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X-RAY STRUCTURE OF A DERIVATIVE OF THE "SIMPLEST METALLOCENE: CYCLOPENTADIENYLLITHIUM", $[Li\{\eta\text{-}C_5H_4(SiMe_3)\}\{NMe_2(CH_2)_2NMe_2\}]$ (i.e., LiCp′(TMEDA)) *

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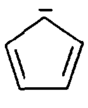
Summary

Crystalline monomeric tetramethylethylenediamine(trimethylsilylcyclopentadienyl)lithium [LiCp′(TMEDA)] was prepared by addition of an equimolar mixture of n-butyllithium and TMEDA in n-hexane to trimethylsilylcyclopentadienene, and recrystallisation from n-pentane at −30°C. X-ray data show that the lithium atom may be regarded as trigonal planar, with bonds to (a) the two nitrogen atoms (2.142(8) and 2.119(10) Å) of the chelating TMEDA and (b) the centroid of the planar η^5-cyclopentadienyl ring (1.928 Å). The Li–C bonds range from 2.257(10) to 2.286(10) Å (the carbon bearing the $SiMe_3$ substituent), and the cyclopentadienyl C–C bonds from 1.38(1) (the two bonds furthest removed from $C\text{–}SiMe_3$) to 1.421(8) Å.

Introduction

In principle, the cyclopentadienyl ligand may bind to a metal in various ways, as illustrated by some of the canonical forms (I–III) of the carbanion, giving rise to h^1-, h^2-, h^3-, or h^5-cyclopentadienylmetal complexes.


(I)


(II)


(III)

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* No reprints available.

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The fertile area of metallocene chemistry originated with the discovery of ferrocene [Fe(η-Cp)$_2$] (Cp = C_5H_5) in 1953. Problems relating to the structures and bonding (including the possibility of fluxional behaviour in solution) of metallocenes have occupied a pivotal role in the organometallic chemistry of the intervening three decades.

We take the term "metallocene" to describe a metal complex having one or more pentahapto ligated Cp$^-$. In that sense, the designation of η^5-cyclopentadienyllithium as "the simplest metallocene", a phrase coined by Alexandratos, Streitwieser, and Schaeffer [1], is entirely appropriate.

These workers carried out ab initio MO calculations (see also earlier MO papers cited in ref. 1) which led them to predict that the most stable configuration of LiCp has the lithium sited symmetrically above the ring, i.e., it has the formula [Li(η-Cp)]; the distance of Li to the centroid of the planar Cp ring was calculated as 1.649 (STO-3G) or 1.820 (DZ basis sets) Å. It was proposed that the hydrogens are bent out of the C_5 plane away from the lithium. This is the opposite to the experimental (gas-phase electron-diffraction data) findings [2] on molecules such as [Cr(η-Cp)$_2$]. The anomaly was attributed [1] to the ionic nature of the Li$^+$ η-Cp-bonding, whereby Coulombic attraction is enhanced by maximising negative charge on the side facing the Li$^+$ cation.

The most recent publication dealing inter alia with the same problem but from a different theoretical standpoint, namely that of "aromaticity in three dimensions" or the "$4n + 2$ interstitial electron rule", is by Jemmis and Schleyer [3]. They treated metallocenes as aromatic 6-membered *nido*-polyhedra, belonging to the same family as, for example, many boranes, carbaboranes, or suitable isolobal transition-metal systems. Using STO-3-21G basis sets, the Li–C and C–C distances in [Li(η-Cp)] were calculated as 2.039 and 1.406 Å, respectively, with the 5 H's also bent away from the Li. Starting with an ionic (C_{5v}) model for cyclopentadienyllithium, the six π-electrons of Cp$^-$ ("the ring") were assumed to be delocalised to the Li$^+$ ("the cap") (the term "interstitial" being used to designate the electrons that bind cap to ring). The *a*- and *e*-π-orbitals of Cp$^-$ were thus said to interact with the Li *s*- and *p*-orbitals of the same symmetry, so giving rise to three stabilised MO's.

