highest purity available.

Bis(trifluoroacetato-*O*)(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (3). Mercuric trifluoroacetate (1.36 g, 3.19 mmol) was added to a solution of 1,2,3,4-tetramethylbenzene (0.211 g, 1.57 mmol) in trifluoroacetic acid (8 mL). The mixture was stirred at 25 °C for 15 min and then poured into water (40 mL). The resulting precipitate was separated by centrifugation, washed thoroughly with water, and dried in vacuo. Sublimation (10^{-5} Torr, 100 °C) removed the product of monomercuration[6] and left a residue of the bis(trifluoroacetate) **3** (0.898 g, 1.18 mmol, 75.2%). Recrystallization from chloroform/acetonitrile provided colorless crystals of an analytically pure sample: mp >300 °C; IR (KBr) 1680, 1445, 1210, 1160 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 2.17 (s, 6 H), 2.38 (s, 6 H); ^{199}Hg NMR (53.6 MHz, DMSO-d_6, 0.1 M) δ −1493. Anal. Calcd for $C_{14}H_{12}F_6Hg_2O_4$: C, 22.14; H, 1.60. Found: C, 22.10; H, 1.56.

(μ-3,4,5,6-Tetramethyl-1,2-phenylene)(μ-oxo)dimercury (1b). Bis(trifluoroacetate) **3** (410 mg, 0.54 mmol) was heated at reflux for 20 min in aqueous NaOH (0.16 N, 35 mL). The mixture was cooled, and the suspended solid was separated by centrifugation, washed thoroughly with water, and dried in vacuo to give the oligomeric oxide **1b** as a white powder (300 mg, 0.54 mmol, 100%): mp >300 °C; IR (KBr) 2950 (br), 1470, 645, 460 cm^{-1}. This product was used for the following reaction without further purification.

1:4 DME Adduct of the Macrocyclic Mercuric Hexafluoroglutarate 2b. Oxide **1b** (40.9 mg, 74.4 μmol) was added at 25 °C under dry N_2 to a solution of hexafluoroglutaric acid (19.0 mg, 79.1 μmol) in DME (30 mL). The mixture was stirred for 15 min; then the flask was opened to the atmosphere, and the solvent was allowed to evaporate slowly. This yielded colorless crystals of the 1:4 DME adduct of macrocyclic mercuric hexafluoroglutarate **2b**, which were removed by filtration and dried in vacuo (54.1 mg, 28.4 μmol, 76.3%): mp 236–237 °C dec; IR (KBr) 1700, 1380, 1340, 1250, 1145 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.06 (s, 12 H), 2.26 (s, 12 H), 3.22 (s, 24 H), 3.41 (s, 16 H); ^{199}Hg NMR (53.6 MHz, DMSO-d_6, 0.01 M) δ −1474. Anal. Calcd for $C_{46}H_{64}F_{12}Hg_4O_{16}$: C, 29.02; H, 3.40. Found: C, 28.79; H, 3.31.

Crystallographic Data for the 1:4 DME Adduct of Host 2b. The crystal selected for analysis had the dimensions 0.16 × 0.22 × 0.36 mm. It proved to belong to the triclinic space group $P\bar{1}$, with a = 9.141 (3) Å, b = 11.203 (4) Å, c = 14.563 (11) Å, α = 97.34 (4)°, β = 96.70 (4)°, γ = 97.45 (3)°, V = 1453.1 Å^3, Z = 1, and D_{calcd} = 2.175 g cm^{-3}.

Crystallographic Measurements and Structure Resolution. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data according to a procedure described elsewhere.[7] Seven standard reflections checked every 1 h showed random fluctuations of less than ±2.1% about their respective means. A set of 7586 Mo K$\bar{\alpha}$ reflections ($2\theta \leq 45°$) was collected at 220 K. Of these, 2963 ($I > 3\sigma(I)$) were retained for structure resolution and refinement after averaging to the Laue $\bar{1}$ symmetry. These measurements were corrected for the Lorentz effect, polarization, and absorption (Gaussian integration technique) before averaging. The structure was solved by using direct methods (EEES) and difference-Fourier calculations (SHELX), and it was refined on $|F_0|$ by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions (C–H = 0.95 Å, B_{iso} = 7 Å^2 (phenyl) and 8 Å^2 (others)). Disorder was introduced at C(43) to account for its large anisotropic behavior. The occupancy was initially refined and then fixed at 0.70/0.30. Refinement converged to R = 0.025, R_w = 0.027, and goodness-of-fit ratio S = 1.67 for 363 parameters refined. The final ΔF map was essentially featureless, with a general background below ±0.18 e Å^{-3} and 15 peaks of 0.20–0.54 e Å^{-3} within 1.15 Å from Hg. The scattering curves for the non-hydrogen atoms[8] and the hydrogen atoms[9] were taken from standard sources. The contributions of Hg to anomalous dispersion were included.[10]

Selected interatomic distances, bond angles, and torsion angles are listed in Table I, and atomic coordinates and isotropic thermal parameters are provided in Table II. Tables of hydrogen atom coordinates, anisotropic thermal parameters, interatomic distances, bond angles, and structure factors are included as supplementary material.

