not unrealistic to consider. This could result in an interchange (I_d) contribution associated with a less positive ΔV^*, as reported for all the reactions with pip in Table II.

The results of this study once again underline the importance of investigating the solvent concentration dependence in an effort to distinguish between various possible solvent displacement mechanisms. This is not always possible, since innocent solvents are not always available to perform such mixed-solvent investigations. In addition, the extended series of ΔV^* data now available for solvent displacement reactions of pentacarbonyl complexes enable a more complete comparison and emphasize the important role of the bonding mode of the solvent and its competition with related nucleophiles.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5$pip, 15710-39-1; FB, 462-06-6; HEP, 142-82-5; hex, 592-41-6; piperidine, 110-89-4.

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Formation of a Highly-Ordered Polymeric, Supersandwich Metallocene: The First X-ray Crystal Structure of a Base-Free Lithium Cyclopentadienide, $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$[1]

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Summary: Crystals of $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$ form in the space group $P\bar{1}$ with a = 8.402 (2) Å, b = 11.778 (3) Å, c = 14.740 (4) Å, α = 81.25 (2)°; β = 80.76 (2)°, γ = 77.30 (2)°, V = 1394.1 (5) Å^3, and D_{calcd} = 1.03 g cm^{-3} for Z = 2. Least-squares refinement of the model based on 2902 reflections ($|F_o| > 3.0\sigma|F_o|$) converged to a final R_F = 5.44%. The structure consists of parallel chains of $LiC_5H_4SiMe_3$ units which extend along the b-axis. In each chain, lithium atoms alternate with the $C_5H_4SiMe_3$ rings to form a continuous polymeric sandwich structure. Within a chain, the dihedral angles between cyclopentadienyl planes are 5.1–8.1° and the Li–(ring centroid) distances range from 1.957 to 1.982 Å. The orientation of the $SiMe_3$ substituents in the trimetallic $(LiC_5H_4SiMe_3)_3$ repeat unit found in the chains generates a highly ordered interchain structure.

Introduction

Organolithium complexes hold a prominent position in organometallic chemistry, not only as readily accessible reagents but also as organometallic compounds of the electronically simplest metal.[2] Although organolithium species have been quite attractive for theoretical studies, it has proven to be difficult experimentally to obtain the crystallographic data necessary for optimizing theoretical evaluations. The highly reactive nature of organolithium reagents is compounded by the fact that these complexes tend to oligomerize into noncrystalline materials.

This situation extends even to the cyclopentadienide ligand, which historically has provided so many crystallizable complexes in organometallic chemistry.[3] In recent years, access to crystallographically characterizable lithium cyclopentadienyl complexes has been provided through the use of substituted cyclopentadienides and coordinating bases.[4-14] Table I lists the lithium as well as sodium[9-11] and potassium[10,12,13] structures reported to date. Unfortunately, the extent to which the chelating bases affect the bonding parameters in these compounds is not known since crystal data on the requisite base-free analogs are not available for comparison. Calculations on ammonia adducts of LiC_5H_5 have suggested that there is a significant effect on bonding parameters.[15] The recently reported $\{[C_{24}H_{14}(SiMe_3)_2]Li_2(THF)_2\}_2$[14] has both THF-solvated and

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Table I. Bond Distances (Å) in Alkali-Metal Cyclopentadienide Complexes

compd	Li–(ring centroid) dist	Na–(ring centroid) dist	K–(ring centroid) dist	C–C (ring) av dist	ref
$[\eta^5\text{-}C_5H_2(SiMe_3)_3]Li\cdot$(quinuclidine)	1.79			1.44 (3)	4
$[\eta^5\text{-}C_5H_2(SiMe_3)_3]Li\cdot THF$	1.80			1.41 (3)	5
$[\eta^5\text{-}C_5H_4Me]Li\cdot TMEDA$	1.91			1.40 (0)	6
$[\eta^5\text{-}C_5H_4(SiMe_3)]Li\cdot TMEDA$	1.92			1.38 (1)	7
$[\eta^5\text{-}C_5H_2(SiMe_3)_3]Li\cdot PMDETA$	1.92–1.98				2g, 4
$[\eta^5\text{-}C_5H_2(SiMe_3)_3]Li\cdot TMEDA$	1.98			1.43 (1)	4
$[\eta^5\text{-}C_5H_5]Li\cdot$(12-crown-4)	2.06			1.39 (1)	8
$\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$	1.96			1.41 (1)	this work
$\{[C_{24}H_{14}(SiMe_3)_2]Li_2(THF)_2\}_2$	2.04, 2.05, 2.09				14
$\{[\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4(C(O)Me)]Na\cdot THF\}_n$		2.69–2.94		1.40 (3)	9
$[\eta^5\text{-}C_5Me_5]Na\cdot 3py$		2.79		1.39 (1)	10
$\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_5]Na\cdot TMEDA\}_n$		2.92		1.38 (1)	11
$\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5]K\cdot 2py\}_n$			2.79	1.41 (0)	10
$\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_3)]K\}_n$[a]			2.78		12
$[\eta^5\text{-}C_5(CH_2C_6H_5)_5]K\cdot 3THF$			2.79	1.41	13

