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Lithium-Induced Cyclization of Tribenzocyclyne: Synthesis and Structural Characterization of a Novel Helicene Dianion, Its Protonated Form, Silylated Isomers of a Substituted Fulvalene Ligand, and a Novel Dimeric Lithium Complex

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A novel lithium-induced cyclization reaction of tribenzocyclotriyne (TBC) (**1**) leads to the formation of a helical fulvalene dianion derivative $Li_2(\eta^5,\eta^5\text{-}C_{24}H_{14})$ (**2**) in high yield. The helical nature of the dianion is observed in the crystal structure of the 1:2 adduct with TMEDA (**2a**), which crystallizes in the triclinic space group $P\bar{1}$ with a = 12.379 (3) Å, b = 16.043 (3) Å, c = 16.902 (4) Å, α = 95.42 (2)°, β = 96.64 (2)°, γ = 90.27 (2)°, V = 3318.6 (13) Å^3, and Z = 4. Reaction of the fulvalene dianion **2** with methanol gives a protonated neutral compound $C_{24}H_{16}$ (**3**) which crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 5.460 (9) Å, b = 13.675 (2) Å, c = 20.552 (3) Å, V = 1534.74 (4) Å^3, and Z = 4. Reaction of the fulvalene dianion **2** with trimethylchlorosilane leads to the formation of bis(trimethylsilyl) trans and cis isomers of $C_{24}H_{14}(SiMe_3)_2$. The structures of the two isomers have been determined by single crystal X-ray diffraction. The trans isomer (**4a**) crystallizes in the monoclinic space group $P2_1/a$ with a = 12.066 (4) Å, b = 18.129 (4) Å, c = 13.253 (4) Å, β = 116.41 (2)°, V = 2596.6 (13) Å^3, and Z = 4. The cis isomer (**4b**) crystallizes in the triclinic space group $P\bar{1}$ with a = 8.3694 (13) Å, b = 11.446 (2) Å, c = 14.807 (3) Å, α = 110.058 (13)°, β = 96.901 (13)°, γ = 99.810 (13)°, V = 1288.0 (4) Å^3, and Z = 2. The *trans*-bis(trimethylsilyl) compound **4a** has the most pronounced helical character. Dimetalation of the disilylated isomers **4a** and **4b** with 2 equiv of *n*-butyllithium results in the formation of a new dimeric organolithium compound $\{Li_2(THF)_2[\eta^5:\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2\}_2$ (**5**) which shows unusual modes of coordination for lithium atoms. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ with a = 13.663 (3) Å, b = 14.509 (3) Å, c = 18.494 (4) Å, β = 107.50 (3)°, V = 3496.5 (13) Å^3, and Z = 4. This is the first example of a crystal structure of an organolithium having lithium atoms bound in an η^5,η^5 fashion to cyclopentadienyl (Cp) moieties forming a sandwich system and is the only inverse sandwich structure with Li–Cp–Li–Cp interactions.

Introduction

Reactions of alkynes with transition metal complexes can lead to a variety of products. Metal complexes of alkynes are important as intermediates for catalytic processes in the cyclodimerization, cyclotrimerization, and cyclotetramerization of alkynes to benzenes and cyclooctatetraenes.[2] A number of research groups have investigated alkyne cyclization reactions with most of these being transition metal catalyzed.[3] For the last few years our research group has been studying the synthesis of cyclic polyalkynes (cyclynes) and metallocyclynes and the reaction chemistry of these unique compounds with the primary interest being the synthesis of conducting materials based on these new compounds.[4] In our studies of the interaction of transition metal complexes with cyclynes,[4a–f] we have isolated transition metal cyclyne complexes but, consistent with the results of other researchers[5] we have not observed transition metal-induced [2 + 2 + 2] alkyne cyclization of the cyclynes. Recently in our investigation of the interaction of lithium metal with a cyclyne ligand we have discovered an unprecedented lithium-induced cyclization reaction of tribenzocyclotriyne[6] (TBC) (**1**) to form the novel helicene dianion **2**.[7] This is the first example of a helicene dianion based on a fulvalene fragment. The synthesis, structural characterization of the helical dicyclopentadienyl dianion, its reaction chemistry, and the characterization of the reaction products are presented here.

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Experimental Section

General Procedures. Unless otherwise stated, all manipulations were performed under argon or vacuum by using standard inert atmosphere techniques.[8,9] Tetrahydrofuran (Aldrich) was distilled from sodium/benzophenone ketyl under argon. Tetramethylethylenediamine (TMEDA) (Aldrich) was purified by vacuum distillation from barium oxide. Trimethylchlorosilane (Aldrich) was degassed and distilled from calcium carbonate under vacuum. Methanol (Aldrich) was degassed with argon prior to use. Lithium sand (Aldrich) contained a 1% sodium impurity. *n*-Butyllithium (Aldrich) was standardized with diphenylacetic acid prior to use.[10] Flash chromatography[11] was carried out using silica gel (40 μm, Baker).

Infrared spectra were recorded on either a Matson Cygnus 25 FT-IR or Bomem-Michelson FT-IR spectrometer. Nuclear magnetic resonance spectra were recorded on either a Varian Gemini-300 or a Brucker MSL-400 FT-NMR spectrometer.[12] X-ray intensity data were collected at ambient temperatures with the use of graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nicolet R3m/v diffractometer except complex **5** whose data were collected on a Syntex P2_1 diffractometer. Microanalytical determinations were performed at the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points were obtained using a Thomas-Hoover Unimelt apparatus and are uncorrected.

Synthesis of TBC (1). TBC was prepared via the Stephens–Castro coupling[13] of copper(I) *o*-iodophenylacetylide.[6c] *O*-Iodophenylacetylene was synthesized from phenylacetylene by a modification of a literature procedure.[14]

Reduction of TBC with Lithium. Synthesis of $[Li(TMEDA)]_2(\eta^5,\eta^5\text{-}C_{24}H_{14})$ (2a). TBC (**1**) (0.10 g, 0.33 mmol) was dissolved in THF (40 mL) to give a pale yellow solution. Lithium metal (0.010 g, 1.44 mmol) and TMEDA (1 mL) were added to the solution. The color turned pale blue upon stirring, deepened over a period of 1 h and turned purple in 2 h. After 4 h the solution started turning red and turned completely red after approximately 6 h. No further color change was noted after 20 h. The reaction mixture was filtered using a medium frit. THF and excess TMEDA were removed in vacuo. The red solid was washed with hexane to give an extremely air-sensitive orange solid: yield 0.17 g $[Li(TMEDA)]_2(\eta^5,\eta^5\text{-}C_{24}H_{14})$ (**2a**), 92% based on TBC; IR (Nujol, KBr, cm^{-1}) 1612 m, 1462 m, 1321 s, 734 m; ^{1}H NMR (C_6D_6, δ) 0.9 (s, 8 H, CH_2 TMEDA), 1.10 (s, 24 H, CH_3 TMEDA), 7.30–7.33 (m, 6 H), 7.55 (dd, $J_1 = 3.3$ Hz, $J_2 = 6$ Hz, 2 H), 8.05–8.11 (m, 2 H), 8.69 (dd, $J_1 = 3.3$ Hz, $J_2 = 6$ Hz, 2 H), 9.40–9.46 (m, 2 H); ^{13}C NMR (THF-d_8, δ) 45.91 (TMEDA, CH_3), 58.57 (TMEDA, CH_2), 110.56, 112.31, 115.79, 119.05, 123.46, 123.83, 124.06, 124.44, 130.34, 132.18, 159.14.

Reduction of TBC with Lithium without TMEDA. Synthesis of $[Li(THF)]_2(\eta^5,\eta^5\text{-}C_{24}H_{14})$ (2b). The same procedure as above was followed without TMEDA. No more color changes were observed after approximately 18 h, the solution was filtered using a medium frit, and THF was removed in vacuo to give an air-sensitive red solid which was then washed with toluene and hexane. Attempts to obtain crystals of this compound were unsuccessful: yield 0.17 g, $[Li(THF)]_2(\eta^5,\eta^5\text{-}C_{24}H_{14})$ (**2b**), 92% based on TBC; IR (Nujol, KBr, cm^{-1}) 1591 m, 1377 s, 728 m; ^{1}H NMR (THF-d_8, δ): 1.72–1.76 (m, 4 H, THF), 3.16 (d, $J = 1.01$ Hz, 4 H, THF), 3.52–3.60 (m, 4 H, THF), 6.47–6.64 (m, 4 H), 6.74 (s, 2 H), 7.07 (dd, $J_1 = 3.3$ Hz, $J_2 = 6.0$ Hz, 2 H), 7.45 (d, $J = 2.13$, 2 H), 8.28 (dd, $J_1 = 3.4$ Hz, $J_2 = 6.0$ Hz, 2 H), 8.81 (d, $J = 7.5$ Hz, 2 H).

Reduction of TBC with Lithium in THF-d_8. The same reaction procedure was followed using deuterated THF with TMEDA. The resulting orange solid was washed with hexane to give $[Li(TMEDA)]_2(\eta^5,\eta^5\text{-}C_{24}H_{12}D_2)$, 92% based on TBC: ^{1}H NMR (THF-d_8, δ) 2.06 (s, 8 H, CH_2, TMEDA), 2.08 (s, 24 H, CH_3, TMEDA), 6.52–6.66 (m, 4 H), 7.09 (dd, $J_1 = 3.3$ Hz, $J_2 = 6.0$ Hz, 2 H), 7.47 (d, $J = 7.7$ Hz, 2 H), 8.27 (dd, $J_1 = 3.4$ Hz, $J_2 = 6.0$ Hz, 2 H), 8.82 (d, $J = 7.6$ Hz, 2 H).

