

Table III. Calculated (Observed) Geometrical Parameters

molecule	bond lengths (Å)		bond angles (deg)	
	calcd	(obsd)	calcd	(obsd)
ZnMe ₂	ZnC, 1.89	(1.930) ^a	CZnC, 179.4	(180.0) ^a
ZnEt ₂	ZnC, 1.91	(1.950) ^a	CZnC, 177.0	(180.0) ^a
			ZnCC, 118.7	(114.5) ^a
			CCC, 115.3	(113.6) ^a
Zn(Pr- <i>n</i>) ₂	ZnC, 1.91	(1.952) ^a	CZnC, 179.0	(180.0) ^a
			ZnCC, 118.0	(114.5) ^a
ZnF ₂	ZnF, 1.68	(1.810) ^b	FZnF, 180.0	(180.0) ^b
ZnCl ₂	ZnCl, 2.12	(2.050) ^b	ClZnCl, 180.0	(180.0) ^b
ZnBr ₂	ZnBr, 2.23	(2.210) ^b	BrZnBr, 180.0	(180.0) ^b
ZnI ₂	ZnI, 2.38	(2.38, 2.42) ^b	IZnI, 180.0	(180.0) ^b

^a Almenningen, A.; Halgaker, T. U.; Haaland, A.; Samdal, S. *Acta Chem. Scand., Part A* 1982, A36, 159. ^b Akishin, P. A.; Spiridonov, V. P. *Sov. Phys. Crystallog.* 1957, 2, 472.

an atom belongs are the relevant overlap integrals. MO-PAC provides for their calculation for all elements.

Results and Discussion

Table I shows the final parameters for zinc, in the notation used previously.^{3,4}

Table II shows the heats of formation (ΔH_f°), first ionization energies, and dipole moments (μ) calculated for molecules containing zinc, together with available experimental values for comparison. The ionization energies were estimated from orbital energies, using Koopmans' theorem.

The errors in the heats of formation calculated for ZnS and Zn²⁺ are both large: 83 and 55 kcal/mol, respectively. MNDO is known⁴ to perform poorly for diatomic molecules, and the formalism of MNDO is not sufficiently flexible to include multiply charged atoms. Omitting these two species, the average error in the calculated ΔH_f° 's is 13 kcal/mol, comparable with those for other metals.¹⁸⁻²⁰ While the average error in the dipole moments is small (0.1 D), this relates to experimental values determined in so-

lution, usually in *n*-heptane. The average error in the ionization potentials is 1 eV, similar again to that for other metals.¹⁸⁻²⁰

The calculated geometries compare well with experiment, the only significant errors being the shortness of the ZnF bond (calculated 1.68 Å; observed 1.81 Å) and the inability to handle sandwich compounds. Thus while MNDO predicts cyclopentadienylmethylzinc (CpZnMe) to have the classical η^1 structure, gas-phase studies²⁶ have indicated it to be a half-sandwich with a η^5 -cyclopentadienyl group. This weakness (i.e., the inability to handle nonclassical bonding) has been noted previously in the case of boron,²⁷ tin,¹⁸ and lead.²⁰ The geometry of η^5 -CpZnMe is therefore not included in Table III. The same is true for bis(pentamethylcyclopentadienyl)zinc, which has one η^5 -bonded and one η^1 -bonded (or σ -bonded) Cp ring.²⁸ MNDO again predicts a classical structure.

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Registry No. ZnMe₂, 544-97-8; ZnEt₂, 557-20-0; Zn(Pr-*n*)₂, 628-91-1; Zn(Bu-*n*)₂, 1119-90-0; ZnF₂, 7783-49-5; ZnCl₂, 7646-85-7; ZnBr₂, 7699-45-8; ZnI₂, 10139-47-6; ZnMeF, 102436-61-3; ZnMeCl, 5158-46-3; ZnMeBr, 18815-74-2; ZnMeI, 18815-73-1; ZnF, 20654-98-2; ZnCl, 18623-80-8; ZnBr, 13550-22-6; ZnI, 31246-29-4; ZnH, 13981-87-8; ZnMe⁺, 47936-33-4; Zn, 7440-66-6; Zn⁺, 15176-26-8; Zn²⁺, 23713-49-7; ZnCl₂⁺, 102436-59-9; ZnMe₂⁺, 102436-60-2; ZnO, 1314-13-2; ZnS, 1314-98-3; ZnCpEt, 38097-43-7; ZnCpPh, 94980-39-9.

