

previously reported, the distances in **2** are large compared to other lithium cyclopentadienides and this was attributed to a primarily electrostatic bonding in that complex.¹²

Conclusion

Base-free [(trimethylsilyl)cyclopentadienyl]lithium forms a highly-ordered polymeric structure which explains its low solubility. Although the supersandwich structure is composed of a trimetallic repeating unit, 3-fold symmetry is not present in the stacks of C₅H₄(SiMe₃)Li units. Instead, the trimethylsilyl groups are oriented in a complicated three-dimensional arrangement of substituent

bulk and space. The structure provides the experimental basis for future calculations on lithium cyclopentadienides which should include bridged oligomers.

Acknowledgment. For support of this research, we thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (9 pages). Ordering information is given on any current masthead page.

OM920435Y

Rare Example of a Monomeric Aryllithium Complex. X-ray Crystal Structure of (2,4,6-Triphenylphenyl)lithium-Bis(diethyl ether)

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Received April 9, 1992

Summary: Lithiation of 1-bromo-2,4,6-triphenylbenzene with *n*-butyllithium in diethyl ether gives (2,4,6-triphenylphenyl)lithium-bis(diethyl ether), whose X-ray crystal structure has been determined. This compound is a rare example of a monomeric organolithium reagent: the lithium atom adopts a planar three-coordinate geometry defined by the ipso carbon of the 2,4,6-triphenylphenyl group and two oxygen atoms of the diethyl ether solvate molecules; Li-C = 2.08 (2) Å, Li-O = 1.93 (1) Å, O-Li-C = 124.0 (4)°, O-Li-O = 112.0 (8)°. Crystal data for LiC₃₂H₃₇O₂ at 26 °C: monoclinic, space group *I2/a*, with *a* = 11.732 (7) Å, *b* = 20.538 (13) Å, *c* = 11.723 (9) Å, β = 95.06 (6)°, *V* = 2814 (3) Å³, *Z* = 4, *R_F* = 0.067, *R_{wF}* = 0.064 for 153 variables and 783 reflections.

Introduction

Organolithium reagents are almost without exception oligomeric in both solution and the solid state: the most commonly encountered oligomers are tetramers and hexamers.¹ Solvated organolithium reagents are often dimeric as in the *N,N,N',N'*-tetramethylethylenediamine² adduct of phenyllithium, Li₂Ph₂·2tmed.³ The first monomeric aryllithium reagents, LiPh·pmdt⁴ and LiC₆H₂(*t*-Bu)₃·tmpn,⁵ have only recently been structurally characterized, and monomeric *alkyl*lithium reagents with one Li-C interaction per lithium atom remain scarce: among these are the bulky alkyls LiCH(SiMe₃)₂·pmdt,⁶ LiC(SiMe₂Ph)₃·thf,⁷ and LiCH(SiMe₂)₂(CH₂)₂·tmed,⁸ the 2,6-dithiacyclohexyl reagents LiC₄S₂H₇·tmed⁹ and

Table I. Crystal Data for LiC₆H₂Ph₃·Et₂O at 26 °C

space group: <i>I2/a</i>	<i>V</i> = 2814 (3) Å ³
<i>a</i> = 11.732 (7) Å	<i>Z</i> = 4
<i>b</i> = 20.538 (13) Å	mol wt = 460.59
<i>c</i> = 11.723 (9) Å	<i>d</i> _{calcd} = 1.087 g cm ⁻³
β = 95.06 (6)°	<i>μ</i> _{calcd} = 0.61 cm ⁻¹
α = γ = 90°	size = 0.3 × 0.4 × 0.4 mm

diffractometer: Syntex P2₁
radiation: Mo Kα, λ = 0.710 73 Å
monochromator: graphite crystal, 2θ = 12°
scan range, type, speed: 3.0 < 2θ < 53.0°, ω/2θ, 2-15° min⁻¹
no. of rflctns: 3274, 2935 unique, 783 with *I* > 2.58σ(*I*)
internal consistency: *R_i* = 0.039

R_F = 0.067
R_{wF} = 0.064
variables = 153
p factor = 0.020

LiC₄S₂H₆Ph·tmed·thf,¹⁰ and the phosphinoalkyls LiCH(PMe₂)(SiMe₃)₂·pmdt¹¹ and LiCH₂PPh₂·tmed.^{12,13}