From the experimental side, X-ray data were previously available only for benzocyclopentadienyl- (i.e., indenyl- [4]) and dibenzocyclopentadienyl- (i.e., fluorenyl- [5])-lithium, in the form of their TMEDA or bisquinuclidine adducts, respectively. Rhine and Stucky [4] concluded that the molecular structure of crystalline Li(C_9H_7)(TMEDA) was best described in terms of a trihapto (i.e., quasi-allylic) mode of ligation of the $C_9H_7^-$ moiety with respect to the Li(TMEDA)$^+$ cap. Although the lithium atom was positioned above the five-membered ring, it was shifted towards C(2) with the closest approaches of Li being to C(1), C(2), and C(3); Li($C_{13}H_9$)(quinuclidine)$_2$ showed an even more pronounced allylic (or h^3) (as distinct from h^5) structure [5]. In both molecules the carbanions were significantly non-planar, with the most negatively charged carbon atoms displaced towards the lithium [4,5].

From ^{1}H NMR data, in dimethoxyethane (DME) solution, Li(C_9H_7)(TMEDA) was considered to be a solvent-separated ion pair, but probably a contact (or tight) ion pair in benzene [4,5]. Use of ^{7}Li NMR data led to the suggestion that Li(Cp) in THF, DME, or *p*-dioxane had a pentahapto (or h^5) arrangement of the ligand with respect to the cap [6].

Results and discussion

Although trimethylsilylcyclopentadienyllithium (LiCp′) has long been known, it is normally prepared in situ in solution and then employed directly as a Cp′-transfer reagent. For example, we have previously obtained the Group IVA transition-metallocene(IV) dichlorides $[M(\eta\text{-}Cp')_2Cl_2]$ (M = Ti, Zr, or Hf) [7] in this fashion, from the appropriate metal(IV) dichloride and two molar equivalents of a solution of LiCp′ in n-hexane; the latter was obtained from $C_5H_5SiMe_3$ (Cp′H) [8] in n-C_6H_{14} and a solution of $LiBu^n$ in n-C_6H_{14}.

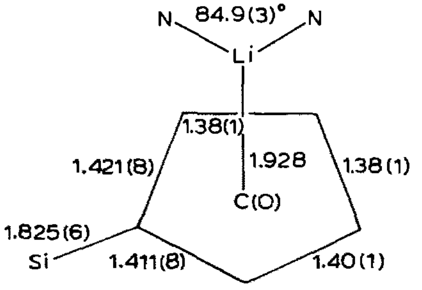
We have recently drawn attention to some of the advantages that may accrue when using isolated crystalline lithium reagents, e.g., $[Li\{CH(SiMe_3)_2\}(TMEDA)]$ [9] or $[\{Li(\mu\text{-}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)(OEt_2)\}_2]$ [10], and to the role of the ligated base. These features include (a) confidence in reagent purity and stoicheiometry, and (b) control of reagent selectivity and reactivity. Moreover, an important "spin-off" from this exercise is the opportunity of investigating the structures of the isolated reagents.

The colourless crystalline [LiCp′(TMEDA)] was prepared as shown in eq. 1. Suitable crystals for X-ray investigation were obtained by recrystallisation from n-C_6H_{14}.

X-Ray structure of [LiCp′(TMEDA)]

The structure of tetramethylethylenediamine(trimethylsilylcyclopentadienyl)lithium is illustrated in Fig. 1, while Fig. 2 shows the unit cell contents projected down the *c* axis; both also show the non-hydrogen atom numbering scheme. Some of the salient structural parameters are indicated schematically in IV and V. The non-hydrogen atom coordinates are in Table 1 and the non-hydrogen atom geometry is summarised in Table 2.

