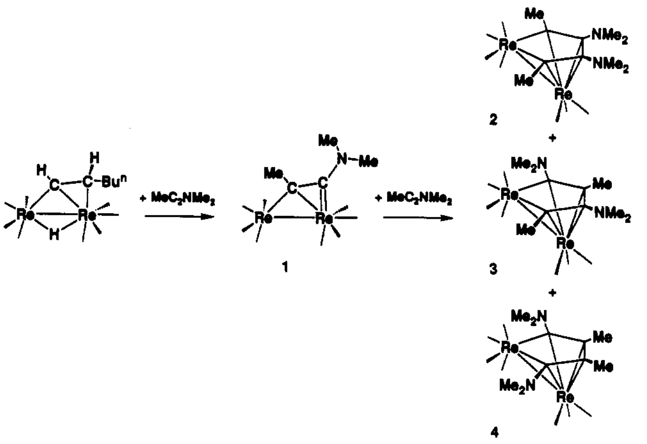
Scheme I



ture, and the observation of a single N-methyl resonance in the ^{1}H NMR spectrum (2.89 ppm) indicates that rotation about the C–N bond is rapid on the NMR time scale at 25 °C.

The infrared spectra of compounds **3** and **4** in the carbonyl region are very similar to that of **2** and indicate that the structural dispositions of the carbonyl ligands in all three complexes are also very similar. The mass spectra of **3** and **4** show parent ions m/e = 734 and ions due to the loss of each of seven carbonyl ligands. This supports the notion that **2**–**4** are isomers. The ^{1}H NMR spectrum of **3** shows two resonances of intensity 6 (2.90 and 2.57 ppm) that we attribute to two inequivalent but rapidly rotating NMe_2 groups and two resonances of intensity 3 that we attribute to inequivalent C-methyl groups. On this basis, we propose that the structure of **3** is analogous to that of **2** but contains two ynamine ligands coupled in a head-to-tail fashion. On the other hand, the ^{1}H NMR spectrum of **4** shows only one N-methyl resonance and one C-methyl resonance. Accordingly, we propose that the structure of **4** is analogous to that of **2** and **3** but that the ynamine ligands are coupled in a tail-to-tail fashion (see Scheme I). All four products **1**–**4** were obtained when $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ was allowed to react with an excess of MeC_2NMe_2 at 50 °C. As found for the bridging ynamine ligands in other complexes, we believe that further studies will show that the amine-substituted carbon atom in **1** also contains a substantial amount of carbene-like character. The reactivity of **1** is currently being investigated in hopes of finding additional evidence for this.

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for both crystal structure analyses (7 pages); listings of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Synthesis and Structural Characterization of the Sandwichlike Compound [(12-crown-4)Li(η^5-C_5H_5)] and the η^0-Substituted-Cyclopentadienide Salt [Li(12-crown-4)$_2$][1,2,4-(Me_3Si)$_3C_5H_2$]

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The addition of 12-crown-4, in stoichiometric amounts or in excess, to a solution of LiC_5H_5 in THF affords the complex [(12-crown-4)Li(η^5-C_5H_5)] (**1**). X-ray structural data demonstrate that it possesses a unique sandwichlike structure in which the Li^+ ion is coordinated on one side by four oxygens from a 12-crown-4 ligand and on the other side by the cyclopentadienide anion, $[C_5H_5]^-$, in an η^5 fashion. In contrast, the addition of 12-crown-4 to THF solutions of Li(1,2,4-(Me_3Si)$_3C_5H_2$) gives the ion pair [Li(12-crown-4)$_2$]$^+$[1,2,4-(Me_3Si)$_3C_5H_2$]$^-$ (**2**), which has a free (η^0) substituted-cyclopentadienide ion as part of its lattice. The latter complex represents a very rare example of the structure of an η^0 delocalized carbanion, and the structure of **1** is the first of a new class of sandwich structures. Crystal data at 130 K: **1**, $C_{13}H_{21}LiO_4$, a = 7.729 (5) Å, b = 11.268 (7) Å, c = 15.618 (8) Å, orthorhombic, $P2_12_12_1$, Z = 4; **2**, $C_{30}H_{61}LiO_8Si_3$, a = 11.924 (4) Å, b = 12.565 (4) Å, c = 14.530 (3) Å, α = 92.65 (2)°, β = 90.03 (2)°, γ = 120.28 (2)°, triclinic, $P\bar{1}$, Z = 2.