Protonation of the Dianion 2. Synthesis of the Neutral Compound $C_{24}H_{16}$ (3). Compound 1 (0.10 g, 0.33 mmol) was dissolved in THF (40 mL) under argon. Lithium metal (0.01 g, 1.44 mmol) was added to the pale yellow solution. After 18 h the color of the solution was bright red. The reaction mixture was filtered using a frit and 1 mL of degassed methanol was added to the solution via a syringe. The solution turned brown-yellow immediately. The solvents were removed in vacuo. The solid residue was dissolved in toluene and passed through a plug of Celite to give a yellow solution. Removal of the solvent in vacuo afforded a yellow solid of the neutral compound **3**: yield 0.06 g, $C_{24}H_{16}$, 60% based on TBC; ^{1}H NMR ($CDCl_3$ δ) 4.22 (s, 4 H), 7.26–7.54 (m, 6 H), 7.68 (d, $J = 7.30$ Hz, 2 H), 8.03 (dd, $J_1 = 3.30$ Hz, $J_2 = 4.80$ Hz, 2 H), 8.52 (d, $J = 7.30$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, δ) 36.91 (methylene C on C_p ring), 123.89, 125.5, 126.58, 127.09, 129.85, 141.71, 143.44, 144.56, 142.83. Anal. Calcd: C, 94.70%; H, 5.30% Found: C, 94.48%; H, 5.00%.

Silylation of the Dianion 2. Synthesis of 4a and 4b. Compound 1 (0.5 g, 1.66 mmol) and lithium metal (0.06 g, 8.64 mmol) were dissolved in THF (120 mL) and stirred at room temperature for 18 h. The solution was filtered through a frit and trimethylchlorosilane (1 mL) was then added to the solution via syringe. The reaction mixture was stirred at room temperature for 3 h resulting in a yellow-brown solution. The solvent was removed in vacuo giving a yellow solid. At this point all further operations were conducted in air. Hexane (100 mL) was added to dissolve the product and then filtered over a plug of Celite to remove lithium chloride. The volume of the solution was reduced to ca. 20 mL on a rotary evaporator. Thin-layer chromatography (TLC) showed the presence of two compounds. The solution was subjected to flash chromatography on silica gel (elution with chloroform/hexanes mixture 1:9 ratio).

The first compound to elute was the trans isomer, *trans*-$C_{24}H_{14}(SiMe_3)_2$ (**4a**), a pale yellow solid (mp 201–202 °C): yield 0.56 g, 75% based on TBC; ^{1}H NMR ($CDCl_3$, δ) −0.13 (s, $SiMe_3$, 18 H), 4.55 (s, 2 H), 7.31 (dt, $J_1 = 1.1$ Hz, $J_2 = 7.41$ Hz, 2 H), 7.38–7.47 (m, 4 H), 7.63 (d, $J = 7.57$ Hz, 2 H), 8.01 (m, 2 H), 8.55 (d, 7.48 Hz, 2 H); ^{13}C NMR ($CDCl_3$, δ) −1.85 (CH_3 on Si) 43.88 (methylene C on C_p ring), 122.80, 123.66, 124.34, 124.79, 126.38, 128.23, 132.62, 141.65, 143.58, 147.21 (aromatic C). Anal. Calcd: C, 80.30%; H, 7.19%. Found: C, 80.30%; H, 7.06%.

The second compound to elute was the cis isomer, *cis*-$C_{24}H_{14}(SiMe_3)_2$ (**4b**) also a pale yellow solid (mp 180–181 °C) yield 0.14 g, 19% yield based on TBC; ^{1}H NMR ($CDCl_3$, δ) −0.24 (s, $SiMe_3$), 4.65 (s, 2 H), 7.34 (td, $J_1 = 1.1$ Hz, $J_2 = 7.40$ Hz, 2 H), 7.37–7.48 (m, 4 H), 7.63 (d, $J = 7.48$ Hz, 2 H), 8.02 (m, 2 H), 8.69 (d, $J = 7.9$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, δ) −1.91 (CH_3), 43.37 (methylene C on C_p ring), 123.41, 123.86, 124.47, 124.78, 126.73, 128.21, 132.90, 141.21, 142.83 (aromatic C). Anal. Calcd: C, 80.30%; H, 7.19%. Found: C, 80.47%; H, 7.15%.

Conversion of the Silylated Compounds 4a and 4b to the Diketone ($C_{24}H_{12}O_2$) 6. Compound **4a** or **4b** was left to stand in air at room temperature in the solid state for several weeks. The compounds changed color from yellow to orange-red during that period. Addition of a minimum amount of chloroform resulted in a dark orange-red solution. TLC showed the presence of at least two compounds. The solution was subjected to column chromatography on silica gel. Elution with a 1:9 mixture of chloroform/hexane gave the original compound **4a** or **4b**. Further elution with a 1:1 mixture of chloroform/hexane produced a red compound, the diketone **6**, in low yields (ca. 10%): IR (Nujol, KBr, cm^{-1}) 1701 m (C=O); ^{1}H NMR ($CDCl_3$, δ) 7.35 (dt, $J = 7.4$

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Table I. Summary of Crystallographic Data for Compounds 2a and 3

	2a	**3**
formula	$C_{36}H_{46}Li_2N_4$	$C_{24}H_{16}$
formula wt	548.7	304.4
space group	$P\bar{1}$	$P2_12_12_1$
crystal system	triclinic	orthorhombic
cell constants		
a, Å	12.379(3)	5.4604(9)
b, Å	16.043(3)	13.675(2)
c, Å	16.902(4)	20.552(3)
α, deg	95.42(2)	
β, deg	96.64(2)	
γ, deg	90.27(2)	
V, Å^3	3318.6(13)	1534.7(4)
Z	4	4
D(calcd) g cm^{-3}	1.034	1.317
absorp coeff mm^{-1}	0.057	0.069
F(000)	1056	640
temp, K	291	291
2θ range, deg	3.5 to 45.0	3.5 to 45.0
scan type	ω	ω
scan speed, deg/min in ω	3.00 to 14.65	2.00 to 14.65
scan range (ω), deg	1.20	1.20
no. of reflns collcd	7509	1214
no. of indep reflns	7024	1195
R_{int} %	1.75	0.00
no. of obsd reflns, $F > 6\sigma(F)$	1920	753
$R(F)$ %	10.53	3.69
$R_w(F)$ %	15.15	3.72
GOF	0.99	1.27

Table II. Summary of Crystallographic Data for Compounds for 4a, 4b, and 5

	4a	**4b**	**5**
formula	$C_{30}H_{32}Si_2$	$C_{30}H_{32}Si_2$	$C_{38}H_{46}Li_2O_2Si_2$
formula wt	448.7	448.7	1219.6
space group	$P2_1/a$	$P\bar{1}$	$P2_1/n$
cryst system	monoclinic	triclinic	monoclinic
cell constants			
a, Å	12.066(4)	8.3694(13)	13.663(3)
b, Å	18.129(4)	11.446(2)	14.509(3)
c, Å	13.253(4)	14.807(3)	18.494(4)
α, deg		110.058(13)	
β, deg	116.41(2)	96.961(13)	107.50(3)
γ, deg		99.810(13)	
V, Å^3	2596.6(13)	1288.0(4)	3496.5(13)
Z	4	2	4
D(calcd), g cm^{-3}	1.148	1.157	1.149
absorp. coeff, mm^{-1}	0.146	0.147	1.127
F(000)	960	480	1296
temp, K	291	298	293
2θ range, deg	3.5 to 45.0		3.0 to 45.0
scan type	ω	ω	2θ-θ
scan speed, deg/min	3.00 to 14.65 in ω	4.00 to 15.00 in ω	4.19 in 2θ
scan range, deg	1.40 (ω)	1.20 (ω)	2.00 (2θ) plus Kα-separation
no. of reflns collcd	7160	3583	4740
no. of indep reflns	3396	3313	4524
R_{int} %	2.35	1.87	0.99
no. of obsd reflns, $F > 6\sigma(F)$	1858	1951	3525 ($F > 4\sigma(F)$)
$R(F)$ %	5.37	5.01	5.83
$R_w(F)$ %	5.65	6.05	7.26
GOF	1.87	1.62	2.62

Hz, 2 H), 7.46–7.59 (m, 4 H), 7.71 (d, *J* = 7.2 Hz, 2 H), 8.02 (d, *J* = 7.6 Hz, 2 H), 8.97–9.03 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 123.59, 124.50, 124.54, 129.50, 129.75, 131.21, 133.20, 134.63, 134.47, 134.77, 139.99, 143.04, (aromatic C), 194.16 (C=O).

