due to the orientation of the four $SiMe_3$ groups on each phosphorus toward each other across the Li_2P_2 plane. This steric congestion then gives rise to a lengthening in the Li–P bonds.

With the exception of the P(*t*-Bu)$_2$ compound (**5**),[9] the C–P–C angles in the rest of the complexes average close to 103° and are almost identical with those seen in PPh_3. The anomalous angle of ca. 112.7° in the P(*t*-Bu)$_2$ complex **5** is somewhat surprising in view of the fact that **6**, which has the larger $CH(SiMe_3)_2$ substituent, has an average C–P–C angle of 102.0 (5)°. The explanation for the difference in angles again lies in the way the two $CH(SiMe_3)$ groups orient relative to each other. In the case of **6** and many other complexes[17–19] involving the $CH(SiMe_3)_2$

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ligands, the substituents are arranged so that their α-CH's point toward each other, allowing relief of steric interference between the large $SiMe_3$ groups. For the $P(t\text{-Bu})_2$ moiety, however, all the α-CH's are replaced by CH_3 groups and the steric congestion necessitates a wide angle at P. Steric interference for α-CH_3 groups does not, of course, arise for **1**, **2**, or **3** so that the angles observed are smaller. Angles of phosphorus(III) compounds also depend markedly on the electronic properties of the ligand so that more electronegative substituents, such as those in $[P(CN)_2]^-$[13] or $P(CN)_3$,[20] $P(NMe_2)_3$,[21] and $P(OEt)_3$,[22] have much lower angles at phosphorus of ca. 96°.

The overall structures of complexes **1**–**3** are also worthy of comment. Their polymeric skeletons have a resemblance to those found in some alkali-metal salts of delocalized carbanions, either as linear polymers[3,4,24,25] or as monomers in the presence of good complexing agents. If a sufficiently good Li^+ complexing agent is added, then complete cation and anion separation may ensue. Thus, **1** or **2** readily form **4** as free $[PPh_2]^-$ and $[Li(12\text{-crown-}4)_2]^+$ ions upon the addition of 12-crown-4.[8] The parallel with delocalized carbanions involves crown ether salts of $[CHPh_2]^-$ or $[CPh_3]^-$.[23] For the infinite-chain structure, the complex $[\{Li(Et_2O)CH_2Ph\}_\infty]$[24] has a structural resemblance to **1** as do many other delocalized complexes involving TMEDA or related donors.[3,4,25]

Much evidence also exists which shows that, in solution, the delocalized carbanions exist as ion pairs with varying degrees of solvation. There are, unfortunately, no extensive studies on alkali-metal diorganophosphide solutions. Nonetheless, the structural similarities and behavior toward crown ethers tend to support a more ionic picture of $LiPR_2$ compounds in ethers than the proposed covalent dimeric structures. Another feature of the structures that may support a more ionic formulation involves the Li–P–Li angles. For example, within **1** there is a difference of about 9° in this parameter between the two molecules of the unit. A similar difference exists between **1** and **3**. Less variation might be expected in a more covalent structure, which would involve tetrahedrally disposed bonding orbitals on phosphorus. In addition, we also note that solvation of lithium compounds by donor molecules is well-known and is widely understood to increase their ionic character compared to that of their unsolvated analogues.[4]

The degree of solvation in **1**–**3** appears to reflect steric effects. Due to the larger size of C_6H_{11} vs. Ph, only one THF is coordinated to Li in **3** whereas, in **2**, Li is solvated by an extra THF. Similarly, the solvation of **1** and **2** reflects the larger size of Et_2O vs. THF. Compounds **5** and **6** have structures different from those of **1**–**3** for steric reasons. In the case of the $P(t\text{-Bu})_2$ complex (**5**), the bulky t-Bu groups will not allow as much THF solvation, i.e. as seen in **1** or **3**. Instead, the stoichiometry in **5** corresponds to $Li(THF)_{0.5}P(t\text{-Bu})_2$ so that replacement of C_6H_{11} by t-Bu effectively halves the amount of THF solvation. The structure of **5** may be considered as a two-unit fragment of two chains terminated by THF and cross-linked by Li–P interactions. The very large groups seen in **6** effectively prevent any solvent coordination. This steric congestion also probably prevents polymer formation, which results in the dimeric structure shown.

An additional feature of the polymer structures of **1**–**3** is that they are consistent with ^7Li and ^{31}P NMR data for their Et_2O solutions. This data showed splitting patterns of 1:2:1 for ^7Li NMR and 1:2:3:4:3:2:1 for the ^1H-decoupled ^{31}P spectrum. These spectra imply a ^7Li nucleus coupled to two equivalent ^{31}P ($I = {}^1/_2$) nuclei and a ^{31}P nucleus coupled to two equivalent ^7Li ($I = {}^3/_2$, abundance 92.6%) nuclei. These results were interpreted in terms of a dimeric structure similar to that in **6** with the lithiums presumably solvated by Et_2O or THF. However, the chain structures of **1**–**3**, which may have considerable similarity to their structures in concentrated solution, are also in agreement with the NMR data. The molecular weight measurements cited in support of the dimeric formulation also suggested a considerable amount of monomer was present.[7] We have been unable to obtain crystals of a dioxane–$LiPPh_2$ adduct suitable for X-ray studies, but the arsenic analogue $[Li(1,4\text{-dioxane})_3AsPh_2]$ has been crystallized and is monomeric in the crystalline state.[26] These data tend to favor the view that 1,4-dioxane adducts might have structures different from those of their Et_2O or THF analogues, and it may be inaccurate to make extrapolations from one solvent to the other. Further solution studies involving, perhaps, more extensive molecular weight determinations, EXAFS, or conductivity experiments are necessary to establish the solution structures with a degree of confidence.

In conclusion, the evidence that involves (i) the X-ray structures of the solvates, (ii) the crystallization of $[PPh_2]^-$ as a separate ion using crown ethers, and (iii) the agreement of the ^7Li and ^{31}P NMR studies with the alternating-chain structure suggests significant ionic character in the Li–P bonding in **1**–**3**. Partial desolvation seen in **5** and lack of any coordinating donor solvent in **6** suggest a more covalent bonding scheme in these molecules.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8116355) and the Research Corp. for financial support.

Supplementary Material Available: Tables of anisotropic thermal parameters, full tables of bond distances and angles, hydrogen coordinates and temperature factors, and observed and calculated structure factors, and Figures S1–S3, stereoviews of the polymer chains of **1**–**3** (40 pages). Ordering information is given on any current masthead page.

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