Since the sum of the angles directed from Li to N(1), N(2), and C(O) (see IV) (C(O) being the centroid of the planar cyclopentadienyl ring) is 359.7°, we may conclude $LiN_2C(O)$ to be planar and normal to the Cp′ plane. It is shown in V that



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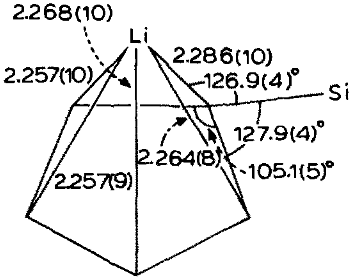

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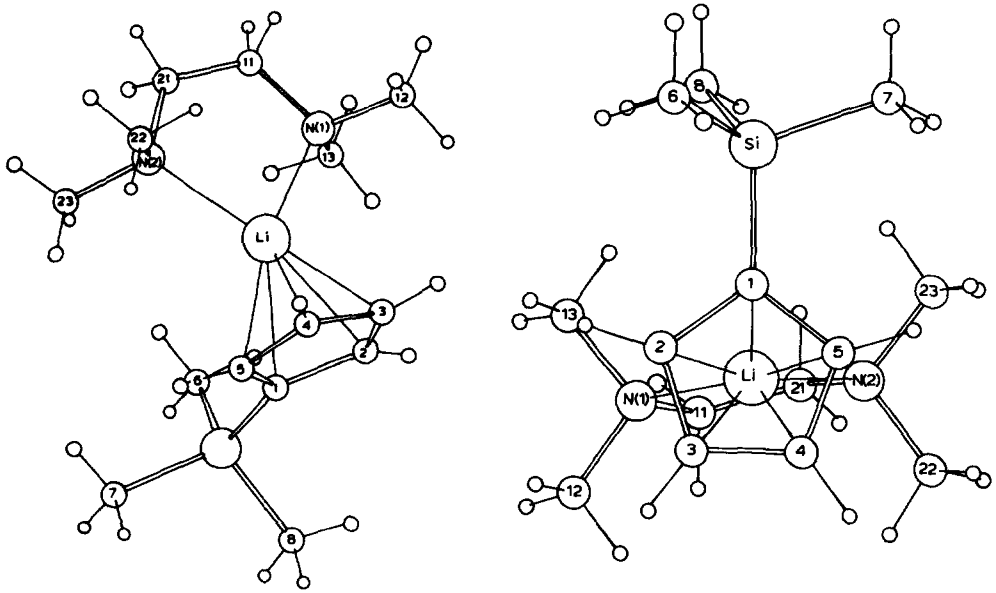


Fig. 1. The structure of a single molecule of Li{$C_5H_4(SiMe_3)$}(TMEDA), with atom numbering.

the sum of the angles at C(1), the carbon atom bearing the $SiMe_3$ substituent, is 359.9°; thus C(1) is trigonal planar, with the silicon atom in the plane of the five-membered ring.