[a] An additional, weak η^2-bonding relationship has been described in this structure.[12]

THF-free lithium atoms coordinated to five-membered rings in a polycyclic aromatic hydrocarbon, but the effect of the fused hexacyclic system on the parameters is uncertain.

We report here the first crystallographic data on a base-free lithium complex of a simple cyclopentadienide. This structure provides data for comparison with the previously characterized base adducts of lithium cyclopentadienides. These data also allow a direct lithium vs potassium comparison to be made with the only other base-free alkali-metal complex of a simple cyclopentadienide in the literature, $\{[C_5H_4(SiMe_3)]K\}_n$.[12]

Experimental Section

All manipulations were performed under dry nitrogen using Schlenk, vacuum line, and glovebox techniques. Solvents were dried and physical measurements were obtained as previously described.[16] Crystals of $\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_3)]Li\}$ were obtained as a byproduct of the reaction of $\{[\eta^5\text{-}C_5H_4(SiMe_3)]Y(OCMe_3)\}_2$[1,17] with $LiCH_2SiMe_3$ in hexane at ambient temperature for 12 h, a complicated reaction system which is not fully understood to date. Removal of solvent and extraction with hexane gave an oil which was a mixture of products by NMR spectroscopy. Crystallization at ambient glovebox temperature over a 6-week period by slow diffusion of hexanes into a THF/DME solution of a portion of this product mixture gave crystals of $\{[\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_3)]Li\}$. It is possible that the crystals formed by the slow decomposition of an intermediate in this reaction.[18] Attempts to grow crystals from pure $LiC_5H_4SiMe_3$ under similar solvent conditions have not been successful.

Collection of X-ray Diffraction Data. Under nitrogen, a colorless crystal of approximate dimensions 0.20 × 0.27 × 0.28 mm was immersed in Paratone-D oil. The oil-coated crystal was then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Siemens P3 diffractometer which is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[19] Low-temperature (158 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation under the conditions given in Table II.

All 3960 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No 2]. With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[20] and was later shown to be the correct choice.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[LiC_5H_4SiMe_3]_n$

compd	$C_{24}H_{39}Li_3Si_3$
mol wt	432.6
space group	$P\bar{1}$
cell constants	
a (Å)	8.402 (2)
b (Å)	11.778 (3)
c (Å)	14.740 (4)
α (deg)	81.27 (2)
β (deg)	80.76 (2)
γ (deg)	77.30 (2)
cell vol (Å^3)	1394.1 (5)
molecules/unit cell	2
D(calc) (Mg/m^3)	1.031
temp (K)	158
μ(calc) (mm^{-1})	0.172
radiation [λ (Å)]	Mo Kα (0.71073)
max cryst dimens (mm)	0.20 × 0.27 × 0.28
scan width (deg)	1.20 (plus Kα separation)
scan rate (deg min^{-1})	3.00 (in ω)
background counting	esd from 96-step profile
no. of std reflns	3960
2θ range (deg)	4.0–45.0
no. of total data	3960
no. of unique data with ($\lvert F_o\rvert > 3.0\sigma\lvert F_o\rvert$)	2902
no. of params varied	271
GOF	1.43
R (%)	5.4
R_w (%)	6.0
max Δ/σ in final cycle	<0.001

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out using either the UCI-modified version of the UCLA Crystallographic Computing Package[21] or the SHELXTL PLUS program set.[22] The analytical scattering factors for neutral atoms were used throughout the analysis;[23] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[23] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0007(|F_o|)^2$.