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council of Canada and by the Ministère de l'Éducation du Québec. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support. We are grateful to Robert Mayer and Dr. M. T. Phan Viet of the Regional High-Field NMR Laboratory for helping us record our ^{199}Hg NMR spectra.

Registry No. **1b**, 125611-04-3; **2b**, 125640-18-8; **3**, 125611-05-4; $Hg(OOCCF_3)_2$, 13257-51-7; 1,2,3,4-tetramethylbenzene, 488-23-3; hexafluoroglutaric acid, 376-73-8.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and interatomic distances and bond angles for the 1:4 DME complex of macrocyclic mercuric hexafluoroglutarate **2b** (8 pages); a table of structure factors (14 pages). Ordering information is given on any current masthead page.

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Rotational Behavior of *exo*-[1,1,3-Tris(trimethylsilyl)allyl]lithium

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Summary: The title compound, **3**, has been generated by metalation of (*E*)-1,3,3-tris(trimethylsilyl)-1-propene with butyllithium[^{6}Li] in pentane–TMEDA at room temperature. NMR establishes the exo structure of **3** under all conditions used. Compound **3** in THF with 1 equiv of TMEDA exhibits a barrier to rotation about the C_1C_2 bond of $\Delta H^{\ddagger}$ = 17 kcal and $\Delta S^{\ddagger}$ is +25 eu.

Allyllithium and substituted versions thereof have been the subject of extensive investigations of their chemistry[1] by X-ray crystallography,[2] with NMR,[3] and by calculation.[4]

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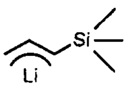
These compounds display an astonishing variety of properties that vary with substitution, temperature, and especially the nature of coordinated ligand. Whereas the synthetic utility of [1-(trimethylsilyl)allyl]lithium[5-7] is well documented, little is known about its structure or of any of the possible [(polysilyl)allyl]lithiums. We recently initiated an investigation of these interesting species,[8-10] the results of which, so far, are summarized by structures 1 and 2. This paper deals with the structure and dynamic



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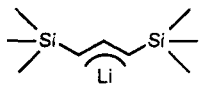
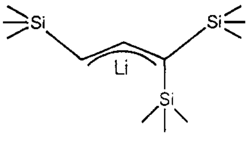


2

behavior of [1,1,3-tris(trimethylsilyl)allyl]lithium, 3.



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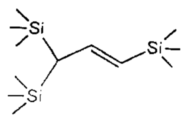

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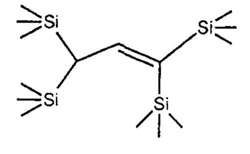
Reaction of *exo,exo*-[1,3-bis(trimethylsilyl)allyl]lithium, 2, in diethyl ether containing 1 equiv of TMEDA (*N,N,N',N'*-tetramethylethylenediamine) with chlorotrimethylsilane at -78 °C gave exclusively (*E*)-1,3,3-tris(trimethylsilyl)-1-propene, 4.[8] This compound underwent smooth allylic metalation on treatment with *n*-butyllithium[^{6}Li] and one equiv of TMEDA in pentane at room temperature over 24 h to form the [tris(silyl)allyl]lithium 3, the subject of this note.

A portion of crude 3 prepared in pentane–TMEDA (see Experimental Section) was treated with chlorotrimethylsilane, yielding 1,1,3,3-tetrakis(trimethylsilyl)propene, 5;



5

none of the isomeric 1,3,3,3-tetrakis(trimethylsilyl)-1-propene could be detected in this reaction mixture. Compound 5 was inert to metalation by *n*-butyllithium in THF–TMEDA or pentane–TMEDA at -78 °C or room temperature. Failure to metalate 5 allylically can be ascribed to crowding about the allylic carbon.

