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Communications

Synthesis and Crystal Structure of the Dimer $\{Li_2(THF)_2[C_{24}H_{14}](SiMe_3)_2\}_2$: An Example of a Li–Cp–Li–Cp Supersandwich

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Summary: The new organolithium compound $\{Li_2(THF)_2[C_{24}H_{14}](SiMe_3)_2\}_2$ has been synthesized and structurally characterized by X-ray crystallography. In this unique compound there are two modes of coordination for lithium ions. In the first mode one lithium ion is coordinated in a η^5:η^5 fashion to two cyclopentadienyl rings of two substituted fulvalene ligands, resulting in a sandwich system. In the second mode one lithium ion is η^5-bonded to a cyclopentadienyl ring of the ligand and to two THF molecules. This compound is a dimer of $Li_2(THF)_2[C_{24}H_{14}](SiMe_3)_2$ 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. This is the first example of a crystal structure of an organolithium species having lithium ions bound in a η^5:η^5 fashion to cyclopentadienyl rings, forming a sandwich system, and is the only inverse sandwich structure with Li–Cp–Li–Cp interactions.

Organolithium compounds play an important role as synthetic intermediates, leading to the formation of many compounds, including a variety of transition-metal and main-group organometallics. Lithium compounds exhibit fascinating structures and bonding patterns[1] and thus have generated much interest among experimentalists and theoreticians in recent years. Several crystallographic studies have focused on plain and substituted lithium cyclopentadienyl (Cp) compounds. These studies, including that of our monomeric fulvalene derivative $\{Li_2(TMEDA)_2[C_{24}H_{14}]\}$ (2·2TMEDA),[2] indicate that the Li–Cp(centroid) distance is very dependent on the nature of the basic ligand bound to the lithium atom.[1b,3] This communication reports the synthesis and spectral and crystallographic characterization of a novel disilylated derivative of 2, the dimeric $\{Li_2(THF)_2[C_{24}H_{14}](SiMe_3)_2\}_2$ (4). Compound 4 exhibits two bonding modes which are unusual in lithium cyclopentadienyl compounds: (1) two lithium atoms are not bound to a basic ligand but each is bound in a η^5:η^5 fashion to two Cp ligands and (2) two of the four Cp ligands are involved in inverse sandwiches with Li–Cp–Li–Cp interactions.

We recently reported the lithium-induced cyclization reaction of the tribenzo cyclotriyne compound 1 that led to the formation of the substituted fulvalene dianion 2.[2] Reaction of the dianion 2 with 2 molar equiv of trimethylsilyl chloride has resulted in the isolation of the silylated compound 3.[4] Reaction of 3 with 2 molar equiv of n-butyllithium under anaerobic conditions in tetrahydrofuran yielded 4 (Scheme I). In a typical reaction, the silylated compound 3 (0.10 g, 0.22 mmol) was allowed to react with n-butyllithium[5] (2.5 M, 0.18 mL, 0.45 mmol) in 35 mL of tetrahydrofuran at −78 °C for 1 h. After the mixture was slowly warmed to room temperature, the solvent was removed. Compound 4 was isolated in 98%

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[1] For reviews see: (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 354. (b) Jutzi, P. *Pure Appl. Chem.* **1989**, *61*, 1731.

[2] Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089.

[3] (a) Stucky, G. *Polyamine-Chelated Alkali Metal Compounds*; Advances in Chemistry 130; American Chemical Society: Washington, DC, 1974; Chapter 3. (b) Bloom, R.; Faegri, K., Jr.; Midtgaard, T. *J. Am. Chem. Soc.* **1991**, *113*, 3230. (c) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991**, *10*, 1282.

[4] Malaba, D.; Djebli, A.; Tessier, C. A.; Youngs, W. J.; Zarate, E. A. Unpublished results.

[5] n-Butyllithium was standardized with diphenylacetic acid prior to use; see: Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