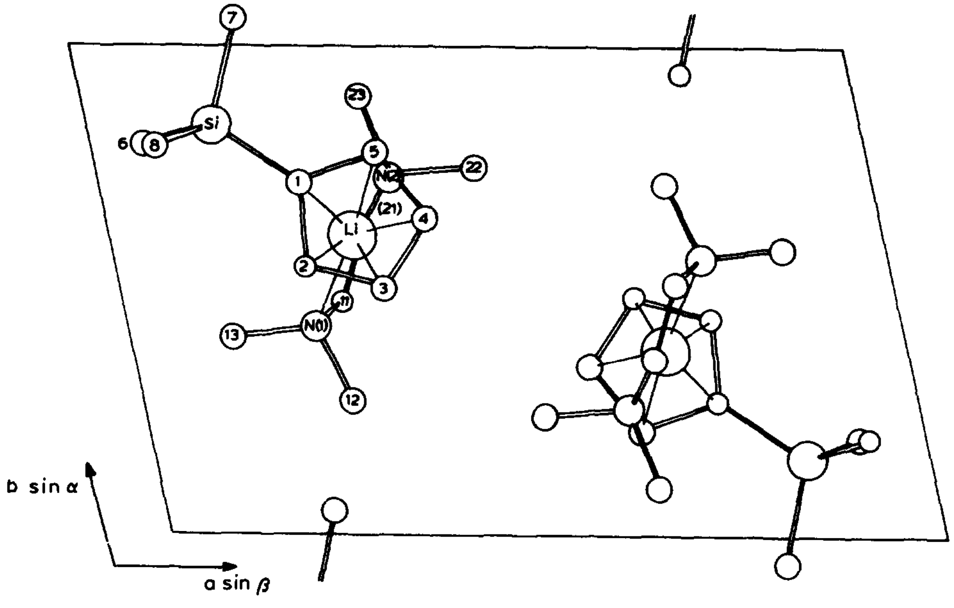


Fig. 2. Unit cell contents of Li{$C_5H_4(SiMe_3)$}(TMEDA), projected down the *c* axis, with atom numbering.

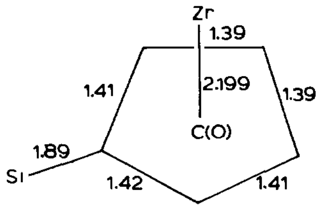
TABLE 1

NON-HYDROGEN ATOM COORDINATES (C(O) is the cp′ ring centroid)

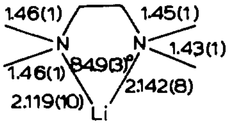
Atom	*x*	*y*	*z*
Li	0.3143(6)	0.6167(10)	−0.1813(9)
TMEDA ligand			
N(1)	0.2422(4)	0.4294(5)	−0.3857(5)
C(11)	0.2834(9)	0.4813(10)	−0.5235(9)
C(12)	0.2692(8)	0.2780(9)	−0.3598(9)
C(13)	0.1345(7)	0.4080(13)	−0.4156(11)
N(2)	0.3770(4)	0.7366(6)	−0.3615(6)
C(21)	0.3295(7)	0.6345(12)	−0.5187(9)
C(22)	0.4878(6)	0.7527(9)	−0.3208(10)
C(23)	0.3574(7)	0.8973(10)	−0.3639(10)
Cp′ ligand			
C(0)	0.3255(−)	0.6436(−)	0.0564(−)
C(1)	0.2596(4)	0.7218(6)	0.0446(5)
C(2)	0.2463(4)	0.5535(7)	0.0401(6)
C(3)	0.3404(6)	0.5118(8)	0.0561(6)
C(4)	0.4148(4)	0.6508(9)	0.0741(6)
C(5)	0.3662(4)	0.7800(7)	0.0670(6)
Si	0.1599(1)	0.8370(2)	0.0370(2)
C(6)	0.0836(7)	0.7956(13)	0.1940(13)
C(7)	0.2170(7)	1.0514(9)	0.0785(14)
C(8)	0.0724(8)	0.7965(15)	−0.1623(11)

The parameters associated with Cp'^- ligand agree favourably with those found previously for η-Cp′-metal complexes. For example, in $[Zr(\eta\text{-}Cp')_2Cl_2]$ the mean bond lengths are summarised in VI [11], and are available for comparison with IV. It is apparent that the influence of the $SiMe_3$ substituent at C(1) of Cp'^- is to make the C(2)–C(3) and C(3)–C(4) bonds significantly the shortest in the C_5 ring; consideration of the thermal parameters, however, suggests that the predominant contribution to this variation is likely to arise from the lack of correction for libration, rather than bonding effects.

Some of the geometrical features associated with the TMEDA ligand in LiCp′(TMEDA) are outlined in VII and may be compared with those shown in VIII for $Li(C_9H_7)(TMEDA)$ [4]. In both structures there is, however, very high thermal motion associated with the TMEDA moeity rendering comparison futile. The NLiN′ angle of ca. 85° is characteristic of many TMEDA-lithium compounds [4].