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Structure of a Lithiated Phosphoylide, [[Li(CH₂)P(C₆H₅)₂(CH₂)]₂(dioxane)₃]₂•(dioxane)

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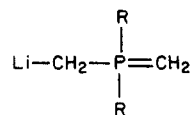
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Pale yellow, air-sensitive crystals of [Li(CH₂)(CH₂)P(C₆H₅)₂]₄•(C₄H₈O₂)₇ belong to space group $P\bar{1}$ with cell constants of $a = 13.529$ (3) Å, $b = 14.472$ (1) Å, $c = 11.771$ (1) Å, $\alpha = 109.017$ (8)°, $\beta = 90.05$ (1)°, and $\gamma = 94.009$ (9)°. The structure was solved by a combination of direct methods and difference Fourier maps and refined by least-squares methods to final error indices of $R = 10.9\%$ and $R_w = 10.4\%$ by using the 3552 unique reflections with $I > 3\sigma(I)$ from the data set containing 5954 unique reflections. The molecular structure consists of two eight-membered rings in the saddle conformation, each composed of two [(CH₂)(CH₂)P(C₆H₅)₂]⁻ ligands bridging two lithiums. The two rings are joined by a disordered bridging dioxane molecule which is coordinated to a Li in each ring. The coordination about the lithiums is completed by additional dioxanes which are also disordered.

Lithiated phosphoylides, [Li(CH₂)(CH₂)PR₂], have been known [Li(CH₂)(CH₂)P(C₆H₅)₂]₄•(C₄H₈O₂)₇ the mid 1960s and have been used as starting materials for the synthesis of organometallic compounds.¹⁻⁴ NMR studies demon-

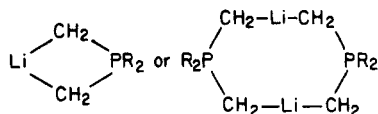
strated¹ that does not exist in solution and suggested that



are the most probable structures for this class of molecules.

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The lithiated phosphoylides, however, have proven to be difficult to crystallize, and their structure in the solid state has, consequently, not yet been reported. During our studies of metal-ylide chemistry at least five of our co-workers tried without success to obtain single crystals for X-ray diffraction. Finally, we serendipitously obtained crystals from a reaction of ThCl_4 with $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_n$ in a THF-dioxane mixture which proved to be the title compound.

Data Collection and Refinement

Pale yellow, air sensitive crystals of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4(\text{C}_4\text{H}_8\text{O}_2)_7$ were obtained as unreacted starting material from a 4:1 mixture of $\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2$ and ThCl_4 in a THF-dioxane solvent mixture. An irregularly shaped crystal was mounted in a 0.5-mm capillary tube under a N_2 atmosphere.

Data collection and reduction parameters are listed in Table I. The instrumentation and data reduction procedures have been described previously.⁵ The cell constants and their standard deviations were determined as $a = 13.529$ (3) Å, $b = 14.472$ (1) Å, $c = 11.771$ (1) Å, $\alpha = 109.017$ (8)°, $\beta = 90.05$ (1)°, $\gamma = 94.009$ (9)° by a least-squares treatment of the angular coordinates of 15 intense independent reflections with 2θ values between 14° and 78°. The complete data set of 6090 reflections was collected from the ($\pm h, \pm k, \pm l$) hemisphere with ($3.5^\circ < 2\theta < 115^\circ$) and was merged by SHELX-76⁷ into 5954 unique reflections with the final data set used for the structure solution consisting of the 3552 unique reflections with $I > 3\sigma(I)$.