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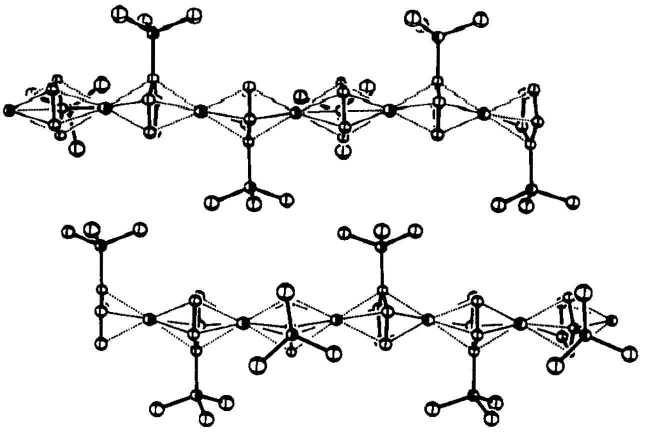

Figure 1. Side view of two of the chains in $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$. The *b*-axis is horizontal.

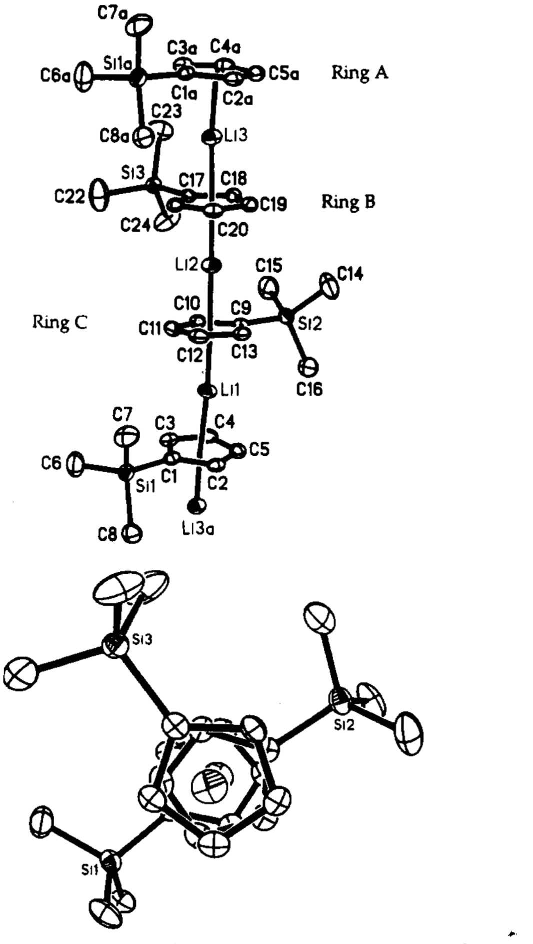

Figure 2. (a, top) Isotropic ORTEP representation of a side view of the three independent $LiC_5H_4SiMe_3$ units which constitute the repeating unit of a chain. (b, bottom) Top view down the *b*-axis of the three independent $LiC_5H_4SiMe_3$ units.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. The molecule is polymeric as shown in Figure 1. Refinement of the model led to convergence with R_F = 5.4%, R_wF = 6.0%, and GOF = 1.43 for 271 variables refined against those 2902 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 0.35 e Å^{-3}.

Results and Discussion

[(Trimethylsilyl)cyclopentadienyl]lithium crystallizes as a "supersandwich"[12] of stacked metal ring units, $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}$, as shown in Figure 1. The unit cell contains two of these infinite chains which are parallel to the *b*-axis. Within a chain, the structural repeat unit is composed of three crystallographically independent $LiC_5H_4SiMe_3$ moieties (Figure 2a). Although the stacking of the cyclopentadienyl rings if fairly regular, their planes are not rigorously parallel. The dihedral angles between rings A and B, rings A and C, and rings B and C are 8.1, 5.2, and 5.1°, respectively. The three independent Li–(ring centroid)–Li angles are 177.0, 177.9, and 177.5° and the three independent (ring centroid)–Li–(ring centroid) angles are 173.6, 174.8, and 175.3° (see Table III). The Li(1)–Li(2)–Li(3) angle is 174.5°.