Synthesis of the Dimer {$Li_2(THF)_2[\eta^5{:}\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2$}$_2$ (5). Compound **4a** or **4b** (0.10 g, 0.22 mmol) was dissolved in THF (35 mL) and cooled to -78 °C. *n*-BuLi in hexanes (0.18 mL, 0.45 mmol, 2.5 M) was added to the solution dropwise via a syringe with stirring. The solution immediately turned red. The cold bath was removed and the mixture was allowed to warm to room temperature. Stirring was continued for 1 h after which the solvent was removed under vacuum to give an extremely air and moisture-sensitive orange solid: yield 0.13 g, 98%; ^{1}H NMR (C_6D_6, δ ppm) 0.78 (s, 36, H, $SiMe_3$), 0.70 (16 H, THF), 2.28 (16 H, THF), 7.03–7.08 (broad, 8 H), 7.23–7.28 (broad, 4 H), 8.10–8.20 (broad, 4 H), 8.34–8.50 (broad, 4 H).

X-ray Data Collection, Structure Determination and Refinement for [Li(TMEDA)]$_2$(η^5,η^5-$C_{24}H_{14}$) (2a). An orange-red crystal of approximate dimensions 0.10 × 0.30 × 0.30 mm selected from a crop of crystals obtained by slow recrystallization from ether was mounted in a glass capillary under argon and accurately aligned on the diffractometer. Lattice parameters were obtained by least-squares refinement of the indices and angles of 25 general reflections with 20.0° < 2θ < 30.0°. Crystal data, data collection and reduction, and structure refinement details are listed in Table I. Background measurements were made at the beginning and end of each scan, each equal to a quarter of the total scan time. Crystal stability was monitored by measuring three standard reflection every 100 measurements. Data were corrected for Lorentz and polarization factors and reduced to unscaled *F* values. Those 1920 data with $F > 6.0\sigma(F)$ were considered observed. Crystallographic calculations were performed by using the Nicolet SHELXTL PLUS (MicroVAX II) program set.[15] The positions of most of the carbon atoms for the molecule **2a** were determined by direct methods and positions of the remaining carbon atoms and other non-hydrogen atoms were determined by successive cycles of difference-Fourier synthesis and least squares refinement. The quantity minimized during full-matrix least-squares refinement was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2 F_o + 0.00243 F_c^2$. The hydrogen atoms were included by using a riding model with *d*(C–H) = 0.95 Å and the isotropic thermal parameters were fixed at 0.08 Å^2. The structure for this molecule could not be refined anisotropically because of the low data to parameter ratio. The carbon atoms of the TMEDA group were put in a model. The final agreement factors for the 1920 data with $F > 6.0\sigma(F)$ were R_F = 10.53% and R_{WF} = 15.15% and GOF = 0.99.

X-ray Data Collection, Structure Determination and Refinement for the Neutral Compound $C_{24}H_{16}$ (3). Crystals of $C_{24}H_{16}$ (**3**) were grown from a toluene solution. A yellow crystal measuring 0.50 × 0.50 × 0.50 mm was mounted on a glass fiber and aligned on the diffractometer. Final cell parameters were determined from 25 high angle reflections. Crystal stability was monitored by measuring three standard reflections every 50 measurements. Crystal data, data collection and reduction, and structure refinement details for **3** are also listed in Table I. Crystallographic calculations were performed by using the Nicolet SHELXTL PLUS (MicroVAX II) program set. A careful survey of the preliminary data set revealed the systematic absences (*h*00, *h* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1; 00*l*, *l* = 2*n* + 1) indicating the noncentrosymmetric orthorhombic space group $P2_12_12_1$. The noncentrosymmetric space group was later determined to be the correct choice by successful solution of the structure. Data were corrected for Lorentz and polarization factors and reduced to unscaled *F* values. The positions of all the carbon atoms were found by direct methods. The structure was refined via a series of difference-Fourier syntheses. All hydrogen atoms, except those on the cyclopentadienyl (Cp) rings and those on carbon C(6) and C(11), whose approximate positions could not be obtained from the electron density maps, were placed in calculated idealized positions (*d*(C–H) = 0.95 Å,[16] *B* = +1 Å^2 of the B_{iso} of the carbon to which the hydrogen atom is bonded). Finally, all non-hydrogen atoms were refined anisotropically. The final agreement for the 753 data ($F > 6.0\sigma(F)$ were R_F = 3.69% and R_{WF} = 3.72% and GOF = 1.27.

X-ray Data Collection, Structure Determination, and Refinement for *trans*-$C_{24}H_{14}(SiMe_3)_2$ (4a). Crystals of *trans*-$C_{24}H_{14}(SiMe_3)_2$ (**4a**) were grown from a hexane solution. A yellow crystal measuring 0.20 × 0.40 × 0.50 mm was mounted on a glass fiber and aligned on the diffractometer. Lattice parameters for a monoclinic cell were determined from 25 high angle reflections.

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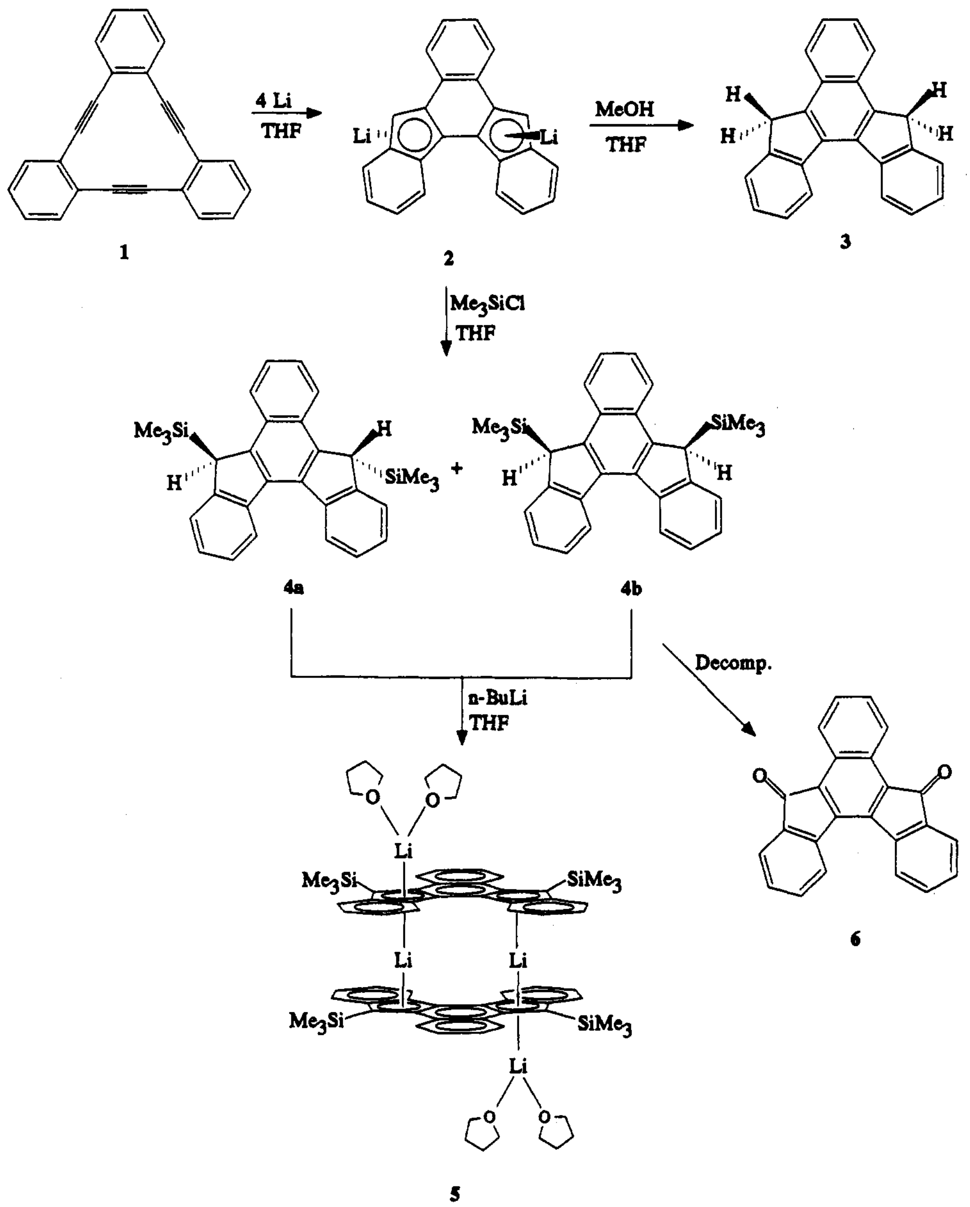
Scheme I



Intensity statistics suggested the space group $P2_1/a$ and was confirmed by successful solution and refinement of the structure. During data collection, the intensities of three standard reflections measured every 100 reflections showed no decay. Data were corrected for Lorentz and polarization factors. Crystal data, data collection and reduction, and structure refinement details for **4a** are listed in Table II. Crystallographic calculations were performed by using the Nicolet SHELXTL PLUS (MicroVAX II) program set. The positions of all non-hydrogen atoms were determined by direct methods and were refined anisotropically by use of full matrix least-squares methods. The B values of the carbon atoms of the methyl groups on the silicon atoms are relatively higher than those of the rest of the carbon atoms. The final agreement for the 1858 data ($F > 6.0\sigma(F)$) were $R_F = 5.37\%$ and $R_{WF} = 5.65\%$ and GOF = 1.87.