The structure was solved in the space group $P\bar{1}$. An initial direct methods solution, obtained by using MULTAN 80,⁶ gave a set of atomic positions for two phosphorus atoms, the eight carbon atoms bonded to them, and four additional carbon atoms of a phenyl ring. The remaining carbon, oxygen, and lithium atoms were located in a series of difference Fourier maps and least-squares refinements using SHELX-76. Atomic scattering factors for H^0 , C^0 , and P^0 were supplied by SHELX-76, and those for Li^0 were taken from the literature.⁸

Refinement proceeded to $R = 16\%$ with rigid body phenyl rings and all atoms isotropic. At this point disordering in the dioxane units was indicated by large thermal parameters and large peaks in the difference map in the vicinity of the rings. This disorder was modeled by assuming that each ring adopts two different positions but that the oxygen atom which is coordinated to lithium occupies nearly the same site regardless of the location of the remaining ring atoms. Each of the dioxane oxygen atoms which are bound to a lithium was, thus, refined anisotropically with a fixed occupancy of one. Two sets of the remaining four carbon and one oxygen in each ring were refined with the restrictions that all sites within an individual set had identical occupancies, and the sum of the occupancies was one for the each atom between the two sets. This resulted in an $R = 12.5\%$. The relatively large thermal parameters of the ring atoms indicate that the disorder has not been completely modeled and may be the reason for the overall poor fit and high refinement indices obtained for the

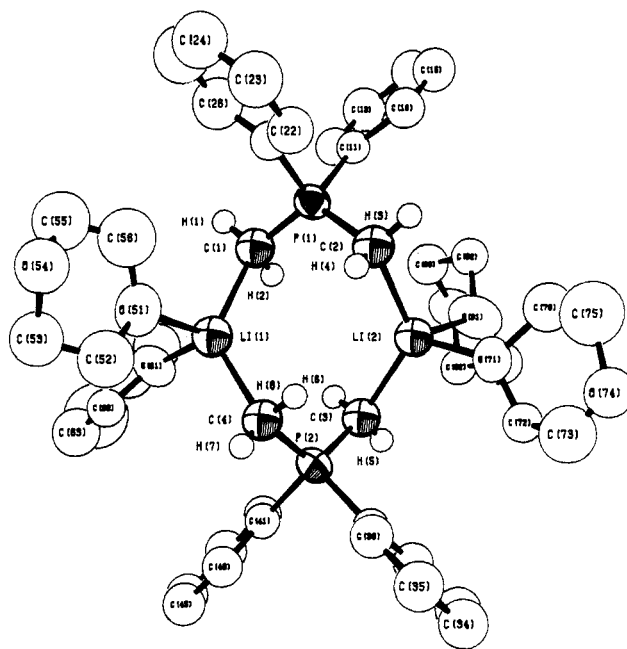


Figure 1. Ortep drawing of the independent unit of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4(\text{C}_4\text{H}_8\text{O}_2)_7$. For clarity the hydrogens on the phenyl and dioxane fragments have been omitted, the thermal parameters of the methylene hydrogens have been reduced to equivalent arbitrary values, and only one of the disordered dioxanes is shown at each position.

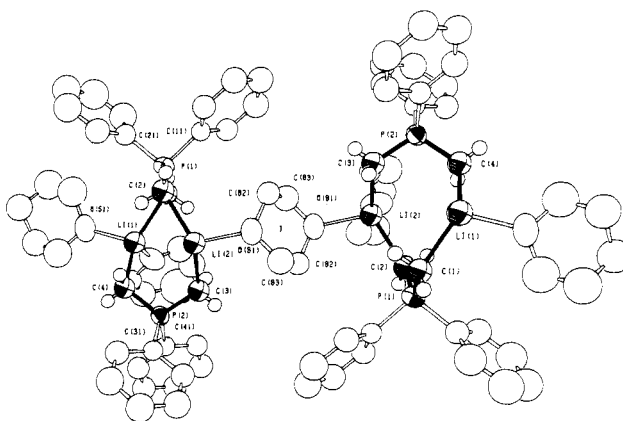


Figure 2. Ortep drawing of the $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4(\text{C}_4\text{H}_8\text{O}_2)_7$ molecule. For clarity two dioxanes which are located above the plane of the figure and the hydrogens on the phenyl and dioxane fragments have been omitted, the thermal parameters of the methylene hydrogens have been reduced to equivalent arbitrary values, and only one of the disordered dioxanes is shown at each position.

structure. The possibility of more complex disordering, perhaps involving the substitution of dioxane by occasional THF molecules, was considered, but no more complex models were attempted.