We have been interested for several years in the use of 2,4,6-triphenylphenyl substituents to prepare sterically encumbered metalloporphyrin centers.¹⁴⁻¹⁶ This bulky aryl group may also be of utility as a ligand in transition-metal and main-group chemistry. Trisubstituted aryl ligands such as the 2,4,6-trimethylphenyl group (mesityl) and the 2,4,6-tris(*tert*-butyl)phenyl group ("supermesityl") have already proven to be highly useful substituents in main-group chemistry.¹⁷⁻²² Such groups, by virtue of their

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(2) Abbreviations used: tmed = *N,N,N',N'*-tetramethylethylenediamine, pmdt = *N,N,N',N',N''*-pentamethyldiethylenetriamine, tmpn = *N,N,N',N'*-tetramethylpropylenediamine, thf = tetrahydrofuran.

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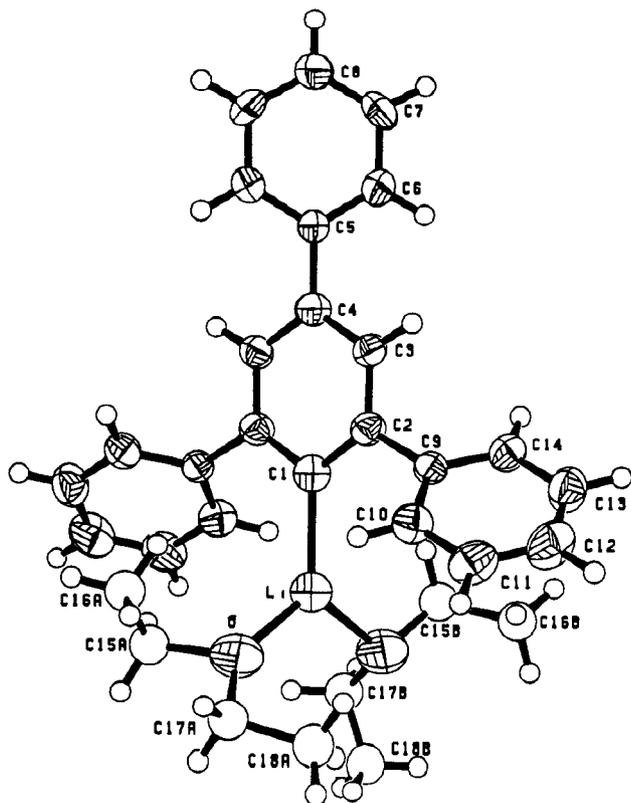


Figure 1. ORTEP diagram of $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$ (1). Thermal ellipsoids are drawn at the 35% probability level, while hydrogen atoms are represented by arbitrarily-sized spheres.

steric size, inhibit catenation reactions and permit the isolation of compounds that contain multiple bonds between main-group elements. The bulky groups can also considerably reduce the coordination number about a transition metal; for example, one-coordinate copper and silver complexes have recently been isolated that contain the 2,4,6-triphenylphenyl ligand.²³ We now describe the synthesis and X-ray crystal structure of the unusual monomeric aryllithium reagent $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$.²⁴

Results and Discussion

Synthesis of (2,4,6-Triphenylphenyl)lithium. Metalation of 1-bromo-2,4,6-triphenylbenzene with *n*-butyllithium in diethyl ether followed by addition of pentane and cooling to -20°C yields the crystalline aryllithium reagent $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$ (1) in high yield. This com-

$$(\text{C}_6\text{H}_2\text{Ph}_3)\text{Br} + \text{Li}(n\text{-Bu}) + 2\text{Et}_2\text{O} \rightarrow \text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O} + n\text{-BuBr}$$

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ound is readily soluble in ethers and aromatic hydrocarbons, and its ^1H and ^{13}C NMR spectra confirm its pu-

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 (24) Professor P. P. Power has informed us that he has also prepared and crystallographically characterized $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$. Interestingly, his crystals were orthorhombic, space group *Pcab*, and possessed approximately twice our cell volume. Otherwise, the molecular structure of the (2,4,6-triphenylphenyl)lithium reagent based on our results and his are very similar. We thank Professor Power for communicating this result to us. See: Olmstead, M. M.; Power, P. P. *J. Organomet. Chem.* 1991, 408, 1–6.