Introduction

Although the term π-complex is normally associated with transition-metal species, most notably ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, numerous compounds that feature π-complexation of a ligand to a main-group element are now known. A recent review[1] of this area cited almost 300 references and showed that complexes which involve gallium[2] and antimony in π-complexation have been known for over a century.

Lithium π-complexes have been studied for a number of years,[3] and they are of importance because, like σ-

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bonded lithium organometallics,[4] they can be used as synthetic precursors of other species. Lithium salts of cyclopentadienyl and related ligands also are of interest in their own right, and their structure and bonding has been of widespread interest to theoreticians and experimentalists.[4] Although the structure of the simplest derivative LiC_5H_5 is currently unknown, a number of lithium cyclopentadienide derivatives of relevance to the work in the paper have been structurally characterized. These include the quinuclidine complex $[(quinuclidine)Li\{\eta^5\text{-}1,2,4\text{-}(Me_3Si)_3C_5H_2\}]$,[5] the TMEDA–$Li^+$ complexes (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) of the $[\eta^5\text{-}(Me_3Si)_3C_5H_2]^-$ ion[5] and the related species $[\eta^5\text{-}Me_3SiC_5H_4]^-$,[6] and the THF–$Li^+$ complex (THF = tetrahydrofuran) of the $[\eta^5\text{-}(Me_3Si)_3C_5H_2]^-$ ion.[7] Treatment of solutions of $Li\{\eta^5\text{-}1,2,4\text{-}(Me_3Si)_3C_5H_2\}$ with PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) did not effect Li^+ separation but gave the complex $[(PMDETA)Li\{\eta^5\text{-}1,2,4\text{-}(Me_3Si)_3C_5H_2\}]$, in which PMDETA is η^2-bound to Li^+.[8] In addition, the structures of the TMEDA–Li^+ complex of indenyllithium[9] and bis(quinuclidine)fluorenyllithium[10] have appeared. The structure of the lithium sandwich complex $[Li(indenofluorene)]_2$, in which the Li^+ ions are bound in an η^6 fashion, has also been published.[11] Recently, the structure of the "η^0" $[C_5H_5]^-$ anion has been determined in connection with the ligand-stripping reactions of PMe_3 with $[Re(\eta^5\text{-}C_5H_5)(NO)(CO)(Me)]$.[12] In addition, prior work in this laboratory has shown that certain free carbanions and related species can be synthesized by reactions of their lithium salts and 12-crown-4.[13]

In this paper the structures of the products derived from the addition of 12-crown-4 to lithium salts of cyclopentadiene and the substituted-cyclopentadienide ion $[1,2,4\text{-}(Me_3Si)_3C_5H_2]^-$ are now described.

Experimental Section

All reactions were performed by using modified Schlenk techniques under an N_2 atmosphere or by using a Vacuum Atmosphere HE43-2 drybox. Solvents were freshly distilled from Na/K alloy or Na/K benzophenone ketyl and degassed twice immediately before use. *n*-BuLi (as a 1.6 M hexane solution) was used as purchased. Cyclopentadiene was synthesized by thermal cracking of a commercial sample of dicyclopentadiene. Commercially available 12-crown-4 was dried by distilling it off molten potassium under reduced pressure. The compound 1,2,4-tris(trimethylsilyl)cyclopentadiene was synthesized as described in the literature.[14] Compounds 1 and 2 gave satisfactory C and H elemental analyses.