X-ray Data Collection, Structure Determination, and Refinement for *cis*-$C_{24}H_{14}(SiMe_3)_2$ (4b). Crystals of *cis*-$C_{24}H_{14}(SiMe_3)_2$ (**4b**) were grown from a hexane solution. A yellow crystal measuring 0.44 × 0.29 × 0.23 mm was mounted on a glass fiber and aligned on the diffractometer. Final lattice parameters of a triclinic cell are based on a least-squares analysis of 25 high angle reflections. The centrosymmetric space group $P\bar{1}$ was determined to be the correct choice by successful solution of the structure. Data were corrected for Lorentz and polarization factors. Crystal data, data collection and reduction, and structure refinement details for **4b** are also listed in Table II. Crystallographic calculations were performed by using the Nicolet SHELXTL PLUS (MicroVAX II) program set. The positions of all non-hydrogen atoms were determined by direct methods and were refined anisotropically by use of full matrix least-squares methods. The hydrogen atoms were included by using a riding model with $d(C-H) = 0.95$ Å and the isotropic thermal parameters was fixed at 0.08 Å^2. The final agreement for the 1951 data ($F > 6.0\sigma(F)$) were $R_F = 5.01\%$ and $R_{WF} = 6.05\%$ and GOF = 1.62.

X-ray Data Collection, Structure Determination, and Refinement for $\{Li_2(THF)_2[\eta^5:\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2\}_2$ (5). An orange crystal of approximate dimensions 0.50 × 0.30 × 0.60 mm selected from a crop of crystals obtained from a saturated solution of **5** in benzene was mounted in a glass capillary under argon and accurately aligned on a Syntex $P2_1$ diffractometer. Final unit-cell parameters were obtained by least-squares refinement of 25 well-centered high angle reflections. Crystal data, data collection and reduction, and structure refinement details are listed in Table II. Background measurements were made at the beginning and end of scan, each equal to a half of the total scan time. Crystal stability was monitored by measuring three standard reflections every 100 measurements. Data were corrected for Lorentz and polarization factors and reduced to unscaled F values. Those 3525 data with $F > 4.0\sigma(F)$ were considered observed. Crystallographic calculations were performed by using the Siemens SHELXTL PLUS (PC Version)[17] program library. The quantity minimized during full-matrix least-squares refinement was $\sum w(F_o$

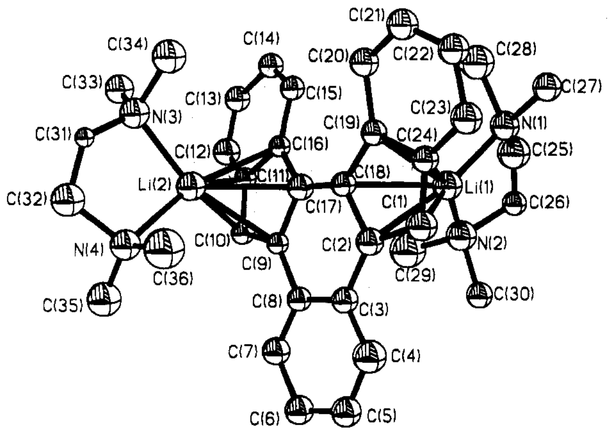


Figure 1. Thermal ellipsoid labeling diagram of **2a**. The thermal ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity.

$- F_c)^2$ were $w^{-1} = \sigma^2 F_o + 0.004 F_c^2$. All non-hydrogen atoms were located with little difficulty by direct methods except Li2 (bound to two Cp rings) which was found by increasing the numbers in difference Fourier map to 50. All non-hydrogen atoms were then refined anisotropically leading to a half molecule. Hydrogen atoms were included using a riding model with $d(\mathrm{C-H}) = 0.95$ Å and the isotropic thermal parameters were fixed at 0.08 Å^2. The final agreement factors for the 3525 data with $F > 4.0\sigma(F)$ were $R_F = 5.83\%$ and $R_{WF} = 7.26\%$ and GOF = 2.67.

Results and Discussion

According to the Hückel rule cyclic conjugated hydrocarbons with $4n\pi$ electrons are predicted to be antiaromatic. The addition of two electrons to these compounds should result in an aromatic dianion. The reduction of TBC with alkali metals has been studied previously by us[4f] and others.[6b] In all these cases the alkali metal was used to generate the corresponding aromatic dianion. Thus the reaction of TBC with 2 mol equiv of lithium metal gave the blue-purple dianion accompanied by a small amount of the monoanion. The IR spectrum of TBC dianion is very characteristic with a C≡C stretch at 2090 cm^{-1} with a shoulder due to contamination with the monoanion. The observation of one C≡C stretch is consistent with a delocalized dianion. An attempt to take an NMR spectrum of the dianion was unsuccessful due to the presence of the paramagnetic monoanion. When this dianion is exposed to oxygen it is oxidized back to TBC implying that this process is reversible.

The reaction of TBC (Scheme I) with 4 mol equiv of lithium in THF yields an extremely air- and moisture-sensitive dianion **2**. The formation of the dianion **2** (Scheme II) involves bond formation between carbons 1 and 3 and between 4 and 6, protonation at carbons 2 and 5, and conversion of the triple bonds of TBC into one tetrasubstituted and two trisubstituted double bonds. These new bonds are arranged in a fused ring system consisting of two five membered-rings and a six-membered ring. The Cp rings in **2** are like fulvalene moieties, but unlike the nonrigid fulvalene system in which the Cp rings are connected only by a carbon–carbon single bond and may be rotated relative to each other, the Cp rings in **2** are held in the same plane and cannot be rotated because of the central aromatic ring.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic and Displacement Coefficients (Å^2 × 10^3) for Compound 2a

atom	*x*	*y*	*z*	*U*(eq)[a]
C(1)	8935(18)	4569(12)	2997(12)	68(6)
C(2)	7947(17)	4864(11)	3254(12)	58(6)
C(3)	7624(18)	5125(11)	4031(12)	54(6)
C(4)	8354(21)	5111(13)	4705(14)	85(7)
C(5)	8060(18)	5355(11)	5461(12)	69(6)
C(6)	7008(17)	5620(12)	5565(12)	68(6)
C(7)	6255(17)	5628(11)	4839(11)	65(6)
C(8)	6590(17)	5376(11)	4098(11)	48(5)
C(9)	5798(15)	5342(10)	3394(10)	40(5)
C(10)	4633(16)	5423(10)	3316(11)	50(5)
C(11)	4171(17)	5161(10)	2557(11)	45(5)
C(12)	3122(19)	5042(12)	2199(12)	71(7)
C(13)	2877(17)	4720(11)	1428(12)	64(6)
C(14)	3729(16)	4469(11)	951(12)	59(6)
C(15)	4791(16)	4580(10)	1282(10)	52(5)
C(16)	5055(15)	4935(10)	2073(10)	40(5)
C(17)	6047(18)	5052(12)	2612(12)	59(6)
C(18)	7202(17)	4892(10)	2531(11)	48(5)
C(19)	7815(15)	4691(10)	1852(11)	48(5)
C(20)	7582(17)	4695(11)	947(11)	61(6)
C(21)	8432(18)	4529(12)	529(13)	68(6)
C(22)	9450(18)	4323(11)	852(12)	63(6)
C(23)	9712(17)	4291(11)	1661(12)	65(6)
C(24)	8913(17)	4483(11)	2166(11)	50(5)
C(25)	7493(37)	1764(22)	2407(25)	49(12)
C(25)	6809(52)	1862(31)	2222(33)	98(18)
C(26)	6983(45)	1959(25)	2946(27)	54(15)
C(26)	6341(42)	2038(24)	2913(24)	52(14)
C(27)	8651(39)	2093(26)	747(28)	74(15)
C(27)	8403(38)	2256(26)	1312(28)	64(14)
C(28)	7037(47)	2618(31)	967(32)	101(18)
C(28)	6519(38)	2513(24)	1301(25)	58(12)
C(29)	5829(24)	3216(16)	3626(16)	122(10)
C(30)	7342(42)	2795(25)	4183(26)	60(14)
C(30)	7891(48)	2712(30)	4049(30)	77(19)
C(31)	5942(53)	7895(34)	1923(34)	102(24)
C(31)	5369(36)	7898(21)	1869(20)	28(11)
C(32)	5334(19)	8180(14)	2671(14)	87(7)
C(33)	3827(43)	6901(32)	1265(29)	71(18)
C(33)	3801(42)	7270(32)	1465(30)	71(18)
C(34)	5170(20)	7751(14)	4041(14)	95(8)
C(36)	6968(66)	7419(48)	3247(46)	118(35)
C(36)	6853(55)	7607(37)	3514(36)	70(22)
Li(1)	7710(31)	3509(21)	3589(21)	71(11)
Li(2)	5194(32)	6382(21)	2577(22)	72(11)
N(1)	7544(15)	2449(10)	1820(10)	70(5)
N(2)	6866(16)	2834(11)	3369(11)	82(6)
N(3)	4972(15)	7059(10)	1582(10)	72(5)
N(4)	5696(16)	7548(10)	3279(10)	73(5)

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

When the reduction of TBC is carried out in THF in the presence of TMEDA, the reaction takes approximately 6 h, and a TMEDA adduct of **2**, in which the lithium cations are chelated by TMEDA molecules, is isolated in almost quantitative yield. When TMEDA is not used, the cyclization reaction is much slower taking approximately 20 h and the same cyclized product is isolated in approximately the same yield with two THF molecules being coordinated to each of the lithium atoms instead of TMEDA. This activating effect of TMEDA on metalation reactions of organolithium compounds and alkynes is well established.[4f,18] The ^{1}H NMR spectrum of **2a** shows that all protons of the ligand are found downfield because of ring current effects of the aromatic rings. The protons attached to the Cp rings are expected to be deshielded and are assigned to the downfield resonance at 7.31 ppm. This assignment is also based on the results from the reaction of TBC with lithium in THF-d_8. The resonances for the Cp protons are absent for the deuterated product resulting from this experiment. The compound **2** is soluble

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(17) Nicolet Instrument Corp., Madison, WI, 1988.