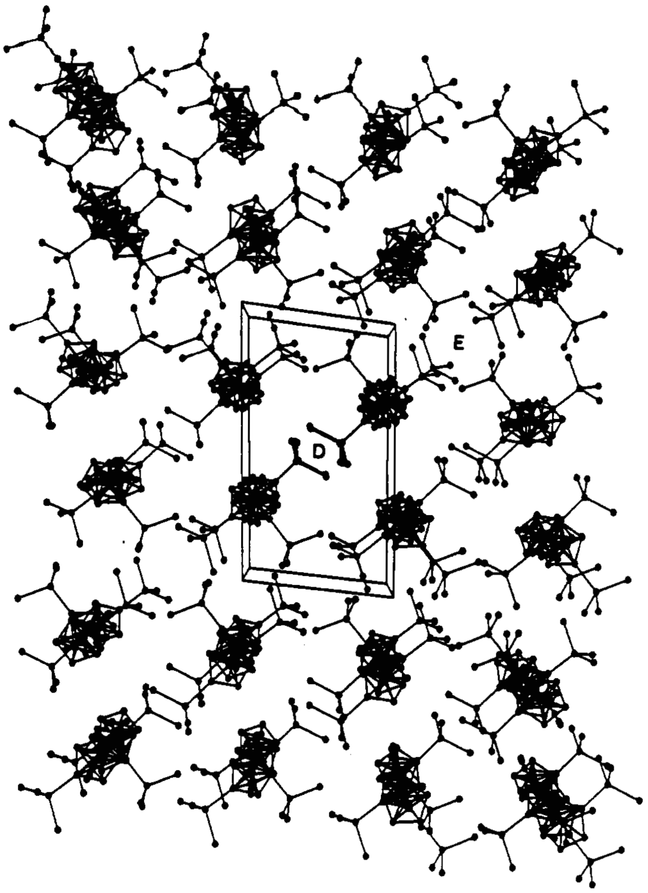

Figure 3. Packing diagram of $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$ viewed down the *b*-axis. Labeled areas D and E show vacancies in the lattice.

The interchain arrangement shown in Figure 3 is determined by the Me_3Si groups in the trimetallic repeating unit. The orientation of the three Me_3Si groups within the trimetallic unit with respect to each other is shown in Figure 2b. The Si(1)–(ring A centroid)–(ring B centroid)–Si(2) torsional angle is 174.2°, the analogous Si(2)–(B)–(C)–Si(3) angle is 90.7°, and the Si(3)–(C)–(A)–Si(1) angle is 95.0°. This variation in Me_3Si group placement generates a pattern of steric bulk and holes perpendicular to the *b*-axis which leads to the three-dimensional structure in this crystal.

The trimethylsilyl groups of the parallel chains point toward each other to generate two types of Me_3Si regions in the structure, as seen in Figure 3 and a stereoview (Figure 4). One of these regions involves Me_3Si groups containing Si(1) and is labeled as D in the center of the unit cell in Figure 3. Although it appears that the trimethylsilyl groups from the two chains point toward each other, these groups are actually staggered along the *b*-axis. As shown in Figure 1, one trimethylsilyl group per trimetallic repeat unit points toward a vacant position in the

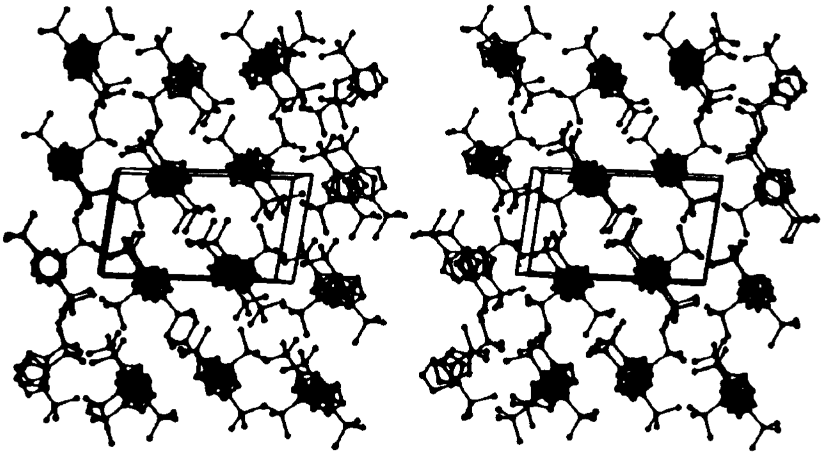

Figure 4. Stereoview of the packing diagram of $\{[\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$, viewed down the *b*-axis.