Synthesis of 1 and 2. Freshly obtained cyclopentadiene (0.24 g, 3.64 mmol) in THF (30 mL), cooled in an ice bath, was treated dropwise with an *n*-BuLi solution in hexane (2.34 mL of a 1.6 M solution) with vigorous stirring. After the mixture was stirred for 1 h, 12-crown-4 (1.16 mL, 7.2 mmol) was added by syringe. The solution was stirred for a further 1 h, and the solvents were pumped off until about 15 mL of solution remained. Cooling overnight in a −20 °C freezer gave the product 1 as colorless crystals: yield 0.64 g, 71%; mp 180 °C dec. ^1H NMR: $\delta(CH_2O) = 2.6$ (s, 16 H); $\delta(C_5H_5) = 5.52$ (s, 5 H).

Table I. Crystallographic Data for Compounds 1 and 2

	1	2
compd	$[(12\text{-crown-4})Li(\eta^5\text{-}C_5H_5)]$	$[Li(12\text{-crown-4})_2][1,2,4\text{-}(Me_3Si)_3C_5H_2]$
formula	$C_{13}H_{21}LiO_4$	$C_{30}H_{61}LiO_8Si_3$
fw	248.90	641.01
a, Å	7.729 (5)	11.924 (4)
b, Å	11.268 (7)	12.565 (4)
c, Å	15.618 (8)	14.530 (3)
α, deg		92.65 (2)
β, deg		90.03 (2)
γ, deg		120.28 (2)
V, Å^3	1360 (1)	1877.2 (8)
Z	4	2
space group	$P2_12_12_1$	$P\bar{1}$
T, K	130	130
λ, Å	0.71069	0.71069
d(calcd), g/cm^3	1.22	1.13
μ(Mo Kα), cm^{-1}	0.81	1.6
range of trnsmsn fctrs	0.97–0.98	0.94–0.96
R(*F*)	0.035	0.037
$R_w(F)$	0.035	0.038

In a similar manner $1,2,4\text{-}(Me_3Si)_3C_5H_3$ (0.28 g, 1 mmol) in THF (20 mL), cooled in an ice bath, was treated with 1.6 mL of the *n*-BuLi solution. After the mixture was stirred for 1 h, 12-crown-4 (0.4 mL) was added by syringe and stirring was continued for a further 30 min. The volume of the solution was reduced until incipient crystallization was apparent. Cooling in a −20 °C freezer for 20 h afforded the product 2 as colorless crystals: yield 0.3 g, 48%; mp 130–132 °C. ^1H NMR: $\delta(SiMe_3) = 0.39$ (s, 9 H), 0.48 (s, 18 H); $\delta(C_5H_2) = 6.85$ (s, 2 H); $\delta(CH_2O) = 2.6$ (s, 32 H).

X-ray Data Collection, Solution, and Refinement of the Structures. All data were collected on a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 device, and the crystal was cooled to 130 K. Calculations were carried out with the SHELXTL program system. The atom form factors, including anomalous scattering, were from ref 15. Crystals 1 and 2 were transferred from the Schlenk tubes under N_2 to Petri dishes and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, mounted on a glass fiber, and immediately placed in a low-temperature N_2 stream. Some details of the data collection and refinement are given in Table I. Further details are provided in the supplementary material. The structures were solved by direct methods. An empirical absorption correction (XABS) was applied. Hydrogen atoms were included in the refinement at calculated positions by using a riding model, with C–H = 0.96 Å and $U_H = 1.2U_C$. All non-hydrogen atoms were refined anisotropically. Atom coordinates and isotropic thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. The largest features on the final difference maps were 0.15 and 0.32 e Å^{-3} for 1 and 2, respectively. The mean shift/esd's were 0.013 and 0.072. Important structural data for 1, 2, and related species are collected in Table IV.