In the final least-squares cycle, phosphorus and the oxygen atoms bound to lithium were refined anisotropically and the hydrogens on the methylene carbons C(1), C(2), C(3), and C(4) were refined independently. The phenyl carbon and hydrogen atoms were treated as rigid groups with idealized geometry assuming $\text{C}-\text{C} = 1.395$ Å and $\text{C}-\text{H} = 0.950$ Å and with a common isotropic thermal parameter for all phenyl hydrogen atoms. Hydrogen atoms were added to the dioxane carbons at calculated positions and were allowed to "ride" on their respective carbon during refinement. The dioxane hydrogen atoms were refined with a common isotropic thermal parameter. Final values of $R = 10.9\%$ and $R_w = 10.4\%$ were obtained. The atomic positions and thermal parameters of the independently refined atoms are listed in Table II. Table III (supplementary material) gives the positional, occupancy, and thermal parameters for the disordered dioxane carbon and oxygen atoms. The positional and thermal

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(6) MULTAN 80, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data by P. Main, 1980.

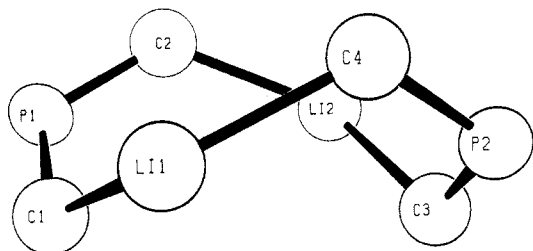
(7) SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(8) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1967; Vol. 4, pg 99.

Table I. Crystal, Data Collection, and Reduction Parameters for $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$

formula	$\text{C}_{84}\text{H}_{112}\text{Li}_4\text{O}_{14}\text{P}_4$
fw	1497.46
space group	$P\bar{1}$
a , Å	13.529 (2)
b , Å	14.472 (1)
c , Å	11.771 (1)
α , deg	109.017 (8)
β , deg	90.05 (1)
γ , deg	94.009 (9)
V , Å ³	2172.8 (4)
Z	1
d , g/cm ³	1.144 (calcd)
cryst dimen, mm	$0.7 \times 0.4 \times 0.5$
cryst shape	irregular prism
radiatn	Cu $K\alpha$; $\lambda = 1.5418$ Å
scan type	$2\theta/\theta$
scan rate, deg/min	2.0–24
2θ range, deg	3.5–115
total observns	6090
unique observns	5954
unique data with $I > 3\sigma(I)$	3552
no. of parameters	301
over determination ratio	11.8
R^a	0.109
R_w	0.104

$$^a R = \sum (|F_o - F_c|) / \sum (F_o); R_w = \sum (|F_o - F_c(w)|)^{1/2} / \sum (F_o(w))^{1/2}; w = k / (\sigma^2(F) + |g|F^2).$$

**Figure 3.** Ortep drawing of the eight member $\text{Li}(1)-\text{C}(1)-\text{P}(1)-\text{C}(2)-\text{Li}(2)-\text{C}(3)-\text{P}(2)-\text{C}(4)$ ring of $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$.

parameters for the rigid phenyl group carbon atoms appear in Table IV (supplementary material), Table V (supplementary material) tabulates the positional, occupancy, and thermal parameters for the fixed hydrogen atoms, and Table VI (supplementary material) is a listing of the observed and calculated structure factors.