(18) Mulvaney, J. E.; Newton, D. J. *J. Org. Chem.* **1969**, *34*, 1936.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Compound 2a[a]

Distances			
Li(1)–N(1)	2.035(35)	Li(2)–N(3)	2.080(41)
Li(1)–N(2)	2.141(43)	Li(2)–N(4)	2.166(37)
Li(1)–Cp(c1)	1.995	Li(2)–Cp(c2)	1.993
Li(1)–C(1)	2.276(40)	Li(2)–C(9)	2.335(40)
Li(1)–C(2)	2.351(37)	Li(2)–C(10)	2.228(42)
Li(1)–C(18)	2.317(38)	Li(2)–C(11)	2.322(40)
Li(1)–C(19)	2.377(40)	Li(2)–C(16)	2.395(37)
Li(1)–C(24)	2.368(42)	Li(2)–C(17)	2.387(40)
N(1)–C(25)	1.558(54)	N(3)–C(31)	1.626(37)
N(1)–C(27)	1.480(52)	N(3)–C(33)	1.477(54)
N(1)–C(28)	1.508(51)	N(3)–C(34)	1.533(29)
N(2)–C(26)	1.528(42)	N(4)–C(32)	1.544(29)
N(2)–C(29)	1.516(35)	N(4)–C(35)	1.518(31)
N(2)–C(30)	1.538(50)	N(4)–C(36)	1.442(69)
Angles			
N(1)–Li(1)–N(2)	86.3(15)	N(3)–Li(2)–N(4)	87.5(14)
Cp(c1)–Li(1)–N(1)	137.3	Cp(c2)–Li(2)–N(3)	136.9
Cp(c1)–Li(1)–N(2)	135.4	Cp(c2)–Li(2)–N(4)	135.3

[a] Cp(c1) and Cp(c2) are the centroids of the C(1),C(2),C(18),C(19),C(24) ring and the C(9),C(10),C(11),C(16),C(17) ring, respectively.

in basic solvents and is insoluble in nonpolar solvents such as hexane. It is however sparingly soluble in benzene.

The compound **2a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per asymmetric unit, with these being enantiomorphs. A thermal ellipsoid labeling diagram for one enantiomer is shown in Figure 1. Table III lists the atomic coordinates and equivalent isotropic displacement coefficients for non-hydrogen atoms of one of the enantiomers. Selected bond distances and bond angles are listed in Table IV.

The structure of **2a** shows that the two helicene enantiomers cocrystallize with each of the Cp rings π-bound to a lithium atom, which in turn is chelated by a TMEDA molecule. The two lithium atoms are on opposite sides of the molecule. The Li–C distances tend to be fairly constant throughout the Cp rings with an average value of 2.336 (17) Å. The Li–N distances are in the range of 2.035 (35) to 2.166 (37) Å with an average value of 2.106 (30) Å. The average Li–Cp(centroid) distance is 1.994 (1) Å and the Cp(centroid)–Cp(centroid) distance is 3.880 Å. These values are comparable to experimental[19] and theoretical[20] parameters of similar systems. The two hydrogen atoms on the Cp groups were observable on electron density maps, however they were calculated and put in idealized positions. The main feature, however, is the helical character of the structure (Figure 2). The Cp and benzene rings are strictly planar, whereas the substituted fulvalene ligand as a whole is slightly bent, the angle of tilt or the dihedral angle between the two benzene rings being 25.6°. The distance between the two hydrogen atoms facing each other (H20A, H25A) is 2.001 Å.

The mechanism of the lithium-induced cyclization reaction is not fully understood and is still under investigation. A possible mechanism for cyclization reaction is that the initial stage involves the generation of the diradical dianion **1b** (Scheme II) as a result of the reduction of TBC (**1**) by 2 mol equiv of lithium metal. Our data are consistent with a delocalized dianion **1b**, though we also draw a localized version to make further reaction easier to visualize. The diradical dianion **1b** could then undergo internal cyclization resulting in bond formation between carbons 1 and 3 and between carbons 4 and 6 to form **1c**. The dianion **1c** could be further reduced by another 2 mol equiv of lithium and then immediately protonated at carbons 2 and 5 to form **2**. The solvent THF would act as a weak Brönsted acid and would serve as the source of the protons. We have established that THF is the source of the hydrogen atoms of **2** by conducting the reaction in deuterated THF. The resulting product **2(D)** contained two deuterium atoms as shown by ^{1}H NMR analysis.

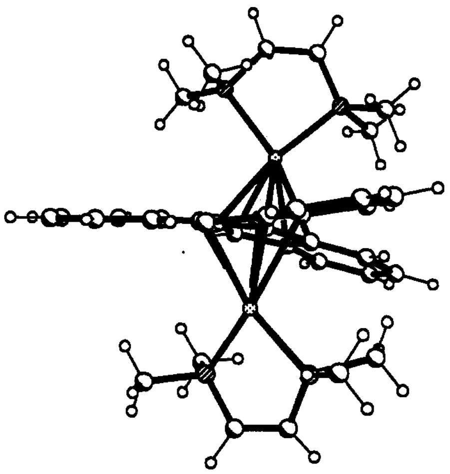
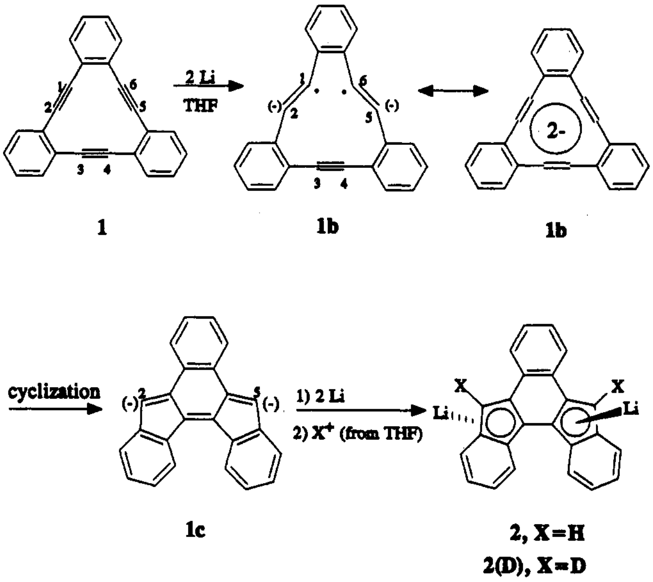


Figure 2. Thermal ellipsoid diagram of **2a** showing the dihedral angle between the two benzene rings fused to the cyclopentadienyl rings.

Scheme II



This mechanism is consistent with the reduction chemistry of simple alkynes by alkali metals. Perhaps the most studied reaction in this class is the reduction of diphenylacetylene with alkali metals.[21] At −78 °C lithium metal reacts with diphenylacetylene in THF to give first the monomer radical anion which may dimerize to give a dianion or may react further with lithium to form a monomeric dianion. The dimerization of the monomer

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(19) (a) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282. (b) Jutzi, P.; Schluter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959. (c) Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1984**, *262*, 271. (d) Jutzi, P.; Leffers, W.; Pohl, S.; Saak, N. *Chem. Ber.* **1989**, *122*, 1449. (e) Jutzi, P.; Schluter, E.; Kruger, C.; Pohl, S. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 994. (f) Rhine, W. E.; Stucky, G. *J. Am. Chem. Soc.* **1975**, *97*, 737. (g) Brooks, J. J.; Rhine, W. E.; Stucky, G. *J. Am. Chem. Soc.* **1972**, *94*, 7339.

(20) (a) Alexandratos, S.; Streitwieser, A. C., Jr.; Schaefer, H. F., III, *J. Am. Chem. Soc.* **1976**, *98*, 7959. (b) Bloom, R.; Faegri, K., Jr.; Midtgaard, T. *J. Am. Chem. Soc.* **1991**, *113*, 3230.