Results and Discussion

The syntheses of the complexes 1 and 2 were accomplished, in a facile manner, by the metalation of the cyclopentadienyl precursors with *n*-BuLi and then by subsequent addition of 12-crown-4. Separation of the cation

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 1 and 2

	x	y	z	U^a
		Compound 1		
O(1)	10092 (2)	6003 (1)	2064 (1)	33 (1)
O(2)	10364 (2)	3598 (1)	1868 (1)	33 (1)
O(3)	9697 (2)	4005 (2)	177 (1)	35 (1)
O(4)	9480 (2)	6448 (2)	357 (1)	43 (1)
C(1)	6143 (3)	4396 (2)	2263 (2)	30 (1)
C(2)	5887 93)	5573 (2)	2042 (2)	34 (1)
C(3)	5574 (3)	5623 (2)	1161 (2)	36 (1)
C(4)	5644 (3)	4460 (2)	843 (2)	35 (1)
C(5)	5999 (3)	3703 (2)	1530 92)	31 (1)
C(6)	10946 (3)	5275 (2)	2692 (2)	37 (1)
C(7)	11745 (3)	4204 (3)	2278 (2)	35 (1)
C(8)	10936 (4)	2780 (2)	1222 (1)	35 (1)
C(9)	11264 (3)	3419 (2)	397 (2)	36 (1)
C(10)	9857 (4)	4797 (2)	−532 (2)	38 (1)
C(11)	10615 (4)	5960 (2)	−265 (2)	41 (1)
C(12)	10231 (4)	7327 92)	899 (2)	41 (1)
C(13)	11240 (4)	6779 (2)	1620 (2)	38 (1)
Li	8457 (5)	4895 (4)	1306 (3)	32 (1)
		Compound 2		
Si(1)	11465 (1)	4138 (1)	2445 (1)	20 (1)
Si(2)	6141 (1)	2322 (1)	1316 (1)	21 (1)
Si(3)	6463 (1)	2552 (1)	3995 (1)	19 (1)
C(1)	9709 (2)	3532 (2)	2504 (1)	19 (1)
C(2)	8810 (2)	3231 (2)	1764 (1)	18 (1)
C(3)	7552 (2)	2832 (2)	2096 (1)	16 (1)
C(4)	7660 (2)	2887 (2)	2090 (1)	18 (1)
C(5)	8980 (2)	3317 (2)	3311 (1)	18 (1)
C(6)	12073 (2)	3764 (2)	3502 (2)	33 (1)
C(7)	12411 (2)	5861 (2)	2382 (2)	29 (1)
C(8)	11852 (2)	3473 (2)	1393 (2)	34 (1)
C(9)	6695 (2)	2868 (2)	129 (1)	37 (1)
C(10)	5106 (2)	592 (2)	1197 (2)	30 (1)
C(11)	5067 (2)	2952 (2)	1676 (2)	28 (1)
C(12)	4934 (2)	1012 (2)	3808 (2)	28 (1)
C(13)	5959 (2)	3746 (2)	4163 (2)	30 (1)
C(14)	7189 (2)	2512 (2)	5132 (1)	30 (1)
O(1)	9113 (1)	6775 (1)	1971 (1)	24 (1)
O(2)	10672 (1)	9169 (1)	1516 (1)	27 (1)
O(3)	10535 (1)	9770 (1)	3374 (1)	26 (1)
O(4)	9009 (1)	7356 (1)	3802 (1)	26 (1)
O(5)	7770 (1)	7816 (1)	881 (1)	28 (1)
O(6)	6674 (1)	6713 (1)	2516 (1)	26 (1)
O(7)	7623 (1)	8839 (1)	3646 (1)	25 (1)
O(8)	8685 (1)	9899 (1)	2005 (1)	22 (1)
C(15)	10296 (2)	7090 (2)	1535 (2)	30 (1)
C(16)	10638 (2)	8178 (2)	968 (1)	30 (1)
C(17)	11830 (2)	9886 (2)	2060 (2)	30 (1)
C(18)	11534 (2)	10588 (2)	2792 (2)	30 (1)
C(19)	10988 (2)	9310 (2)	4075 (1)	26 (1)
C(20)	9810 (2)	8279 (2)	4491 (1)	26 (1)
C(21)	9431 (2)	6498 (2)	3560 (1)	27 (1)
C(22)	8782 (2)	5871 (2)	2654 (1)	24 (1)
C(23)	6637 (2)	6624 (2)	889 (2)	31 (1)
C(24)	5858 (2)	6497 (2)	1734 (2)	31 (1)
C(25)	6103 (2)	6728 (2)	3382 (1)	28 (1)
C(26)	6262 (2)	7976 (2)	3613 (2)	29 (1)
C(27)	7949 (2)	10076 (2)	3476 (1)	26 (1)
C(28)	7843 (2)	10240 (2)	2471 (1)	23 (1)
C(29)	8631 (2)	9958 (2)	1029 (1)	27 (1)
C(30)	7552 (2)	8766 (2)	599 (1)	31 (1)
Li	8765 (3)	8272 (3)	2475 (2)	27 (1)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