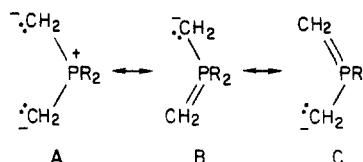
Results and Discussion

Ortep representations of the structure of $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$ are shown in Figures 1 and 2, bond angles and distances for the nondisordered atoms are summarized in Tables VII and VIII, and those for the disordered dioxane atoms appear in Table IX and X (supplementary material). The molecular structure consists of two eight-membered rings in the saddle conformation (Figure 3). Each ring is composed of two $[(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)]^-$ ligands bridging two lithiums. The two rings are joined by a bridging dioxane molecule which is coordinated to Li(2) in each. This dioxane lies on a crystallographic inversion center, denoted as I in Figure 2, which relates one ring to the other. The coordination of Li(2) is completed by a dioxane coordinated in a monodentate fashion and that about Li(1) by two monodentate dioxanes.

The unique eight-membered ring consists of two crystallographically independent $[(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)]^-$ ligands. However, the metrical parameters of the two are very similar and average values will be used in the fol-

lowing discussion. The $\text{P}-\text{C}(\text{C}_6\text{H}_5)$ distance 1.839 (3) Å is a normal $\text{P}-\text{C}$ single bond length, and the $\text{P}-\text{CH}_2$ separation 1.706 (6) Å, which is somewhat greater than 1.64–1.67 Å found in free ylides,^{4,9} is typical for a phosphorane metal complex.^{4,9} In most complexes containing a bridging $[\text{CH}_2-\text{PR}_2-\text{CH}_2]^-$ ligand the bond angles about phosphorus are close to the tetrahedral value.^{4,9} In $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, however, the $\text{CH}_2-\text{P}-\text{CH}_2$ angle 114 (1)° is significantly greater than 109°, and the $\text{C}_6\text{H}_5-\text{P}-\text{C}_6\text{H}_5$ angle 99.7 (2)° is less than this value.

While the nature of lithium-carbon bonding is controversial¹⁰ and cogent arguments can be made to support either an ionic model in which the lithium-carbon bond is described in terms of tight ion pairing¹¹ or a covalent picture often involving delocalized, electron-deficient bonding,¹² organolithium compounds usually adopt structures which can be rationalized by assuming ionic bonding.¹⁰ If the $\text{Li}-\text{C}$ bond is ionic, $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$ can be described as a salt of dioxane solvated Li^+ cations with $[(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)]^-$ anions. The covalent bonding within the anion can be described in terms of the three resonance structures: which indicate



that a sizable partial negative charge should be localized on each methylene carbon atom with a formal positive charge on phosphorus.¹³ Coulombic repulsion of the methylene groups could then open the $\text{CH}_2-\text{P}-\text{CH}_2$ angle. In complexes of less electropositive metals where charge is more equally shared between metal and carbon atoms, this effect would become less important. Unfortunately, structural data are not available for a large number of compounds containing a $\text{M}-\text{CH}_2-\text{PR}_2-\text{CH}_2-\text{M}$ unit, and most of those which have been determined contain metal-metal bonds or small bridging atoms which may themselves influence the geometry of the ylide. Nonetheless, it is interesting that the $\text{CH}_2-\text{P}-\text{CH}_2$ angle has been expanded to 113° in an ethoxide-bridged Ti(IV) complex¹⁴ and an oxo-bridged U(IV) compound,¹⁵ both of which should have quite polar metal-carbon bonds.

The charge distribution within the ring may also be reflected in the large $\text{CH}_2-\text{Li}-\text{CH}_2$, 127 (1)°, and $\text{P}-\text{CH}_2-\text{Li}$, 122 (4)°, angles and in the ring conformation. In the saddle form adopted by the eight-membered rings of $[\text{Li}(\text{CH}_2)(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, the methylene groups define a distorted tetrahedron which, given the constraints imposed by the geometry of $[\text{CH}_2-\text{PPh}_2-\text{CH}_2]^-$, minimizes the repulsion between CH_2 units. The separation of the

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Table II. Atomic Positions and Thermal Parameters for Independently Refined Atoms of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$