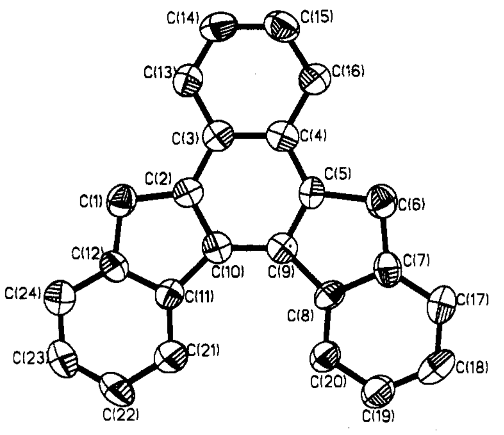

Figure 3. Thermal ellipsoid labeling diagram of **3**. The thermal ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic and Displacement Coefficients ($Å^2 \times 10^3$) for 3

atom	*x*	*y*	*z*	*U*(eq)[a]
C(1)	3275(11)	3540(4)	4941(3)	50(2)
C(2)	1593(11)	3753(4)	5498(3)	40(2)
C(3)	1705(10)	3294(4)	6121(3)	41(2)
C(4)	−25(11)	3595(4)	6596(3)	44(2)
C(5)	−1671(11)	4341(4)	6427(2)	42(2)
C(6)	−3560(12)	4776(4)	6889(3)	53(2)
C(7)	−4807(11)	5519(4)	6464(3)	47(2)
C(8)	−3809(10)	5501(3)	5840(3)	43(2)
C(9)	−1800(11)	4781(3)	5818(3)	41(2)
C(10)	−32(11)	4486(4)	5338(2)	41(2)
C(11)	561(11)	4812(4)	4667(3)	44(2)
C(12)	2491(11)	4248(4)	4437(3)	43(2)
C(13)	3418(11)	2564(4)	6286(3)	54(2)
C(14)	3508(12)	2166(4)	6897(3)	58(2)
C(15)	1806(12)	2446(5)	7360(3)	58(2)
C(16)	47(12)	3137(4)	7229(3)	49(2)
C(17)	−6760(12)	6141(4)	6616(3)	63(2)
C(19)	−6748(12)	6709(4)	5513(3)	59(2)
C(20)	−4823(11)	6093(4)	5357(3)	49(2)
C(21)	−312(13)	5564(5)	4274(3)	69(3)
C(22)	718(15)	5719(5)	3668(3)	78(3)
C(23)	2596(13)	5128(5)	3450(3)	65(3)
C(24)	3559(12)	4397(4)	3827(3)	57(2)

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

radical anion results in C–C bond formation analogous to the C–C bond formations we propose for the conversion of **1b** to **1c**. THF is observed to be a source of protons in the reaction of diphenylacetylene with lithium metal once the reaction mixture is allowed to warm above −78 °C. As discussed above we have shown that THF is the source of protons in the conversion of **1** to **2**.

Protonation of compound **2** by degassed methanol results in the corresponding protonated fulvalene derivative, the neutral species compound **3**, which is isolated in 60% yield (Scheme I). Protonation of **2** with water instead of methanol also gives **3** but in a much lower yield. The neutral species is a light yellow solid and is soluble in most common organic solvents. The ^{1}H NMR spectrum of this compound is similar to that of **2** with the exception of the methylene protons and the decrease in the deshielding effect. Isolation of small quantities of **3** from a Lindlar hydrogenation of **1** has been reported by Staab and coworkers.[22] This compound is insoluble in hexane but soluble in more polar organic media.

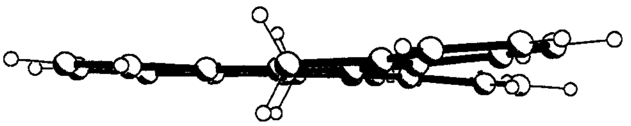

Figure 4. Thermal ellipsoid diagram of the neutral compound **3** showing the dihedral angle between benzene groups.

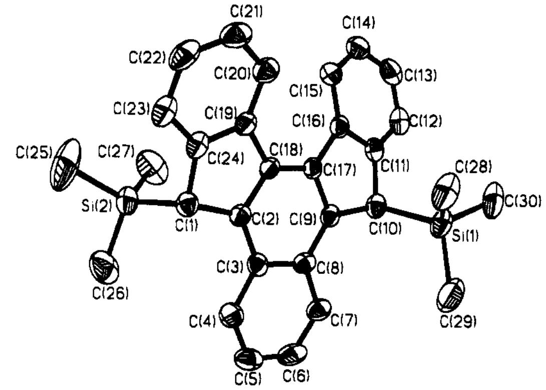

Figure 5. Thermal ellipsoid labeling diagram of **4a**. The thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule per asymmetric unit. The final thermal ellipsoid labeling drawing for this compound is shown in Figure 3. Final positional parameters are listed in Table V. Although the helical strain of compound **3** is less dramatic when compared with that of compound **2a**, the dihedral angle of 10.4° between the two benzene groups indicates that the helical character of the ligand is still present (Figure 4). It is clear from the structure that the two hydrogen atoms facing each other (H20A and H21A) are bent away from one another and from the planes of the benzene rings to which they are attached. The distance separating H20A and H21A is 1.580 Å.

Treatment of both the THF and TMEDA adducts of the dianion **2** with 2 equiv of trimethylchlorosilane produced two isomers of the bis(trimethylsilyl) derivative of **2** (Scheme I). The pure isomers were isolated using flash chromatography on silica gel. One of the isomers, the trans isomer **4a** has the two trimethylsilyl groups on opposite sides of the molecule relative to the least-squares plane of the molecule. The other is the cis isomer **4b** with the trimethylsilyl groups on the same side of the molecule relative to the least-squares plane of the molecule. The ^{1}H and ^{13}C NMR spectra of the two isomers are very similar with minimal differences in their chemical shifts. The two isomers are soluble in virtually all common organic solvents.

Compound **4a** crystallizes in the monoclinic space group $P2_1/a$ with one molecule in the asymmetric unit. A thermal ellipsoid labeling diagram of this compound is listed in Figure 5 and a list of atomic coordinates and equivalent isotropic displacement coefficients for carbon and silicon atoms is listed in Table VI. Selected bond distances and angles are listed in Table VII. The carbon atoms of the methyl groups are slightly disordered with higher thermal parameters.

Comparison between compound **3** (Figure 4) and compound **4a** (Figure 6a) shows a dramatic increase in the

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(21) (a) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268. (b) Levin, G.; Szwarc, M. *J. Chem. Soc. Chem. Comm.* **1971**, 1029. (c) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *Trans. Faraday Soc.* **1971**, 768. (d) Dadley, D.; Evans, A. G. *J. Chem. Soc. B*, **1967**, 418. (e) Dadley, D.; Evans, A. G. *J. Chem. Soc. B*, **1968**, 107. (f) Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1184.

(22) Staab, H. A.; Graf, F.; Doerner, K.; Nissan, A. *Chem. Ber.* **1971**, *104*, 1159 and references cited therein.

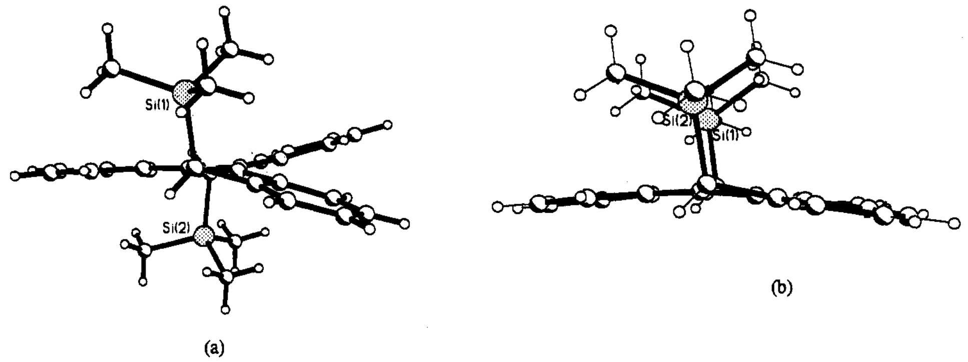

Figure 6. (a) Thermal ellipsoid diagram of **4a** showing the dihedral angle between the two benzene rings fused to the cyclopentadienyl rings. (b) Thermal ellipsoid diagram of **4b** showing no helical character.

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic and Displacement Coefficients (Å² × 10³) for 4a

atom	*x*	*y*	*z*	*U*(eq)[a]
Si(1)	−4231(2)	−1573(1)	2569(2)	73(1)
Si(2)	365(2)	1675(1)	2862(2)	66(1)
C(1)	556(5)	682(3)	3443(5)	54(3)
C(2)	−686(6)	362(3)	3213(5)	48(3)
C(3)	−1409(6)	520(3)	3786(6)	51(3)
C(4)	−1004(7)	960(3)	4759(6)	63(4)
C(5)	−1744(8)	1115(4)	5265(6)	73(4)
C(6)	−2936(8)	822(4)	4820(7)	73(5)
C(7)	−3362(6)	368(4)	3918(6)	62(4)
C(8)	−2603(6)	186(3)	3374(6)	50(4)
C(9)	−3025(5)	−263(3)	2410(5)	49(3)
C(10)	−4240(6)	−669(3)	1813(6)	57(4)
C(11)	−4256(7)	−861(3)	705(6)	55(4)
C(12)	−5239(7)	−1125(3)	−287(8)	69(4)
C(13)	−5041(8)	−1244(4)	−1218(7)	77(4)
C(14)	−3910(8)	−1104(4)	−1195(7)	71(4)
C(15)	−2950(7)	−837(3)	−234(6)	61(4)
C(16)	−3104(6)	−722(3)	739(6)	52(4)
C(17)	−2316(6)	−379(3)	1832(5)	46(3)
C(18)	−1084(6)	−109(3)	2306(5)	46(3)
C(19)	−34(6)	−250(3)	2046(6)	50(3)
C(20)	146(6)	−781(4)	375(6)	65(4)
C(21)	1304(7)	−842(4)	1393(6)	77(4)
C(22)	2249(7)	−377(5)	2054(7)	80(5)
C(23)	2100(6)	136(4)	2738(6)	69(4)
C(24)	943(6)	197(3)	2740(6)	54(3)
C(25)	1743(7)	1944(4)	2708(7)	164(5)
C(26)	193(8)	2349(3)	3808(6)	111(5)
C(27)	−1005(8)	1708(4)	1513(6)	121(5)
C(28)	−2811(6)	−2073(4)	2810(6)	103(5)
C(29)	−4282(8)	−1420(4)	3919(7)	119(6)
C(30)	−5597(6)	−2129(4)	1693(6)	110(5)