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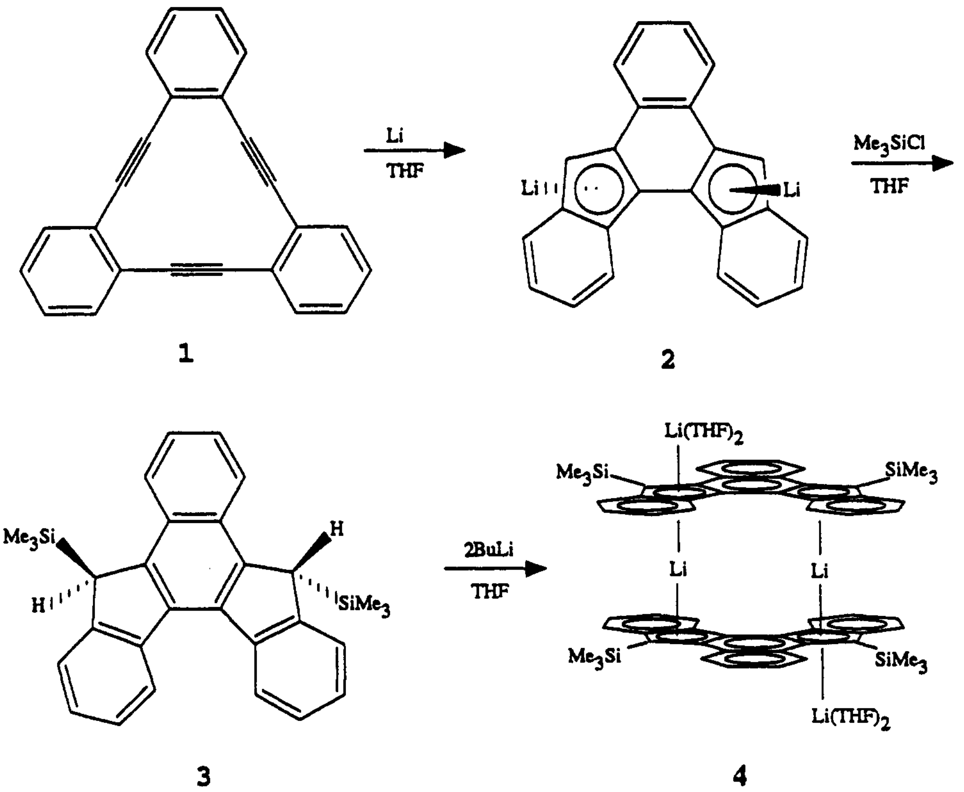
Scheme I



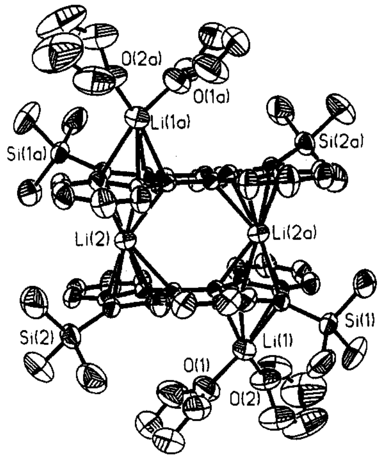


Figure 1. ORTEP labeling diagram for $\{Li_2(THF)_2[C_{24}H_{14}](SiMe_3)_2\}_2$. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are excluded for clarity.

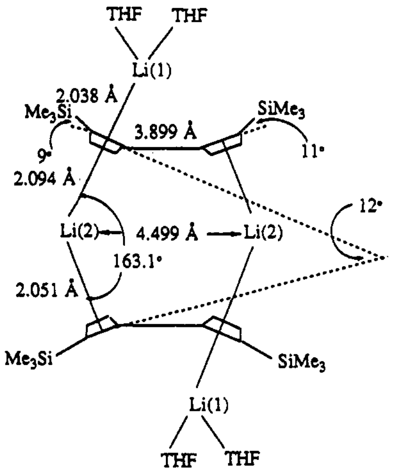


Figure 2. Pictorial representation of selected bonding parameters.

yield as an extremely air- and moisture-sensitive orange solid. The ^1H NMR spectrum[6] of the compound shows broad peaks in the aromatic region and only one $SiMe_3$ resonance, suggesting an exchange process is taking place in solution. Crystals grown from benzene were found suitable for single-crystal X-ray analysis.

The structure of 4 was determined by X-ray crystallography. X-ray diffraction intensity data were collected on a Syntex $P2_1$ diffractometer.[7] The structure was solved by direct methods and refined to convergence (R_F = 5.8%).[8] An ORTEP drawing of the molecular structure of 4 is shown in Figure 1.

Structure solution showed the molecule to be dimeric. The dimer 4 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 ligands, resulting in a sandwich system. Only one other structure showing a lithium atom sandwiched between two aromatic rings has been reported.[9] Lithium atoms sandwiched between Cp rings have been observed only in so-

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[6] The NMR spectrum was recorded on a Varian Gemini 300-MHz spectrometer. ^1H 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).

[7] Crystallographic data: monoclinic, space group $P2_1/n$, 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, ρ_{calcd} = 1.149 Mg/m^3, Z = 4 fw 604.8. The intensity data were collected from 3.0 to 45.0° (Mo Kα radiation, λ = 0.71073 Å) at 293 K. Refinement to convergence of the 3525 unique reflections ($I > 4\sigma(I)$) resulted in final R_F = 5.81% and R_{wF} = 7.40%.

[8] All calculations were performed with the use of the SHELXTL program library (Siemens Corp., Madison, WI).