Table II. Atomic Coordinates for $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C1	0.75	−0.0085 (4)	0.0
C2	0.7010 (5)	0.0303 (3)	0.0835 (5)
C3	0.7031 (5)	0.0974 (3)	0.0853 (5)
C4	0.75	0.1336 (4)	0.0
C5	0.75	0.2052 (4)	0.0
C6	0.7792 (5)	0.2400 (3)	0.0976 (5)
C7	0.7788 (6)	0.3074 (3)	0.0982 (6)
C8	0.75	0.3409 (5)	0.0
C9	0.6410 (5)	−0.0029 (3)	0.1748 (5)
C10	0.5577 (5)	−0.0492 (3)	0.1458 (6)
C11	0.5010 (5)	−0.0799 (3)	0.2316 (6)
C12	0.5287 (6)	−0.0651 (4)	0.3437 (7)
C13	0.6109 (6)	−0.0202 (3)	0.3732 (6)
C14	0.6676 (5)	0.0107 (3)	0.2891 (5)
Li	0.75	−0.1097 (8)	0.0
O	0.6576 (5)	−0.1623 (2)	−0.1090 (5)
C15A	0.685 (1)	−0.1545 (7)	−0.240 (2)
C16A	0.597 (1)	−0.1077 (8)	−0.272 (1)
C17A	0.582 (1)	−0.2136 (10)	−0.120 (1)
C18A	0.578 (1)	−0.2333 (8)	0.005 (1)
C15B	0.898 (2)	−0.120 (1)	0.197 (2)
C16B	0.849 (2)	−0.135 (1)	0.315 (2)
C17B	0.936 (2)	−0.201 (1)	0.052 (2)
C18B	0.937 (2)	−0.264 (1)	0.086 (2)

Table III. Important Bond Distances (Å) and Angles (deg) for $\text{Li}(\text{C}_6\text{H}_2\text{Ph}_3)\cdot 2\text{Et}_2\text{O}$ ^a

Bond Distances			
Li–C1	2.08 (2)	C11–C12	1.36 (1)
Li–O	1.93 (1)	C12–C13	1.36 (1)
C1–C2	1.423 (7)	C13–C14	1.391 (9)
C2–C3	1.378 (8)	C14–C9	1.377 (8)
C3–C4	1.396 (7)	O–C15A	1.60 (2)
C2–C9	1.496 (8)	O–C15B	1.45 (2)
C4–C5	1.47 (1)	O–C17A	1.37 (2)
C5–C6	1.366 (7)	O–C17B	1.55 (2)
C6–C7	1.385 (9)	C15A–C16A	1.44 (2)
C7–C8	1.357 (8)	C15B–C16B	1.57 (3)
C9–C10	1.385 (8)	C17A–C18A	1.52 (2)
C10–C11	1.403 (9)	C17B–C18B	1.35 (3)
Bond Angles			
O–Li–C1	124.0 (4)	C5–C6–C7	121.8 (6)
O–Li–O'	112.0 (8)	C6–C7–C8	120.1 (6)
Li–C1–C2	124.1 (4)	C7–C8–C7'	119.2 (8)
C2–C1–C2'	111.8 (6)	C2–C9–C10	120.3 (5)
C1–C2–C3	124.2 (5)	C2–C9–C14	121.6 (5)
C2–C3–C4	121.9 (6)	C14–C9–C10	118.1 (5)
C3–C4–C3'	115.8 (7)	C9–C10–C11	120.1 (6)
C1–C2–C9	118.7 (5)	C10–C11–C12	120.3 (6)
C9–C2–C3	117.0 (5)	C11–C12–C13	120.1 (7)
C3–C4–C5	122.1 (4)	C12–C13–C14	120.2 (6)
C4–C5–C6	121.5 (4)	C13–C14–C9	121.1 (5)
C6–C5–C6'	116.9 (7)		

^a Primed atoms are related to unprimed atoms by the crystallographic 2-fold axis.

urity (see Experimental Section). The ipso carbon resonance appears at δ 179.0, which may be compared with an ipso carbon shift of δ 171.7 in phenyllithium.²⁵ Although solutions of (2,4,6-triphenylphenyl)lithium²⁶ (and the corresponding Grignard reagent)²⁷ have been reported previously, they were not obtained free from contaminating byproducts. Additionally, the yield of the *n*-butyllithium metalation was reported²⁶ to be a modest 11%, in contrast to our 77% isolated yields.