(VI)



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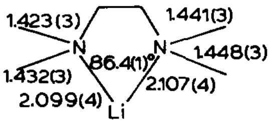

(VIII)

We conclude that, in the crystal, the molecular structure of tetramethylethylene-

TABLE 2

NON-HYDROGEN ATOM GEOMETRY

Distances (Å)		Angles (degrees)	
Li–N(1)	2.142(8)	C(O)–Li–N(1)	135.7(4)
Li–N(2)	2.119(10)	C(O)–Li–N(2)	139.1(4)
Li–C(O)	1.928(–)	N(1)–Li–N(2)	84.9(3)
Li–C(1)	2.286(10)	Li–N(1)–C(11)	104.3(4)
Li–C(2)	2.268(10)	Li–N(1)–C(12)	112.3(4)
Li–C(3)	2.257(10)	Li–N(1)–C(13)	111.2(5)
Li–C(4)	2.257(9)	C(11)–N(1)–C(12)	108.0(7)
Li–C(5)	2.264(8)	C(11)–N(1)–C(13)	111.9(7)
N(1)–C(11)	1.44(1)	C(12)–N(1)–C(13)	109.0(7)
N(1)–C(12)	1.45(1)	Li–N(2)–C(21)	104.8(5)
N(1)–C(13)	1.41(1)	Li–N(2)–C(22)	107.5(5)
C(11)–C(21)	1.34(1)	Li–N(2)–C(23)	113.5(5)
N(2)–C(21)	1.45(1)	C(21)–N(2)–C(22)	112.7(6)
N(2)–C(22)	1.46(1)	C(21)–N(2)–C(23)	110.7(6)
N(2)–C(23)	1.46(1)	C(22)–N(2)–C(23)	107.6(5)
C(1)–C(2)	1.421(8)	N(1)–C(11)–C(21)	121.1(7)
C(1)–C(5)	1.411(8)	C(11)–C(21)–N(2)	120.7(7)
C(1)–Si	1.825(6)	Si–C(1)–C(2)	126.9(4)
C(2)–C(3)	1.38(1)	Si–C(1)–C(5)	127.9(4)
C(3)–C(4)	1.38(1)	C(2)–C(1)–C(5)	105.1(5)
C(4)–C(5)	1.40(1)	C(1)–C(2)–C(3)	109.8(5)
Si–C(6)	1.826(12)	C(2)–C(3)–C(4)	107.8(6)
Si–C(7)	1.826(7)	C(3)–C(4)–C(5)	108.3(6)
Si–C(8)	1.807(9)	C(4)–C(5)–C(1)	109.0(5)
		C(1)–Si–C(6)	111.5(4)
		C(1)–Si–C(7)	110.4(3)
		C(1)–Si–C(8)	112.9(4)
		C(6)–Si–C(7)	107.0(5)
		C(6)–Si–C(8)	107.4(5)
		C(7)–Si–C(8)	107.4(5)

diamine(trimethylsilylcyclopentadienyl)lithium is best described by the formulation [Li{η-$C_5H_4(SiMe_3)$}(TMEDA)], i.e., having the h^5- rather than the h^3-mode of bonding for the five-membered ring. This offers a contrast with the situation found previously in the indenyl- [4] and fluorenyl- [5] analogues. Consistent is the distance from Li(CO) to each of C(1)–C(5) being in the narrow range 2.257(4) to 2.286(10) Å. The occupancy of essentially pure p orbitals of lithium (say p_x and p_y, cf., the NLiN′ angle) for bonding with the TMEDA ligand, allows the s and p_z AO's of Li to be available for combining with the a and e π-orbitals of Cp'^-, compatible with the Schleyer view of the $4n + 2$ interstitial rule. Li–C(O) in the present case is longer than the theoretical estimates but this is only to be expected in view of the TMEDA in the lithium coordination environment.