and anion was only observed in the case of 2. The addition of excess (>2 equiv) 12-crown-4 to solutions of LiC_5H_5 did not effect separation of the $[C_5H_5]^-$ ion.

The structures of 1 and 2 are illustrated in Figures 1 and 2. They consist of discrete molecular units of [(12-crown-4)Li(η^5-C_5H_5)] in the case of 1 and the ions [Li(12-crown-4)$_2$]$^+$ and [η^0-1,2,4-$(Me_3Si)_3C_5H_2$]$^-$ in the case of 2. Neither molecule possesses a symmetry that is crystallographically imposed. The structure of 1 has a unique configuration in which the Li^+ ion is bound to 12-crown-4 and a η^5-cyclopentadienide ion. The average Li–C bond length is very close to 2.38 Å, and the distance between Li^+ and the centroid of the η^5-C_5H_5 ring is 2.06 Å. There is considerable variation apparent in the Li–O bond lengths, which range between 2.135 (4) and 2.426 (4) Å and have an average value of 2.265 (81) Å. The average C–C bond length within the η^5-C_5H_5 ring is 1.395 (6) Å.

The ionic compound 2 is comprised of well-separated cations and anions. The [Li(12-crown-4)$_2$]$^+$ cation has an

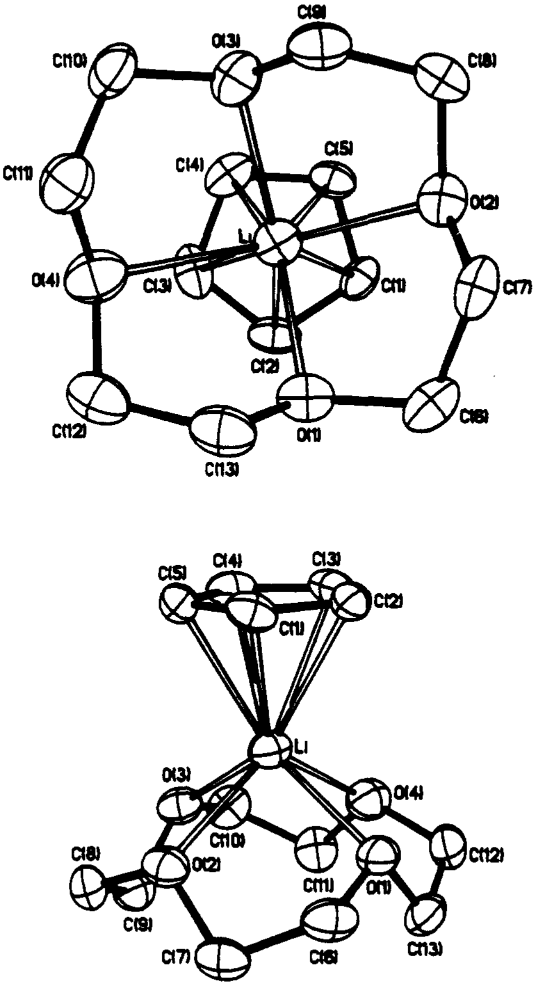

Figure 1. Two views of the complex 1. H atoms are omitted for clarity.