Structure of (2,4,6-Triphenylphenyl)lithium-Bis(diethyl ether). Compound 1 adopts an unusual mo-

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meric structure in the solid state, as shown by a single-crystal X-ray diffraction study (Figure 1). Crystal data are collected in Table I, atomic coordinates are presented in Table II, and important bond distances and angles are given in Table III. Crystals of 1 are composed of discrete monomers that lie on a crystallographic 2-fold axis. The lithium atom is three-coordinate and adopts a planar coordination geometry defined by the ipso carbon atom and two oxygen atoms of the diethyl ether solvate molecules. The Li-C distance of 2.08 (2) Å is one of the shortest known but is comparable to the 2.12 (1) Å distances in the only other monomeric aryllithium reagents, LiPh-pmdt⁴ and LiC₆H₂(*t*-Bu)₃-tmpn.⁵ In contrast, Li-C contacts to bridging phenyl groups are 2.21–2.28 Å, as shown by the structure of the tmed adduct of phenyllithium, Li₂Ph₂·2tmed.³ Other oligomeric aryllithium compounds possess similarly long Li-C distances.^{1,28} The trigonal-planar geometry of the lithium center in 1 resembles the three-coordinate lithium centers in [Li(CH₂Ph)·Et₂O]_x²⁸ and, to some extent, the pseudo-three-coordinate lithium atoms in [1,3:1,3-bis(2,2'-biphenylene)propene]lithium etherate.²⁹

Monomeric alkylolithium reagents typically possess a single Li-C(sp³) contact of 2.13–2.28 Å.^{6–13} Since the radius of an sp² carbon atom is ca. 0.105 Å smaller than that of an sp³ carbon atom,³⁰ the 2.08-Å distance between the lithium and the sp² carbon atom in 1 is near the value expected. Interestingly, however, an ab initio optimization of a disolvated phenyllithium monomer predicted an Li-C contact of only 1.86 Å.³¹ Although 1 is somewhat more crowded sterically than the hypothetical molecule investigated theoretically, there are no significant intramolecular contacts in 1 that would account for the 0.20-Å difference between the observed and calculated Li-C distances.

The central phenyl ring in 1 exhibits distortions from an ideal hexagon that are consistent with its carbanionic character. Specifically, the C-C distance between the ipso and ortho carbon atoms of 1.423 (7) Å is slightly longer than the other C-C distances in the central ring of 1.378 (7)–1.396 (7) Å. Additionally, the interior C-C-C angle at the ipso carbon atom of 111.8 (6)° is significantly more acute than the other interior C-C-C angles around the ring, which vary from 115.8 (7) to 124.2 (5)°. The deviations in both the C-C distances and the C-C-C angles are indicative of a displacement of the ipso carbon atom away from the central ring centroid and toward the lithium atom. The Li-O distances of 1.93 (1) Å between the lithium atom and the ether ligands are unexceptional, as are the other distances and angles in the structure of 1.

The monomeric nature of Li(C₆H₂Ph₃)·2Et₂O is principally a consequence of the steric congestion generated by the two *o*-phenyl substituents. There are no significant Li...C contacts with other carbon atoms in the molecule such as those observed in the alkylolithium complex LiC(SiMe₂Ph)₃·thf.⁷ The closest such contact in 1 of 3.11 (2) Å, which occurs between Li and C(2), is well outside bonding range. The Li-C(9) and Li-C(10) contacts to the *o*-phenyl substituents are even longer at 3.33 (1) and 3.199 (9) Å, respectively.

Concluding Remarks. The X-ray diffraction study of Li(C₆H₂Ph₃)·2Et₂O reveals that this molecule is a rare example of a monomeric σ -bonded organolithium reagent.