We note that the h^5, or pentagonal-based pyramidal structure (a *nido* arrangement), now found for crystalline [Li{η-$C_5H_4(SiMe_3)$}(TMEDA)], is similar to that already reported for gaseous M(η-C_5H_5) (M = In or Tl) [12] or the cation of crystalline [Sn(η-C_5Me_5)][BF_4] [13]. We hope later to examine crystals of Li(C_5H_5)(TMEDA), but X-ray quality crystals are not yet to hand. (We have previously suggested that one of the effects of introducing $SiMe_3$ substituents on to the cyclopentadienyl ring is to increase the covalent character of the derived metal complex compared with the corresponding C_5H_5-metal analogue [14]). The structure of crystalline $Na(C_5H_5)(TMEDA)$ was determined to be polymeric, comprising puckered chains of h^5-cyclopentadienyl rings bridged by Na(TMEDA) units [15]. X-Ray studies on $Li[C_5H_2(SiMe_3)_3]$ adducts are in hand [16].

Experimental

Synthesis

To freshly distilled trimethylsilylcyclopentadiene (3.63 g, 26.25 mmol) in n-hexane (150 cm^3) was slowly added a solution (1.62 *M*) of $LiBu^n$ (16.20 cm^3, 26.24 mmol) with constant stirring during ca. 0.5 h. The solution became viscous, followed by deposition of the white solid $LiC_5H_4SiMe_3$. Solvent was removed under vacuum, and n-pentane (ca. 50 cm^3) was added. To the resulting suspension of (trimethylsilylcyclopentadienyl)lithium in n-pentane TMEDA (4.0 cm^3, 26.50 mmol) was slowly added with stirring during ca. 15 min, whereafter a clear very pale yellow solution was obtained. The reaction mixture was stirred for ca. 3–4 h at ambient temperature and was filtered. The filtrate, on concentration and cooling to −30°C, gave colourless crystals of tetramethylethylenediamine(trimethylsilylcyclopentadienyl)lithium (m.p. 82–84°C, 6.25 g, 91.4%). Found: C, 64.5; H, 11.20; N, 10.74. $C_{14}H_{29}SiN_2Li$ calcd.: C, 64.6; H, 11.22; N, 10.76%. The ^1H NMR spectrum, recorded in C_6D_6, showed signals at δ 0.5 ($SiMe_3$), 1.5 ($N-CH_2$), 1.7 (NMe), and 6.4 (C_5H_4) ppm.

Crystal data. $C_{14}H_{29}LiN_2Si$, $M = 260.4$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 13.592(9), b 8.618(8), c 8.276(5) Å, α 96.71(6), β 100.23(5), γ 101.17(6)°, U 924(1) Å^3, D_c ($Z = 2$) 0.94 g cm^{-3}, $F(000) = 288$. Diffraction data were measured on a Syntex $P2_1$ four-circle diffractomer, using monochromatic Mo-K_α radiation, λ 0.7106_9 Å, μ(Mo) 1.16 cm^{-1}, at 295 K. The crystal, an irregular polyhedron of ca. 0.2 mm diameter, was enclosed in a capillary sealed under argon.

Structure determination

A unique data set was measured to $2\theta_{max} = 45°$ in the conventional $2\theta/\theta$ scan mode. 2341 independent reflections were obtained, 1319 with $I > 3\sigma(I)$ being considered "observed" and used in the 9 × 9 block diagonal least squares refinement without absorption correction after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were estimated and included as constrained invariants. At convergence, R and R' were 0.064 and 0.076, respectively. Neutral atom scattering factors were used, corrected for anomalous dispersion (f', f'') [17].

Computation used the XTAL system, implemented by S.R. Hall on a Perkin–Elmer 3240 computer [18]. Reflection weights were $[\sigma^2(F_o) + 0.0003(F_o)^2]^{-1}$.

The thermal motion in the trimethylsilyl group was found to be very high, indicative of a pronounced tendency toward rotation about the Si–C(1) bond. Similar high thermal motion was observed on the TMEDA moiety.

Tables of non-hydrogen atom thermal parameters, hydrogen atom parameters, and structure factors may be obtained *.

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* From the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

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