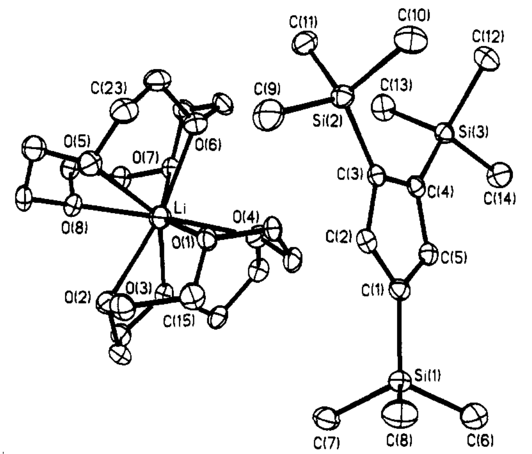

Figure 2. Computer-generated thermal ellipsoid drawing of 2. H atoms are omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for 1 and 2

		Compound 1			
Li–C(1)	2.397 (5)	Li–C(2)	2.419 (5)	Li–C(3)	2.385 (5)
Li–C(4)	2.344 (5)	Li–C(5)	2.353 (5)	Li–O(1)	2.135 (4)
Li–O(2)	2.253 (4)	Li–O(3)	2.245 (4)	Li–O(4)	2.426 (4)
C(1)–C(2)	1.385 (4)	C(2)–C(3)	1.399 (3)	C(3)–C(4)	1.402 (4)
C(1)–C(5)	1.390 (3)	C(4)–C(5)	1.398 (3)		
C(1)–C(2)–C(3)	108.0 (2)	C(2)–C(3)–C(4)	107.8 (2)	C(3)–C(4)–C(5)	107.7 (2)
C(1)–C(5)–C(4)	107.8 (2)	C(2)–C(1)–C(5)	108.7 (2)		
		Compound 2			
C(1)–C(2)	1.414 (3)	C(2)–C(3)	1.413 (3)	C(3)–C(4)	1.446 (3)
C(4)–C(5)	1.414 (3)	C(1)–C(5)	1.414 (3)	Si(1)–C(1)	1.835 (2)
Si(2)–C(3)	1.836 (2)	Si(3)–C(4)	1.842 (2)	Li–O(1)	2.215 (5)
Li–O(2)	2.438 (4)	Li–O(3)	2.338 (3)	Li–O(4)	2.382 (4)
Li–O(5)	2.507 (5)	Li–O(6)	2.268 (3)	Li–O(7)	2.475 (5)
Li–O(8)	2.232 (5)				
C(1)–C(2)–C(3)	110.7 (2)	C(2)–C(3)–C(4)	106.7 (2)	C(3)–C(4)–C(5)	106.3 (2)
C(1)–C(5)–C(4)	110.9 (2)	C(2)–C(1)–C(5)	105.4 (2)	Si(1)–C(1)–C(2)	127.9 (1)
Si(1)–C(1)–C(5)	126.7 (1)	Si(2)–C(3)–C(2)	122.1 (1)	Si(2)–C(3)–C(4)	131.2 (1)
Si(3)–C(4)–C(5)	121.4 (1)	Si(3)–C(4)–C(3)	132.3 (2)		

Table IV. Selected Structural Parameters (Å) for Li–Cyclopentadienyl Derivatives

compd	Li–C	Li–centroid	C–C (ring)[a]	ref
[(quinuclidine)Li{1,2,4-$(Me_3Si)_3C_5H_2$}]	2.157 (22)	1.79	1.440 (13)	5
[(THF)Li{1,2,4-$(Me_3Si)_3C_5H_2$}]	2.166 (16)	1.8	1.411 (20)	7
[(TMEDA)Li(η^5-$Me_3SiC_5H_4$)]	2.266 (9)	1.928	1.40 (1)	6
[(PMDETA)Li{η^5-1,2,4-$(Me_3Si)_3C_5H_2$}]	2.352 (6)	1.98	1.431 (4)	8
[(TMEDA)Li{η^5-1,2,4-$(Me_3Si)_3C_5H_2$}]	2.327 (15)	1.99	1.434 (11)	5
[(TMEDA)Li(η^{3-5}-indenyl)]	2.330 (4)	2.0[b]	1.399 (3)	10
1	2.380 (5)	2.06	1.395 (3)	c
2			1.420 (3)	c

[a] Average values. [b] Li–C = distance from Li^+ to the plane of the cyclopentadienyl ring. [c] This work.

eight-coordinate lithium ion complexed by eight oxygen donors arranged in an approximately D_{4d} fashion. The average Li–O bond length is 2.357 (7) Å and spans the distances 2.215 (5)–2.507 (5) Å. The average C–C bond length in the $[1,2,4\text{-}(Me_3Si)_3C_5H_2]^-$ ring is close to 1.42 Å. Four of these distances are remarkably uniform and are 1.414 (3) Å in length, whereas the C(3)–C(4) bond, which involves the carbons bearing adjacent Me_3Si substituents, is 1.446 (3) Å long.