It is notable that ether and amine adducts of other aryllithium reagents with methyl,²⁸ methoxy,^{32,33} or *tert*-butylthiolato³⁴ groups in the ortho positions are dimeric or tetrameric; evidently, these groups are insufficiently bulky to prevent aggregation of aryllithium species. Thus, the present results demonstrate that the steric bulk of the 2,4,6-tris(*tert*-butyl)phenyl and 2,4,6-triphenylphenyl groups are roughly comparable. Both are useful as bulky substituents in main-group and transition-metal chemistry, but the 2,4,6-triphenylphenyl group is more convenient to employ owing to its greater availability and lower cost.

Experimental Section

All operations were conducted under vacuum or under argon. Diethyl ether was distilled from sodium-benzophenone immediately before use. *n*-Butyllithium (Aldrich) was used as received. 1-Bromo-2,4,6-triphenylbenzene was prepared according to a literature procedure²⁷ and recrystallized from CH₂Cl₂/EtOH.

Microanalyses were performed by Mr. Josef Nemeth and Mr. Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B instrument, and ¹H NMR data were recorded on a General Electric QE-300 or a General Electric GN-300NB spectrometer at 300 MHz. The ¹³C NMR data were recorded on the GN-300NB instrument at 75.4 MHz. Chemical shifts are reported in δ units (positive chemical shifts to higher frequency) relative to tetramethylsilane.

(2,4,6-Triphenylphenyl)lithium-Bis(diethyl ether). A three-necked 300-mL round-bottom flask fitted with a pressure-equalized dropping funnel was flushed with argon and charged with 1-bromo-2,4,6-triphenylbenzene (30.5 g, 79.2 mmol) and diethyl ether (150 mL). The flask was cooled to -78 °C with a dry ice/ethanol bath and the dropping funnel was charged with *n*-butyllithium (60 mL of a 1.5 M solution in hexane, 90.0 mmol). The *n*-butyllithium solution was added dropwise to the stirred reaction solution over 25 min. After being stirred at -78 °C for an additional 4 h and warmed to -20 °C for 30 min, the reaction mixture was allowed to settle for 4 h at -78 °C. The white powdery residue was collected by filtration at -78 °C and extracted with diethyl ether (600 mL) at room temperature. The filtered extract was concentrated to ca. 400 mL and cooled to -20 °C for 12 h to give colorless crystals of the product. Additional material may be obtained by concentrating and cooling the supernatant. Yield: 27.95 g (77%). (Note: isolation of the product is considerably more difficult if the solution is warmed above -20 °C during the lithiation step.) Anal. Calcd for C₃₂H₃₇O₂Li: C, 83.4; H, 8.10; Li, 1.51. Found: C, 83.0; H, 7.97; Li, 1.61. ¹H NMR (C₆D₆, 25 °C): 7.74 (s, *m*-CH), 7.66 (d, *J*_{HH} = 7.5 Hz, *o*'-CH), 7.45 (d, *J*_{HH} = 7.2 Hz, *o*'-CH), 7.31 (t, *J*_{HH} = 7.5 Hz, *m*'-CH), 7.26 ("t", *J*_{HH} = 7.9 Hz, *m*'-CH), 7.15 (t, *J*_{HH} = 7.0 Hz, *p*'-CH), 2.99 (q, *J*_{HH} = 7.6 Hz, OCH₂CH₃), 0.78 (t, *J*_{HH} = 7.6 Hz, OCH₂CH₃). ¹³C{¹H} NMR (C₆D₆, 25 °C): 179.0 (br, s, *i*-C), 154.0 (s, *o*-C), 150.0 (s, *i*'-C), 142.9 (s, *i*'-C), 138.5 (s, *p*-C), 128.9 (s, *m*'-CH), 128.4 (s, *m*'-CH), 127.4 (s, *o*'-CH), 126.9 (s, *p*'-CH), 126.0 (s, *p*'-CH), 125.7 (s, *o*'-CH), 122.5 (s, *m*-CH), 66.1 (s, OCH₂CH₃), 15.1 (s, OCH₂CH₃). For the NMR assignments, atoms in the central ring are unprimed, atoms in the ortho phenyl groups are primed, and atoms in the para phenyl group are doubly primed.