[9] (a) Bladauski, D.; Broser, W.; Hecht, H. J.; Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979**, *112*, 1380. (b) Bladauski, D.; Dietrich, H.; Hecht, H. J.; Rewicki, D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 474.

lution and exist in equilibrium with their monomers.[10] 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.[11] One interesting feature of this compound is that the lithium atoms, two Cp rings, and the THF molecules are in a quasi-linear coordination, forming a Cp–Li–Cp–Li–2THF "*supersandwich*" system. Figure 2 shows a pictorial summary of selected bonding parameters. The Cp(centroid)–Li–Cp(centroid) angle is 163°. 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 ring is 2.038 Å. The Li(2)–Li(2a) distance is 4.499 Å, and the average Li–O distance is 1.916 Å. The Li–C distances vary from 2.272 to 2.518 Å with an average value of 2.397 Å. The distance between the two Cp centroids in the organic ligand is 3.899 Å. These values are comparable to experimental[12] and theoretical[3b,13] parameters of similar systems, including those of 2·2TMEDA. The trimethylsilyl groups are slightly bent out of the planes of the substituted Cp rings pointing away from the internal lithium atoms. Similar out-of-plane bending involving CH bonds in CpLi have been examined theoretically and interpreted as due to simple Coulombic effects.[3c,14] We are currently performing detailed NMR studies of 4 and synthesizing dinuclear main-group and transition-metal complexes from 4.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

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 4 (9 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(10) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Buhl, M.; Fiegel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776.

(11) (a) Rhine, W. E.; Davis, J. H.; Stucky, G. J. *J. Organomet. Chem.* **1977**, *134*, 139. (b) Boche, G.; Etzrodt, H.; Massa, W.; Baum, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 863.

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

(13) (a) Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 7959. (b) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

(14) Waterman, K. C.; Streitweiser, A. C., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3138.

First Isolation of Six-Membered Cyclic Acetylene: Synthesis and Reaction of Tetrasilacyclohexynes

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Summary: Six-membered cyclic acetylenes, namely 1,1,2,2,3,3,4,4-octaalkyl-1,2,3,4-tetrasilacyclohexynes (**1**), have been synthesized directly by the reaction of 1,4-dichlorooctaalkyltetrasilanes with acetylene di-Grignard reagent followed by GC purification. It is found that the tetrasilacyclohexyne **1a** is thermally stable: $t_{1/2}$ = 8 h (decane, 174 °C). Reactions of **1a** with dicobalt octacarbonyl, 2,3-dimethyl-1,3-butadiene, phenyl azide, and diphenyldiazomethane give the corresponding cycloadducts, respectively.

In recent years, there have been a surge of activities in constructing strained cyclic silicon compounds. Two types of compounds, *trans*-cycloalkenes[1] and cycloalkynes,[1a,2] are subjects of considerable interest. We recently reported the first isolation of a seven-membered *trans*-cycloalkene which was stabilized by the long bond distance of Si–Si bonds.[3] On the other hand, many medium-ring cycloalkynes have been generated as reactive intermediates and theoretical studies were carried out.[4] Some silicon-containing cycloalkynes have been reported so far.[5] Previously, we described the synthesis of hexasilacyclooctyne 2 and pentasilacycloheptyne 3.[6] We now report the first

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(1) (a) Greenberg, A.; Liebman, J. F. *Strained Organic Compounds*; Academic Press: New York, 1978. (b) Ziegler, K.; Wilms, H. *Justus Liebigs Ann. Chem.* **1950**, *567*, 1. (c) Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Am. Chem. Soc.* **1965**, *87*, 934. (d) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783. (e) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635. (f) Squillacote, M.; Bengman, A.; Felippis, J. D. *Tetrahedron Lett.* **1989**, *30*, 6805.

(2) (a) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Krebs, A. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969. (c) Nakagawa, M. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: Chichester, England, 1978. (d) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189.

(3) Shimizu, T.; Shimizu, K.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 354.

(4) (a) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 3239. (b) Fitzgerald, G.; Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 690. (c) Olivella, S.; Pericas, M. A.; Riera, A.; Sole, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884. (d) *J. Org. Chem.* **1987**, *52*, 4160. (e) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474. (f) Olivella, S.; Pericas, M. A.; Riera, A.; Serratosa, F.; Sole, A. *J. Am. Chem. Soc.* **1987**, *109*, 5600 and references cited therein.

(5) (a) Karaev, S. F.; Krebs, A. *Tetrahedron Lett.* **1973**, *30*, 2853. (b) As the cyclodiynes: Sakurai, H.; Nakadaira, Y.; Hosomi, A.; Eriyama, Y.; Kabuto, T. *J. Am. Chem. Soc.* **1983**, *105*, 3359 and references cited therein. (c) Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y.; Kabuto, C. *Chem. Lett.* **1984**, 595. (d) Bortolin, R.; Parbhoo, B.; Brown, S. S. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1079. (e) Hengge, E.; Baumegger, A. *J. Organomet. Chem.* **1989**, *369*, C39. (f) Voronkov, M.; Yarosh, O.; Turkina, G.; Vitkovskii, V.; Albanov, A. *J. Organomet. Chem.* **1990**, *389*, 1 and references cited therein. (g) Iwahara, T.; West, R. *Chem. Lett.* **1991**, 545. (h) Sakamoto, K.; Tumura, M.; Sakurai, H. *Chem. Lett.* **1991**, 549.

(6) Ando, W.; Nakayama, N.; Kabe, Y.; Shimizu, T. *Tetrahedron Lett.* **1990**, *31*, 3597.

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