The structures of compounds 1 and 2 are interesting for several reasons. For example, although there are a growing number of structures available for lithium salts of various π-ring systems, there are none for either the unsubstituted lithium cyclopentadienide salt itself or its solvated derivatives. Calculations on LiC_5H_5 predict that the Li is situated 1.82 Å above the center of the cyclopentadienyl ring and that C–C ring distances are optimized at 1.417 Å.[16] In 1 the observed Li–centroid distance is much longer (2.06 Å), while the average C–C distances in the η^5-C_5H_5 ring are shorter and almost identical with the 1.399 (8) Å observed in the free $[\eta^0\text{-}C_5H_5]^-$ ion.[12] This demonstrates that the interaction between the Li^+ and $[\eta^5\text{-}C_5H_5]^-$ ions in 1 has only a very minor effect on the ring C–C bond lengths. In effect, the complex 1 may be described as an essentially ionic contact ion pair. This view of the bonding receives support from the structure of the polymeric species $[(TMEDA)Na(\eta^5\text{-}C_5H_5)]$,[17] which also possesses an ionic structure with short (1.38 (1) Å) C–C ring bonds. Further evidence of ionic bonding comes from the Li–C distances in 1, which, in comparison to the other derivatives in Table IV, are at the longer end of the scale. The increased Li–C distances are due to the higher coordination number (four oxygen donors) of Li^+. The effect of the Li^+ coordination on the strength of the interaction of the Li^+ ion with the cyclopentadienyl ring may also be gauged by a comparison of the Li^+–centroid distances in Table IV. A value of 2.06 Å was observed for 1, whereas a distance of 1.79 Å was observed for [(quinuclidine)Li{η^5-1,2,4-$(Me_3Si)_3C_5H_2$}] and a distance of 1.99 Å was seen in the case of [(TMEDA)Li{η^5-1,2,4-$(Me_3Si)_3C_5H_2$}]. In summary, the close agreement between the C–C distances in 1 and the free $[\eta^0\text{-}C_5H_5]^-$ ion and the observation of the longest Li–centroid distance for any cyclopentadienyl complex confirm that the interaction between the metal ion and the aromatic ring is essentially ionic. It is perhaps worth noting that significantly longer ring C–C distances are normally observed in more covalent structures such as "ferrocene" (C–C = 1.429 (3) Å),[18] where the π-orbitals of the ring are intimately involved in bonding with the low-lying metal valence orbitals.

It was hoped that the addition of excess 12-crown-4 to THF solutions of LiC_5H_5 would afford separation of the Li^+ to give the salt $[Li(12\text{-crown-}4)_2][\eta^0\text{-}C_5H_5]$. Presumably, this did not occur because the lattice energy gained in the formation of this salt is insufficient to disrupt the ionic attraction between Li^+ and $[\eta^5\text{-}C_5H_5]$ in 1. Another possible explanation is that the ions $[Li(12\text{-crown-}4)_2]^+$ and $[\eta^0\text{-}C_5H_5]^-$ are not well matched in terms of size and consequently the lattice energy is relatively low. The substitution of several hydrogens by $-SiMe_3$ groups on the cyclopentadienyl ring allows complete separation of the Li^+ ion upon the addition of 12-crown-4 to give the salt 2. The cation $[Li(12\text{-crown-}4)_2]^+$ possesses the same structure as those previously observed in other complexes.[13] The average Li–O bond length (2.357 (7) Å) is also comparable to those already reported and is consistent with the high (eight) coordination number at lithium. The $[\eta^0\text{-}1,2,4\text{-}(Me_3Si)_3C_5H_2]^-$ ion is well separated from the cations. The ring C–C distances are significantly longer than those observed in 1. It has already been noted that the C(3)–C(4) length in 2 (1.444 (3) Å) is exceptionally long.