Anisotropically Refined Atoms									
atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
P(1)	0.7099 (1)	0.4502 (1)	0.1358 (2)	0.052 (1)	0.048 (1)	0.058 (1)	0.018 (1)	-0.007 (1)	0.002 (1)
P(2)	0.6601 (1)	0.1436 (1)	0.2955 (2)	0.057 (1)	0.047 (1)	0.049 (1)	0.014 (1)	0.001 (1)	0.010 (1)
O(51)	0.9123 (5)	0.2122 (5)	0.0265 (6)	0.106 (5)	0.089 (5)	0.092 (5)	0.010 (4)	0.028 (4)	0.021 (4)
O(61)	0.9498 (4)	0.2799 (4)	0.3043 (6)	0.080 (4)	0.072 (4)	0.112 (5)	0.032 (4)	-0.020 (4)	0.008 (4)
O(71)	0.4047 (4)	0.2560 (5)	0.1815 (6)	0.056 (4)	0.125 (5)	0.134 (6)	0.076 (5)	-0.010 (4)	0.004 (4)
O(81)	0.4663 (5)	0.4326 (5)	0.3901 (5)	0.154 (6)	0.084 (5)	0.074 (5)	0.022 (4)	0.032 (4)	0.048 (5)
Isotropically Refined Atoms									
atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
Li(1)	0.833 (1)	0.265 (1)	0.183 (1)	0.068 (4)	Li(2)	0.5378 (9)	0.3260 (9)	0.262 (1)	0.061 (4)
C(1)	0.8026 (7)	0.4202 (6)	0.2111 (8)	0.066 (2)	C(3)	0.6138 (7)	0.2543 (7)	0.3656 (8)	0.062 (3)
C(2)	0.6009 (7)	0.3803 (7)	0.1257 (8)	0.067 (3)	C(4)	0.7264 (7)	0.1423 (7)	0.1716 (8)	0.062 (2)
H(1)	0.864 (5)	0.463 (5)	0.219 (5)	0.06 (2)	H(5)	0.585 (4)	0.251 (4)	0.423 (6)	0.05 (2)
H(2)	0.786 (4)	0.427 (4)	0.292 (5)	0.05 (2)	H(6)	0.670 (4)	0.299 (4)	0.397 (5)	0.06 (2)
H(3)	0.550 (5)	0.409 (5)	0.093 (7)	0.10 (3)	H(7)	0.743 (4)	0.087 (4)	0.141 (5)	0.04 (2)
H(4)	0.612 (4)	0.322 (5)	0.079 (6)	0.06 (2)	H(8)	0.675 (5)	0.154 (4)	0.123 (5)	0.06 (2)

Table VII. Selected Bond Distances (Å) of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$

P(1)-C(1)	1.695 (9)	P(2)-C(3)	1.71 (1)
P(1)-C(2)	1.71 (1)	P(2)-C(4)	1.71 (1)
P(1)-C(11)	1.842 (6)	P(2)-C(31)	1.836 (5)
P(1)-C(21)	1.842 (7)	P(2)-C(41)	1.837 (5)
Li(1)-C(1)	2.22 (2)	Li(2)-C(2)	2.16 (2)
Li(1)-C(4)	2.18 (2)	Li(2)-C(3)	2.14 (2)
Li(1)-O(51)	2.08 (2)	Li(2)-O(71)	2.07 (1)
Li(1)-O(61)	2.09 (2)	Li(2)-O(81)	2.07 (1)
C(1)-H(1)	0.98 (6)	C(3)-H(5)	0.79 (7)
C(1)-H(2)	0.96 (7)	C(3)-H(6)	0.95 (6)
C(2)-H(3)	0.97 (8)	C(4)-H(7)	0.81 (6)
C(2)-H(4)	0.86 (7)	C(4)-H(8)	0.96 (6)

Table VIII. Selected Bond Angles (deg) of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$