Table I. Carbon-13 Shifts, δ, of 0.5 M [1,3,3-Tris(trimethylsilyl)allyl]lithium with 0.5 M TMEDA in THF-d_8 at Different Temperatures

T, K	C_1	C_2	C_3	NCH_3	CH_2	CH_3Si
185	57.37	160.30	77.91	46.49	58.69	2.558 2.821 4.627
210	56.8	160.32	77.41	46.39	58.84	2.543 2.853 4.612
240	57.29	160.50	77.60	46.27	58.82	2.480 3.997[a]
260	57.30	160.3	77.98	46.28	58.84	2.472 3.848[a]
270	57.30	160.3	77.18	46.18	58.83	2.341 3.788[a]

[a] Signal averaged.

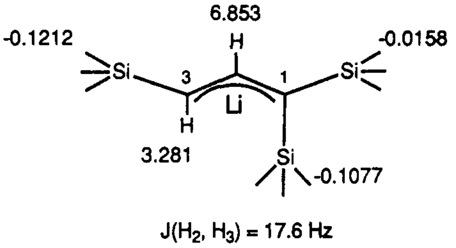


Figure 1. Proton NMR parameters for 3, 0.5 M in THF with 1 equiv of TMEDA (200 K).

The crude reaction product in pentane–TMEDA was found by NMR to consist of 3 and 4 in the ratio 5/1 with minor unidentified impurities and no detectable *n*-butyllithium. After evaporation of solvent there remained an oil that eventually crystallized. This latter material was dissolved in cold THF-d_8 for NMR investigation. The sample still contained TMEDA, though its ^{13}C shifts, NCH_3 at 46.3 and NCH_2 at 55.8. ppm, respectively, were almost the same as those of TMEDA, alone, in THF. Hence the ligand coordinated to 3 must be THF. Furthermore, the NMR parameters for impure 3 in pentane–TMEDA and purified 3 in THF solution were very similar.

Each sample of 3 gave rise to a single NMR spectrum (see Table I and Figure 1). The NMR parameters for 3 in THF varied very little with temperature, implying that the same single species predominated under all conditions used. Proton NMR spectra of all samples show the single trimethylsilyl group at C_3 to be exo as evidenced by the H_2, H_3 vicinal coupling of 17.6 Hz (see Figure 1); the *endo*-3-trimethylsilyl isomer of 3 was not detected in this work. This is consistent with our recent investigations of 1[9,10] and 2[8,10] but stands in sharp contrast to the general observation that in (1-alkylallyl)lithiums *endo*-R is favored over *exo*-R by 2–4 kcal/mol.[11-14]

The NMR data for compound 3 also show interesting dynamic effects. As seen in Figure 2, the trimethylsilyl groups at C_1 are magnetically nonequivalent at 200 K and then progressively undergo signal-averaging on warming the sample to 260 K due to rotation about the C_1C_2 bond. Throughout this temperature range the single ^{13}C peak for

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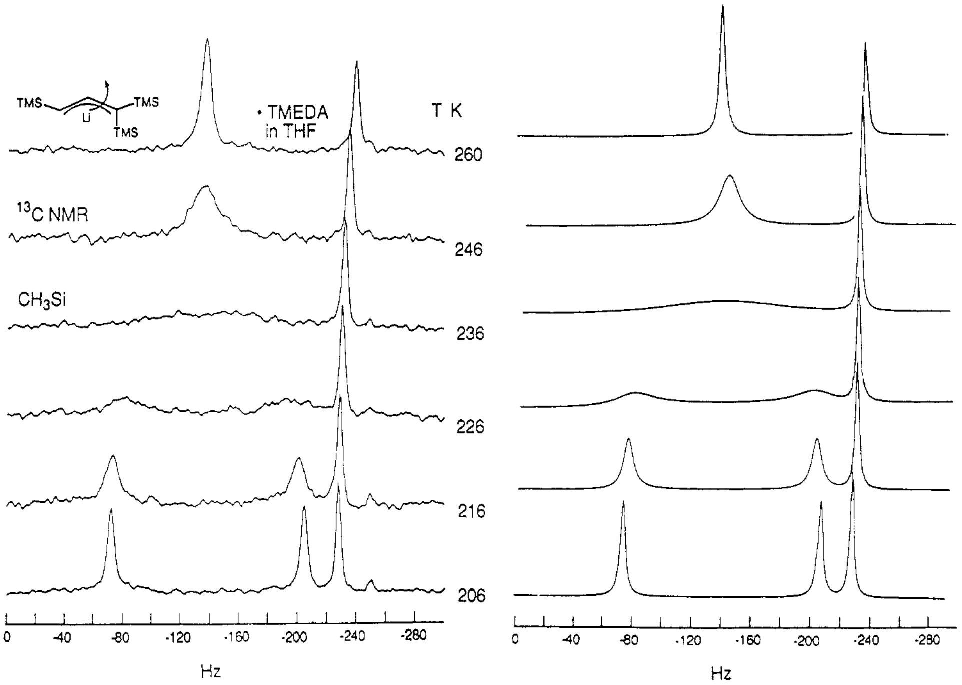

Figure 2. Left: observed ^{13}C NMR line shapes of CH$_3$Si groups of **3** (see Figure 1 caption), at different temperatures (kelvin). Right: calculated line shapes.