Table III. Interatomic Distances (Å) and Angles (deg)[a]

Li(1)–C(1)	2.339 (7)	Li(1)–C(2)	2.305 (6)
Li(1)–C(3)	2.307 (8)	Li(1)–C(4)	2.291 (8)
Li(1)–C(5)	2.280 (7)	Li(1)–C(9)	2.346 (7)
Li(1)–C(10)	2.281 (6)	Li(1)–C(11)	2.275 (6)
Li(1)–C(12)	2.320 (8)	Li(1)–C(13)	2.341 (8)
Li(2)–C(9)	2.307 (7)	Li(2)–C(10)	2.282 (8)
Li(2)–C(11)	2.304 (8)	Li(2)–C(12)	2.328 (7)
Li(2)–C(13)	2.316 (6)	Li(2)–C(17)	2.324 (6)
Li(2)–C(18)	2.314 (7)	Li(2)–C(19)	2.294 (8)
Li(2)–C(20)	2.279 (8)	Li(2)–C(21)	2.284 (6)
Li(3)–C(17)	2.340 (8)	Li(3)–C(18)	2.329 (7)
Li(3)–C(19)	2.325 (6)	Li(3)–C(20)	2.306 (7)
Li(3)–C(21)	2.301 (8)	Li(3)–C(1′)	2.332 (7)
Li(3)–C(2′)	2.292 (8)	Li(3)–C(3′)	2.304 (6)
Li(3)–C(4′)	2.280 (7)	Li(3)–C(5′)	2.281 (8)
Li(1)–Cnt(1)	1.966	Li(1)–Cnt(2)	1.974
Li(2)–Cnt(2)	1.968	Li(2)–Cnt(3)	1.957
Li(3)–Cnt(3)	1.982	Li(3)–Cnt(1′)	1.958
Li(1)–Cnt(2)–Li(2)	177.0	Li(2)–Cnt(3)–Li(3)	177.9
Li(1)–Cnt(1)–Li(3)	177.5	Cnt(1)–Li(1)–Cnt(2)	173.6
Cnt(2)–Li(2)–Cnt(3)	174.8	Cnt(3)–Li(3)–Cnt(1)	175.3

[a] Cnt(1) is the centroid of ring A. Cnt(2) is the centroid of ring B. Cnt(3) is the centroid of ring C. Cnt(1′) is the centroid of ring A′.

neighboring chain. The vacant area arises because the two cyclopentadienyl rings at this level in the neighboring chain have their trimethylsilyl groups oriented in other directions. Figure 1 shows that the size of one trimethylsilyl group is commensurate with the width of two stacked lithium cyclopentadienide moieties. The overall arrangement generates an interlocking pattern in which the shortest interchain C–C distances between methyl groups of Si(1)-containing trimethylsilyl units is 4.1 Å.

The E label in Figure 3 indicates the other interchain orientation of the trimethylsilyl groups with respect to each other. These positions involve the groups containing Si(2) and Si(3). In this case, trimethylsilyl groups from four different chains point toward each other to generate a trimethylsilyl-bounded region of space. The shortest interchain C–C distances between methyl groups of Si(2)- and Si(3)-containing trimethylsilyl groups is 4.3 Å.

It is interesting to note that the trimetallic repeat unit along the chain involves three trimethylsilyl groups, but they are not oriented with 3-fold symmetry (120° torsional angles). Instead, the space around any one chain as viewed down the *b*-axis in Figure 2b or 3 appears to be divisible into four quadrants. One quadrant contains the Si(1) groups which point at Si(1) groups of another chain, two quadrants contain Si(2) and Si(3) groups which point toward space bounded by trimethylsilyl groups from three other chains, and the fourth quadrant is vacant. The alignment is such that this fourth quadrant is adjacent to the positions of the Si(1) groups. Hence, the 3-fold variation along the *b*-axis gets incorporated into a four-component pattern in the three-dimensional arrangement.