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

Table VII. Selected Bond Distances (Å) for Compounds 4a and 4b

4a		**4b**	
Si(1)–C(10)	1.919(7)	Si(1)–C(7)	1.912(4)
Si(1)–C(28)	1.836(8)	Si(1)–C(25)	1.857(5)
Si(1)–C(29)	1.839(10)	Si(1)–C(26)	1.861(7)
Si(1)–C(30)	1.838(7)	Si(1)–C(27)	1.849(6)
Si(2)–C(1)	1.931(6)	Si(2)–C(18)	1.926(5)
Si(2)–C(25)	1.829(10)	Si(2)–C(28)	1.841(5)
Si(2)–C(26)	1.829(8)	Si(2)–C(29)	1.850(7)
Si(2)–C(27)	1.817(6)	Si(2)–C(30)	1.837(7)

dihedral angle between the two benzene groups. The angle of tilt in compound **4a** is 33.1°, about 12.7° larger than that in compound **3**. The calculated distance between the two hydrogen atoms facing each other is 2.006 Å. The two methylene carbon atoms on the Cp groups are projected out of the planes of the corresponding rings and pointing towards the trimethylsilyl groups. The silicon–carbon distance is longer when the carbon atom is a methylene carbon on the Cp group than when it is a methyl carbon. The average Si–C (Cp) distance is 1.925 (6) Å while the Si–C distances range from 1.817 (6) to 1.839 (10) with an average value of 1.831 (3) Å.

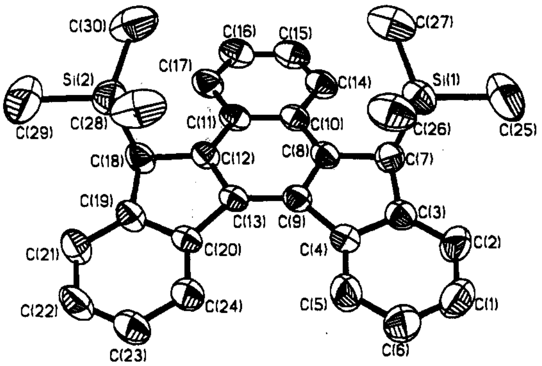

Figure 7. Thermal ellipsoid labeling diagram of **4b**. The thermal ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity.

Compound **4b** crystallizes in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit. A thermal ellipsoid labelling diagram of this compound is shown in Figure 7. Table VIII lists the final positional parameters and equivalent isotropic displacement coefficients for carbon and silicon atoms. Selected bond distances and angles are also listed in Table VII. Compound **4a** shows no helical character and the distance between the two hydrogen atoms facing each other is 1.706 Å.

Compounds **4a** and **4b** are quite stable in air for days and as described above can be separated from each other by chromatography in air. Over extended periods of time (several weeks) they decompose to a red compound, the diketone **6**, which is easily separated by chromatography. Staab and co-workers have previously[22] obtained this compound from an oxidation of **3** using potassium dichromate. Repeated recrystallization of **6** from benzene produced red needles that were not suitable for X-ray analysis. IR and NMR data are consistent with the structure of the diketone.

On the basis of the interesting structure of **2a** and our interest in the synthesis and structural characterization of main group and transition metal complexes of substituted fulvalene ring systems, we explored the dimetalation of **4a** and **4b** with 2 equiv of *n*-BuLi. In THF this reaction leads to the formation of the novel tetrallithium compound $\{Li_2(THF)_2[\eta^5:\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2\}_2$ (**5**) in almost quantitative yields. The presence of the trimethylsilyl groups on this ligand increases its solubility to a point where it is slightly soluble in hexane.

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic and Displacement Coefficients (Å$^2 \times 10^3$) for 4b

atom	*x*	*y*	*z*	*U*(eq)^a
Si(1)	2838(2)	2265(1)	1501(1)	59(1)
Si(2)	–3537(2)	8414(1)	3347(1)	63(1)
C(1)	1954(8)	2851(5)	394(4)	80(3)
C(2)	1046(6)	2498(6)	1000(4)	62(3)
C(3)	407(6)	3390(4)	1654(3)	48(2)
C(4)	680(6)	4660(4)	1703(3)	50(2)
C(5)	1567(8)	4967(5)	1057(4)	84(3)
C(6)	2212(8)	4078(5)	426(5)	99(4)
C(7)	–741(6)	3215(4)	2316(3)	51(2)
C(8)	–830(6)	4545(4)	2895(3)	46(2)
C(9)	–128(5)	5386(4)	2479(3)	42(2)
C(10)	–1516(6)	4950(4)	3746(3)	45(2)
C(11)	–1668(6)	6240(4)	4133(3)	46(2)
C(12)	–1112(6)	7056(4)	3642(3)	43(2)
C(13)	–272(5)	6687(4)	2875(3)	41(2)
C(14)	–1967(6)	4148(4)	4270(4)	56(2)
C(15)	–2546(6)	4603(5)	5108(4)	63(3)
C(16)	–2732(6)	5854(5)	5482(3)	62(3)
C(17)	–2298(6)	6656(4)	4997(3)	56(2)
C(18)	–1322(6)	8393(4)	3864(3)	51(2)
C(19)	–195(6)	8862(4)	3283(3)	48(2)
C(20)	338(6)	7836(4)	2654(3)	43(2)
C(21)	265(6)	10090(4)	3282(3)	58(2)
C(22)	1252(7)	10284(5)	2643(4)	66(3)
C(23)	1756(7)	9295(5)	2018(4)	79(3)
C(24)	1287(7)	8068(5)	2009(4)	70(3)
C(25)	–2698(8)	578(5)	912(5)	100(3)
C(26)	–3283(7)	2965(5)	560(4)	79(3)
C(27)	–4565(7)	2306(5)	2172(4)	88(3)
C(28)	–3900(8)	7674(6)	2000(4)	96(4)
C(29)	–3720(9)	10096(6)	3748(6)	125(5)
C(30)	–5124(7)	7515(6)	3764(5)	96(4)

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

Table IX. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic and Displacement Coefficients (Å$^2 \times 10^3$) for Non-Hydrogen Atoms of 5

atom	*x*	*y*	*z*	*U*(eq)^a
Li(1)	2946(5)	7966(5)	568(4)	64(3)
Li(2)	4315(5)	11420(5)	–166(4)	55(3)
Si(1)	5220(1)	6879(1)	1630(1)	47(1)
Si(2)	2806(1)	12277(1)	1098(1)	59(1)
O(1)	2171(2)	8723(3)	1046(2)	86(2)
O(2)	1972(3)	6980(2)	293(2)	85(2)
C(1)	4746(3)	7743(2)	860(2)	40(1)
C(2)	4532(3)	8727(2)	845(2)	36(1)
C(3)	4932(3)	9409(2)	1442(2)	38(1)
C(4)	5768(3)	9214(3)	2078(2)	49(1)
C(5)	6159(3)	9856(3)	2632(2)	58(2)
C(6)	5752(3)	10733(3)	2559(2)	56(2)
C(7)	4980(3)	10959(3)	1916(2)	50(2)
C(8)	4530(3)	10311(2)	1347(2)	38(1)
C(9)	3735(3)	10555(2)	660(2)	36(1)
C(10)	3138(3)	11399(2)	477(2)	41(1)
C(11)	2547(3)	11294(2)	–300(2)	41(1)
C(12)	1848(3)	11898(3)	–808(2)	53(2)
C(13)	1341(3)	11633(3)	–1519(2)	61(2)
C(14)	1483(3)	10770(3)	–1777(2)	68(2)
C(15)	2174(3)	10175(3)	–1331(2)	60(2)
C(16)	2746(3)	10410(2)	–584(2)	39(1)
C(17)	3496(3)	9952(2)	20(2)	35(1)
C(18)	3926(2)	9022(2)	114(2)	34(1)
C(19)	3808(3)	8226(2)	–378(2)	37(1)
C(20)	3368(3)	8078(3)	–1163(2)	55(2)
C(21)	3396(3)	7229(3)	–1471(2)	64(2)
C(22)	3870(3)	6487(3)	–1027(3)	61(2)
C(23)	4334(3)	6589(3)	–272(2)	53(2)
C(24)	4306(3)	7455(2)	81(2)	40(2)
C(25)	6546(3)	6523(3)	1716(3)	79(2)
C(26)	4424(4)	5812(3)	1422(3)	92(2)
C(27)	5134(5)	7232(3)	2580(3)	96(3)
C(28)	3539(5)	13360(3)	1185(4)	119(4)
C(29)	1438(4)	12608(4)	759(3)	105(3)
C(30)	2925(5)	11853(4)	2079(3)	101(3)
C(31)	1506(5)	6574(5)	798(3)	114(3)
C(32)	1237(7)	5649(6)	545(5)	175(5)
C(33)	1388(8)	5603(6)	–193(6)	198(7)
C(34)	1621(4)	6482(5)	–386(3)	111(3)
C(35)	1286(5)	9190(5)	572(4)	134(4)
C(36)	827(6)	9710(5)	1043(5)	143(5)
C(37)	1396(6)	9482(5)	1811(4)	127(4)
C(38)	2397(4)	9131(4)	1770(3)	93(3)

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

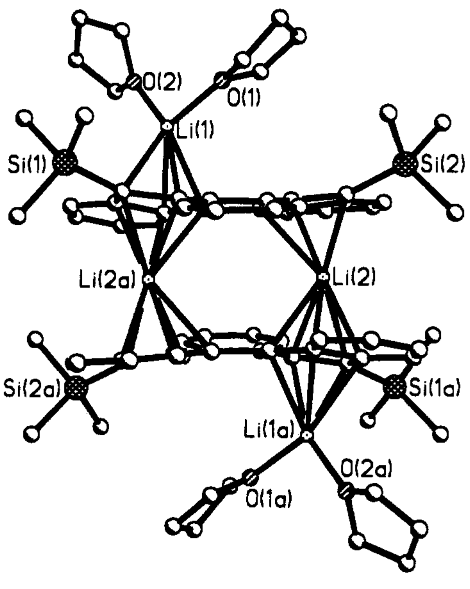

Figure 8. Molecular structure of $\{Li_2(THF)_2[\eta^5{:}\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2\}_2$ (**5**). Hydrogen atoms are excluded for clarity.