C(1)-P(1)-C(2)	114.4 (5)	C(3)-P(2)-C(4)	112.8 (5)
C(1)-P(1)-C(21)	106.4 (4)	C(3)-P(2)-C(31)	105.1 (4)
C(1)-P(1)-C(11)	115.8 (3)	C(3)-P(2)-C(41)	116.6 (4)
C(2)-P(1)-C(11)	105.0 (4)	C(4)-P(2)-C(41)	104.9 (4)
C(2)-P(1)-C(21)	114.9 (4)	C(4)-P(2)-C(31)	117.6 (4)
C(11)-P(1)-C(21)	99.7 (2)	C(31)-P(2)-C(41)	99.6 (2)
C(1)-Li(1)-C(4)	127.9 (7)	C(2)-Li(2)-C(3)	126.4 (7)
C(1)-Li(1)-O(61)	102.5 (7)	C(2)-Li(2)-O(71)	102.0 (7)
C(1)-Li(1)-O(51)	109.6 (7)	C(2)-Li(2)-O(81)	111.7 (7)
C(4)-Li(1)-O(51)	102.6 (7)	C(3)-Li(2)-O(81)	103.8 (7)
C(4)-Li(1)-O(61)	113.0 (7)	C(3)-Li(2)-O(71)	115.9 (7)
O(51)-Li(1)-O(61)	97.2 (6)	O(71)-Li(2)-O(81)	92.0 (6)
P(1)-C(1)-Li(1)	122.0 (6)	P(2)-C(3)-Li(2)	119.9 (6)
P(1)-C(2)-Li(2)	127.0 (6)	P(2)-C(4)-Li(1)	119.1 (6)
P(1)-C(1)-H(1)	113 (4)	P(2)-C(3)-H(5)	108 (5)
P(1)-C(1)-H(2)	113 (3)	P(2)-C(3)-H(6)	106 (3)
Li(1)-C(1)-H(1)	113 (4)	Li(2)-C(3)-H(5)	114 (4)
Li(1)-C(1)-H(2)	89 (3)	Li(2)-C(3)-H(6)	102 (4)
P(1)-C(2)-H(3)	109 (4)	P(2)-C(4)-H(7)	107 (4)
P(1)-C(2)-H(4)	106 (4)	P(2)-C(4)-H(8)	99 (4)
Li(2)-C(2)-H(3)	109 (5)	Li(1)-C(4)-H(7)	119 (4)
Li(2)-C(2)-H(4)	93 (4)	Li(1)-C(4)-H(8)	101 (4)
H(1)-C(1)-H(2)	104 (5)	H(5)-C(3)-H(6)	105 (6)
H(3)-C(2)-H(4)	112 (6)	H(7)-C(4)-H(8)	109 (6)

two lithiums is maximized by their diagonal position in the saddle.

In addition to the two carbons from $[\text{CH}_2\text{-PPH}_2\text{-CH}_2]$ ligands the coordination sphere about each lithium con-

tains two dioxane oxygens. In a covalent bonding model each of the atoms coordinated to Li could be considered as a two-electron donor making the electron count about lithium eight. It is, thus, electron precise. The average Li-C bond length 2.17 (3) Å is, within experimental uncertainty, the same as in $[(\text{tmed})\text{LiCH}_2\text{PMe}_2]_2$, 2.146 (7) Å, which is the most closely related molecule for which a structure has been reported.¹⁶ As is often true with electron-precise organolithium compounds, these distances are at the short end of the 2.1-2.4-Å range observed for Li-C bonds in lithium alkyls.¹⁰

While the structural chemistry of organolithium compounds is complex and there is no assurance that solid state and solution structures of a compound will be the same, it is gratifying that the features observed for $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$ in this study are those proposed on the basis of NMR solution measurements.¹

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Registry No. $[\text{Li}(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, 102307-89-1; $\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2$, 59983-62-9; ThCl_4 , 10026-08-1.

Supplementary Material Available: Table III, atomic positions, occupancy, and thermal parameters for disordered dioxane atoms of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, Table IV, atomic positions and thermal parameters for rigid phenyl group carbon atoms of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, Table V, atomic positions, occupancy, and thermal parameters for fixed hydrogen atoms of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, Table VI, observed and calculated structure factors of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, Table IX, bond distances within disordered dioxane units of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$, and Table X, bond angles within disordered dioxane units of $[\text{Li}(\text{CH}_2)(\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)_7$ (35 pages). Ordering information is given on any current masthead page.