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This pattern of C–C bond lengths observed within the ring is very similar to that for $[(PMDETA)Li(1,2,4\text{-}(Me_3Si)_3C_5H_2)]$.[8] The lengthening may be due to the presence of the two fairly large Me_3Si substituents on adjacent carbon atoms. However, it is apparent from Table IV that the average C–C distances in all the tris(trimethylsilyl)-substituted rings are longer than those observed in 1. The increased C–C distances observed in these rings are most probably a result of the electronic effects of the Me_3Si substituents, whose ability to stabilize, inter alia, negatively charged species such as carbanions is well documented.[19] The three Me_3Si groups in the anion of 2 provide stabilization by lowering the negative charge density through delocalization. As a result, the C–C bond order in the ring is diminished and longer C–C distances are observed. The consequent decrease in the ionic interaction may account for the relative ease with which total separation of the Li^+ ion was achieved in the case of 2. For 1, however, at H substituents on the $[C_5H_5]^-$ ion are not as effective as the silyl groups in removing negative charge density. In effect, the charge remains localized on the ring and a stronger $[Li]^+$–$[C_5H_5]^-$ attraction, which is not amenable to cleavage by 12-crown-4, results.

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Supplementary Material Available: Full tables of crystal data, data collection and refinement details, bond distances and angles, and thermal parameters (13 pages); tables of structure factors (38 pages). Ordering information is given on any current masthead page.

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Synthetic and Structural Studies on Organoiron–Indium Complexes

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The diiron–indium chloride complex $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1), has been synthesized from either the reaction between $InCl_3$ and 2 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ or from the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Compound 1 has been characterized by X-ray crystallography and exists in the solid state as a centrosymmetric dimer involving two chlorine atoms bridging between the indium centers. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.670$ (3), $b = 10.059$ (5), $c = 12.148$ (2) Å and $\alpha = 107.58$ (3), $\beta = 90.97$ (2), $\gamma = 91.32$ (4)°. The iodide complex, $[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (4), was also prepared by analogous synthetic routes by using either InI_3 or InI, although the insertion of InI into the Fe–Fe bond of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ occurs more readily than in the case for InCl. Both 1 and 4 add a further equivalent of halide ion and the compounds $[PPN][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (5), $[Me_4N][InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (6), and $[Et_4N][InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (8) have been prepared and characterized. Compounds 1 and 4 also form adducts with neutral two electron donor ligands, viz. $[InCl(py)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (9) (py = pyridine), $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (10), and $[InI(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (11). The structure of 10 was established by X-ray crystallography and comprises a tetrahedral indium center coordinated to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments, a chlorine atom, and the phosphorus atom of the phosphine PMe_2Ph. Compound 10 crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.646$ (2), $b = 10.621$ (4), $c = 13.586$ (4) Å and $\alpha = 92.66$ (3), $\beta = 103.62$ (2), $\gamma = 99.41$ (2)°. The iron–indium dichloride complex $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (3) has also been prepared from the reaction between $InCl_3$ and 1 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and this complex is also formed as a second product in the reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Full spectroscopic and analytical data are reported for all new complexes.

Introduction

Compounds containing transition metal to indium bonds have been known for many years but continue to attract the attention of a number of groups devoted to synthesis.[1] With reference to compounds containing iron, however, relatively few reports have appeared. Early work by Mays et al. demonstrated the insertion of indium(I) chloride into the Fe–Fe bond of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ which afforded the diiron–indium chloride complex formulated as $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (1).[2] Later work by these authors[3] showed that 1 was also formed in reactions between $InCl_3$ and 2 equiv of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and also by displacement of mercury by InCl from $[Hg\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$. The monoiron complexes $[InX_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (X = Cl, Br) and $[InBr_2(THF)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ were also described,[3] these complexes being formed either by reaction between InX_3 and 1 equiv of $Na[Fe(CO)_2(\eta\text{-}$

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