The structure of $\{[\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$ (1) differs significantly from that of $\{[\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4(SiMe_3)K]\}_n$[12] (2). With the larger metal, a zigzag chain containing bent metallocene units is observed. A "weak bonding relationship"[12] between the potassium atoms and two carbon atoms of a cyclopentadienyl ring in another chain leads to a bent (ring centroid)–K–(ring centroid) angle of 150.7°. The trimethylsilyl groups in 2 appear to be simply oriented to avoid the interchain space. The polymeric lithium alkyl complex, $[LiCH(SiMe_3)_2]_n$, also crystallizes in a zigzag pattern with a 150° C_α–Li–C_α angle and Li–C_α–Li angles of 152 (1)–153 (1)°.[24]

Within the cyclopentadienyl rings in 1, the C–C distances range from 1.400 (5) to 1.436 (5) Å and average 1.416 (22) Å. In comparison, a 1.422-Å distance was calculated[15] for LiC_5H_5 and a 1.41 (3)-Å distance was found[12] in 2. The silicon atoms are coplanar with their attached cyclopentadienyl rings to within 0.05 Å.

There are six independent Li–(ring centroid) distances in this structure, but their range is small, 1.957–1.982 Å. The average Li–(ring centroid) distance 1.967 Å (average Li–C distance = 2.306 (22) Å) is compared to the analogous distances in other alkali-metal cyclopentadienides in Table I. The distance is at the high end of the 1.79–2.04-Å range previously observed for base adducts of lithium cyclopentadienides and is substantially larger than the calculated distance of 1.820 Å for LiC_5H_5.[15] This is consistent with the bridging nature of the cyclopentadienyl ring in 1. For example, in $[(\eta^5\text{-}C_5H_4Me)(THF)Yb(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4Me)_n]$,[25] a polymeric cyclopentadienide complex which has identically substituted rings in both terminal and bridging positions around the same metal, the Yb–(bridging ring centroid) distances of 2.619 and 2.647 Å are longer than the Yb–(terminal ring centroid) distance of 2.483 Å.

The difference between the metal–(ring centroid) distances in 1 and 2, 0.813 Å, is significantly greater than the difference in the ionic radii of the metals: the six-coordinate radii differ by 0.62 Å, and eight-coordinate potassium is 0.75 Å larger than six-coordinate lithium.[26] As

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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 $C_5H_4(SiMe_3)Li$ 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.

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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.

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

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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 $LiC_{32}H_{37}O_2$ 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) Å^3, Z = 4, R_F = 0.067, R_{wF} = 0.064 for 153 variables and 783 observed 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′*-tetramethylethylenediamine[2] adduct of phenyllithium, $Li_2Ph_2{\cdot}2tmed$.[3] The first monomeric *aryl*lithium reagents, LiPh·pmdt[4] and $LiC_6H_2(t\text{-}Bu)_3{\cdot}tmpn$,[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 $LiCH(SiMe_3)_2{\cdot}pmdt$,[6] $LiC(SiMe_2Ph)_3{\cdot}thf$,[7] and $LiCH(SiMe_2)_2(CH_2){\cdot}tmed$,[8] the 2,6-dithiacyclohexyl reagents $LiC_4S_2H_7{\cdot}tmed$[9] and $LiC_4S_2H_6Ph{\cdot}tmed{\cdot}thf$,[10] and the phosphinoalkyls $LiCH(PMe_2)(SiMe_3){\cdot}pmdt$[11] and $LiCH_2PPh_2{\cdot}tmed$.[12,13]

Table I. Crystal Data for $LiC_6H_2Ph_3{\bullet}Et_2O$ at 26 °C

space group: $I2/a$	V = 2814 (3) Å^3
a = 11.732 (7) Å	Z = 4
b = 20.538 (13) Å	mol wt = 460.59
c = 11.723 (9) Å	d_{calcd} = 1.087 g cm^{-3}
β = 95.06 (6)°	μ_{calcd} = 0.61 cm^{-1}
$\alpha = \gamma$ = 90°	size = 0.3 × 0.4 × 0.4 mm

diffractometer: Syntex $P2_1$
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.710 73 Å
monochromator: graphite crystal, 2θ = 12°
scan range, type, speed: $3.0 < 2\theta < 53.0°$, $\omega/2\theta$, 2–15° min^{-1}
no. of rflctns: 3274, 2935 unique, 783 with $I > 2.58\sigma(I)$
internal consistency: R_i = 0.039

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

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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