Crystallographic Studies.³⁵ Single crystals of (2,4,6-triphenylphenyl)lithium-bis(diethyl ether), grown from a mixture of diethyl ether and pentane, were sealed in thin-walled glass capillaries under argon. A suitable crystal was transferred to the diffractometer, and standard peak search and indexing procedures

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gave rough cell dimensions. The diffraction symmetry was supported by examination of the axial photographs. Least squares refinement using 15 reflections yielded the cell dimensions given in Table I.

Data were collected in one quadrant of reciprocal space ($\pm h, +k, +l$) using measurement parameters listed in Table I. Systematic absences for hkl ($h + k + l \neq 2n$) and $h0l$ ($h, l \neq 2n$) were consistent with space groups $I2/a$ and Ia . The average values of the normalized structure factors suggested the centric choice $I2/a$, which was confirmed by successful refinement of the proposed model.³⁶ The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change. Absorption corrections were not applied. Seven questionable reflections were deleted; five flooded the counter, and two were poorly centered. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least squares refinement.

The structure was solved using direct methods (SHELXS-86) and unweighted difference Fourier methods. The positions of the oxygen, lithium, and 18 of the carbon atoms were deduced from an E map. Subsequent difference Fourier calculations revealed the positions of the disordered ethyl carbon atoms. The relative site occupancy factor for the disordered ethyl carbon atoms was 0.588 (6) for the "A" sites. The quantity minimized by the

least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.65/(\sigma(F_o)^2 + (\sigma F_c)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, a group isotropic thermal parameter was varied for the disordered carbon atoms, while all other non-hydrogen atoms were independently refined with anisotropic thermal coefficients. A group isotropic thermal parameter was varied for the hydrogen atoms which were fixed in "idealized" positions with C-H = 0.95 Å. Successful convergence was indicated by the maximum shift/error of 0.035 in the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features. There were no apparent systematic errors among the final observed and calculated structure factors.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the National Institutes of Health (Grant HL 25934) for their support. We particularly thank Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for assistance with the X-ray crystal structure determination. K.S.S. acknowledges an NIH Research Career Development Award and an A. P. Sloan Foundation Research Fellowship. G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship and a Henry and Camille Dreyfus Teacher-Scholar Award.

Supplementary Material Available: Tables S1-S3, giving hydrogen atom positions and anisotropic thermal parameters for $\text{LiC}_6\text{H}_2\text{Ph}_3 \cdot 2\text{Et}_2\text{O}$ (1) (2 pages). Ordering information is given on any current masthead page.

OM920199R

(36) The conventional reduced cell vectors for this I-centered unit cell are $a = 11.723$ Å, $b = 11.732$ Å, $c = 12.967$ Å, $\alpha = 114.36^\circ$, $\beta = 114.34^\circ$, $\gamma = 95.06^\circ$. Axial X-ray diffraction photographs of the data crystal confirmed these reduced cell dimensions. This cell can be transformed into the F-centered pseudoorthorhombic cell $a = 15.837$ Å, $b = 17.301$ Å, $c = 20.538$ Å; however, axial photographs of these axes showed no mirror symmetry for a or b .

Stereochemistry of the Thermal Decomposition of (2-(Acyloxy)alkyl)triorganostannanes

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Received March 24, 1992

Summary: The stereochemical study of the thermal decomposition of (2-(acyloxy)alkyl)triorganostannanes revealed an anti β -elimination of (acyloxy)triorganostannanes. The process is highly stereospecific and not perturbed by the presence of a possible internal chelation favoring syn elimination. It corresponds to an open transition state. Kinetics of β -elimination in cyclohexyl and norbornyl systems showed that the reaction is much more rapid with a 180° dihedral angle between the metal and the ester group than with a 60° angle between the two. Stabilization of the partial positive charge developed during the transition state occurs mainly through hyperconjugation effect.

The β -elimination reaction,¹ which is often an undesirable process because of the induced instability of hetero-substituted organometallic compounds, has been applied to the stereospecific preparation of functional olefins from β -hydroxylated triphenylstannanes.² When treated by acids, these alcohols undergo an anti elimination, whereas their thermal decomposition leads to a syn elimination. Similar processes, based on acid- or base-induced eliminations, occur in organosilicon chemistry where their very

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