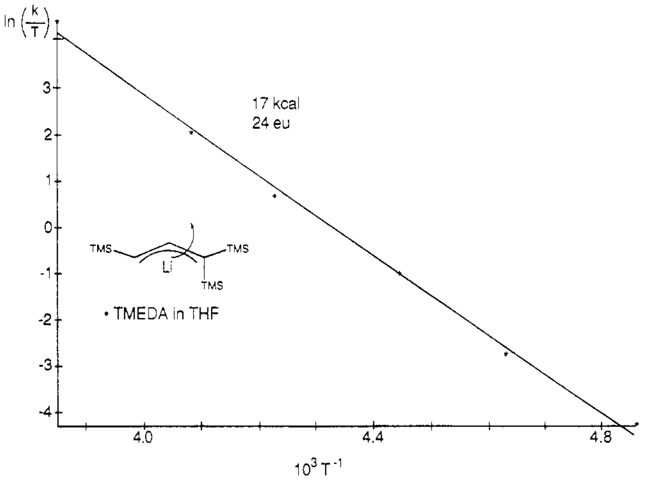

Figure 3. Eyring plot for rotation about the C_1C_2 bond of **3**, as described in Figure 1 caption.

the 3-exo silyl methyls remains sharp and unchanged. NMR line-shape analysis of the collapsing doublet yields $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 16.8 kcal/mol and 25 eu, respectively (Figure 3).

Experimental Section

NMR Analysis. NMR data were obtained under standard conditions by using Bruker AM 250, AM 500, and MSL 300 NMR spectrometers as previously described.[8]

[1,1,3-Tris(trimethylsilyl)allyl]lithium. The alkene, under argon, (*E*)-1,3,3-tris(trimethylsilyl)-1-propene (1.0 g, 3.87 mmol) was weighed into an oven-dried vial, then dissolved in 25 mL of pentane, and transferred to a Schlenk tube. Then, TMEDA at room temperature (0.75 mL, 4 mmol) was added to the solution, and finally *n*-butyllithium[^{6}Li] in pentane (1 mL, 4.4M, 4.4 mmol). This solution was stirred for 24 h at room temperature, by which time it had turned slightly red. Solvent was removed in vacuo, leaving a red black oil. After 1 week crystals were noticed. These were separated with a spatula and carefully washed with a drop of pentane and then dried in vacuo. After drying, they were dissolved in THF-d_8, to ca. 1 M and investigated with NMR methods.

[1,1,3,3-Tetrakis(trimethylsilyl)allyl]lithium. A solution of *n*-butyllithium[^{6}Li] in pentane (5 mL, 2.6 M, 13 mmol) was diluted with 15 mL more of pentane and 13 mmol (1 equiv) of TMEDA. To this solution at room temperature was added (*E*)-1,3,3-tris(trimethylsilyl)-1-propene (2.0 g, 7.7 mmol), and the resulting mixture was stirred at room temperature for 24 h. The resulting reaction mixture was treated with chlorotrimethylsilane (0.85 g, 7.8 mmol) and worked up in the usual way. After evacuation of volatile constituents the residue was vacuum distilled twice, bp 66–67 °C/0.4 Torr, yielding 1 g of a colorless oil; ^{13}C NMR (CDCl$_3$) δ 127.66 (C$_1$), 145.27 (C$_2$), 31.65 (C$_3$) 2.79, 1.04, and 0.19 (1:1:1, CH$_3$Si at C$_1$, C$_1$, and C$_3$, respectively); ^{1}H NMR δ 6.586 (H$_2$), 1.820 (H$_3$), 0.07, 0.075, and 0.14 (1:1:1, CH$_3$Si at C$_3$, C$_3$, and C$_1$, respectively, ^3J(H$_2$,H$_3$) = 13.3 Hz).

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Oxidation of Organoboranes with Sodium Percarbonate

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Summary: Sodium percarbonate, a readily available, inexpensive, and easily handled reagent, efficiently oxidizes a variety of organoboranes. The product yields compare favorably with those obtained by use of the standard sodium hydroxide/hydrogen peroxide oxidation procedure.