Compound **5** is a dimer of $Li_2(THF)_2[\eta^5{:}\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2$ and crystallizes in the monoclinic space group $P2_1/n$ with a = 13.663 (3) Å, b = 14.509 (3) Å, c = 18.494 (4) Å, β = 107.50 (3)°, V = 3496.5 (13) Å^3 and Z = 4. A thermal ellipsoid drawing of the molecular structure of **5** is shown in Figure 8. Positional parameters and equivalent isotropic thermal parameters for **5** are listed in Table IX and selected bond distances and angles are listed in Table X. The dimer **5** crystallizes in a head-to-tail rather than head-to-head fashion. There are two modes of coordination for the lithium atoms. In the first mode, one lithium atom is coordinated in a $\eta^5{:}\eta^5$ fashion to two Cp rings of the substituted fulvalene ligands resulting in a sandwich system. Only one other structure showing a lithium atom sandwiched between two aromatic rings (benzene rings) has been reported.[23] Previous to our earlier report,[24] no X-ray crystal structure of an organolithium compound having two lithium atoms bound in a $\eta^5{:}\eta^5$ fashion to Cp rings forming a sandwich system had been reported. Lithium atoms sandwiched between Cp rings have been observed only in solution and exist in equilibrium with their monomers.[25] In the second mode, a lithium atom is η^5-bonded to a Cp ring and to two THF molecules. These two modes combined lead to an inverse sandwich in which two lithium atoms are π-bonded to opposite sides of one Cp ring. Examples of inverse sandwich structures with two lithium atoms coordinating to opposite sides of the same π-system have been reported.[26] One interesting feature of this compound is that the lithium atoms, two

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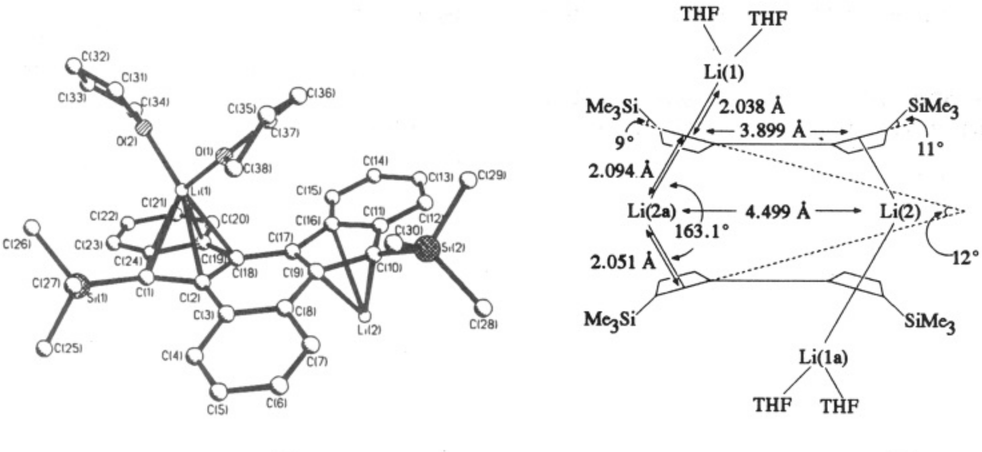

(a) (b)

Figure 9. (a) Thermal ellipsoid labeling diagram of the monomeric unit of **5**. (b) A pictorial representation of selected bonding parameters of **5**.

Table X. Selected Bond Distances (Å) and Angles (deg) for Compound 5[a]

	Distances		
Li(1)–O(1)	1.916(9)	Li(2)–C(2A)	2.300(9)
Li(1)–O(2)	1.915(8)	Li(2)–C(18A)	2.460(8)
Li(1)–C(1)	2.377(8)	Li(2)–C(19A)	2.510(7)
Li(1)–C(2)	2.348(8)	Li(2)–C(24A)	2.461(8)
Li(1)–C(18)	2.351(9)	Si(1)–C(1)	1.861(3)
Li(1)–C(19)	2.414(10)	Si(1)–C(25)	1.845(5)
Li(1)–C(24)	2.413(9)	Si(1)–C(26)	1.864(5)
Li(2)–C(9)	2.294(8)	Si(1)–C(27)	1.867(5)
Li(2)–C(10)	2.271(9)	Si(2)–C(10)	1.859(4)
Li(2)–C(11)	2.361(8)	Si(2)–C(28)	1.844(6)
Li(2)–C(16)	2.519(7)	Si(2)–C(29)	1.848(5)
Li(2)–C(17)	2.478(8)	Si(2)–C(30)	1.876(5)
Li(2)–C(1A)	2.399(9)	Li(1)–Cp(c1)	2.038
Li(2a)–Cp(c1)	2.094	Li(2)–Cp(c1A)	2.051
	Angles		
O(1)–Li(1)–O(2)	96.6(4)	Si(1)–C(1)–Li(2a)	119.5(3)
Li(1)–Cp(c1)–Li(2a)	173.0	Si(1)–C(1)–Li(1)	111.3(3)
O(1)–Li(1)–Cp(c1)	130.5	Si(2)–C(10)–Li(2)	131.0(2)
O(2)–Li(1)–Cp(c1)	132.2	Cp(c1)–Li(2a)–Cp(c2A)	163.1

[a] Cp(c1) and Cp(c2) are the centroids of the C(1),C(2),C(18),C(19),C(24) ring and the C(9),C(10),C(11),C(16),C(17) ring, respectively.

Cp rings, and THF are in a quasilinear coordination forming a Cp–Li–Cp–Li–2THF "*supersandwich*" system, a structure which was first predicted by MO calculations.[24a] The ^{1}H NMR spectrum of the dimer **5** shows broad peaks in the aromatic region and only one SiMe$_3$ resonance suggesting an exchange process is taking place in solution.

The distances between the internal lithium atom and the centroids of the two Cp rings are 2.051 and 2.094 Å and that of the external lithium atom and the Cp rings 2.038 Å. The Cp(centroid)–Li–Cp(centroid) angle is about 163.1°. The lithium atoms Li(2) and Li(2a) are bound to the convex side of the bent ligand and are 4.499 Å apart. Typical separations between lithium atoms in oligomeric organolithium compounds range from 2.1 to 3.0 Å.[27] We have not been able to attribute the long Li–Li separation to any particular factors. If two hypothetical metals were bound on the concave side of the ligand bent like that in **5**, then the metals would be about 3.4 Å apart.[28] We do not know whether the bending in other complexes of a fulvalene type ligand can be greater than that observed in **5**. This ligand is more rigid than fulvalene where distances between transition metals as short as 2.719 Å have been observed.[29] The average Li–O distance is in the range of 1.916 (1) Å while the Li–C distances are in the range 2.272 (9) to 2.518 (8) Å with an average value of 2.397 (6) Å. The distance between the centers of the Cp rings is about 3.9 Å. The helical character of the ligand is still present with the angle of tilt being 13.1°. The trimethylsilyl groups are slightly bent out of the planes of the substituted Cp rings and are pointing away from the internal lithium atoms. Similar out-of-plane bending but involving CH bonds in CpLi have been examined theoretically and interpreted as due to simple coulombic effects.[19a,30] A pictorial summary of selected bonding parameters in **5** is shown in Figure 9, part b.

Comparison of the structures of the four compounds shows an increase in the dihedral angle as well as an increase in the distance separating the two hydrogen atoms on the benzene rings facing each other in the order **4a** > **2a** > **5** > **3** > **4b**. This order corresponds to the increase in the helical character of the four compounds. The lithium-induced cyclization reaction offers a new method for the synthesis of previously unknown fulvalene-containing systems and other polycyclic systems. The new organolithium compounds and the silylated isomers described in this paper are likely to play an important role as synthetic intermediates leading to the formation of a variety of transition metal complexes and main group organometallics of the substituted fulvalene ligand.

Note Added in Proof. Recently, the crystal structure of a polymeric base-free lithium cyclopentadienide in which the lithium atoms are also bound to Cp rings in a η^5,η^5 fashion was reported. See: Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903.

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Supplementary Material Available: Tables of crystal data and data collection details, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances and angles, and hydrogen atom coordinates for all structures (47 pages). Ordering information is given on any current masthead page.

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