Revealing Coordination Patterns in C₅-Cyclic Lithium Organics
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ABSTRACT: Lithium organics with a C₅ perimeter are the most prominent class of compounds in s-block metal organic chemistry to introduce bulky haptotropic bound substituents in organometallic complexes. In this paper we present some coordination patterns. (η⁵-C₅)Li(PMDETA) (1), (η⁵-C₅)Li(TMEDA) (2), and (η⁵-C₅)Li(DME) (3) reveal the electron-releasing capacity of the donor base: The better the density supply from the base, the longer the Li···C₅center distance. The donor base DIGLYME gives the solvent-separated ion pair (SSIP) [(DIGLYME)₂Li][(η⁵-C₅)₂Li] (4). The contact ion pair (η²-Ind)Li(PMDETA) (5) shows an unprecedented strong C–H···π interaction of a PMDETA methyl group to the center of the C₆ perimeter of an indenyl anion. {(η²-Ind)Li(μ-DME)Li(η²-Ind)} (6) is a unique DME-bridged dimer, while [(DIGLYME)₂Li][Ind] (7) crystallizes as a SSIP.

INTRODUCTION

Lithium cyclopentadienyl derivatives are one of the most applied starting materials in organometallic synthesis. At the same time lithium organics with a C₅ perimeter are certainly the most elaborated class of compounds in s-block organometallic chemistry. They are compounds par excellence to generate a huge variety of sandwich or half-sandwich d-block organometallics via transmetalation or salt elimination reactions. The indenyl and fluorenyl substituents contain, apart from the C₅ perimeter, either one or two anellated six-membered carbon rings. In addition to the likely η⁵-bonding mode they feature a potential coordination mode from η¹ up to η₆ to the adjacent C₆ perimeter (Scheme 1), depending on the Lewis acidity of the metal ion, the donor strength, and steric requirement of the cocooordinating species.⁷

The physical properties of parent lithium cyclopentadienyl are reminiscent of those of a typical salt. Like [MeLi]₄, it is insoluble in hydrocarbons and has a high melting point and a low volatility. Developments in powder diffraction techniques⁴ enabled the structure determination of polymeric [C₅Li]₄.⁵ Many lithium organic structures can be rationalized as molecular fractions from that polymeric lithium cyclopentadienyl (a in Scheme 2): a single lithium atom and two rings give the smallest possible metalloenes, the lithocene sandwich anion (b); two solvated lithium atoms and a single ring give the inverted sandwich cation (c); and solvated lithium plus the ring anion in the ratio 1:1 give mono-meric lithium cyclopentadienyl piano chairs, (d).⁶

Scheme 1. Examples for the Variable Hapticity of the Indenyl and Fluorenyl Anions (M = any metal, D = donor), Depending on Donation to the Coordinating Metal Ion

Scheme 2. Solvated Fractions of Polymeric [C₅Li]₄

In this paper we report the preparation and structural characterization of cyclopentadienyl and indenyl lithium donor base complexes to evaluate the factors determining the coordination mode and strength of the lithium cation to the aromatic C₅/C₆ carbanions. The following questions where addressed: How are various Lewis basic donor bases influencing the anion–cation contact? How do they control the hapticity in contact ion pairs?⁶ Are there additional factors causing ring slippage? The answer to

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those questions clearly would also shed some light on the coordination in d-block metal complexes.

RESULTS AND DISCUSSION

The amines PMDETA (N,N,N',N',N''-pentamethyldiethylentriamine), TMEDA (N,N,N',N'-tetramethylethylenediamine), and their oxygen analogues DME (dimethoxyethane) and DIGLYME (diglycol dimethyl ether) are very useful donor bases in organometallic chemistry. By bi- or tridentate coordination of metal ions in reagents such as [MeLi]₆ [n-BuLi]₂₀ and [t-BuLi]₄ the oligomeric aggregation can be reduced and dimeric and monomeric species are formed. The benefit of this kind of deaggregation is the tuning of the reactivity of these species. The other great benefit of these donor bases is the option to stabilize single carbon–metal bonds. By complexation various highly reactive organometallic intermediates could be isolated and structurally characterized by single-crystal X-ray diffraction.

The N- and O-donor bases differ in the type of the coordinating atom and in steric bulk due to the increasing number of methyl groups bound to the donating atom. The lone pairs of nitrogen atoms are less contracted compared to oxygen. This results in a higher electron density shift from the donating nitrogen atom to the metal ion, mirrored by the elongation of the carbanion–metal bond. The nitrogen–metal distances are longer than the corresponding oxygen–metal distances. The shorter local dipole moment of the donating region (NMē₂: μ = 0.61 D, Neıt₂: μ = 0.66 D, Me₂O: μ = 1.30 D, EtOMe: μ = 1.17 D) amplifies this effect. The additional methyl group at every nitrogen atom creates additional steric bulk of the amine ligands in comparison to the ether molecules. The N-coordinated metal ion is more shielded and forms fewer Li–C bonds and hence gives rise to smaller aggregates in contact ion pairs (CIPs). Through their less steric demand DME and DIGLYME tend to form solvent-separated ion pairs (SSIPs).

The donor complexes of cyclopentadienyllithium presented in this paper were prepared by adding an excess of the donor base to a suspension of CpLi in hexane at −15 °C, followed by addition of THF up to the formation of clear solutions. Crystallization from that solution was achieved at −23 and −45 °C. The clear, colorless, and low-melting crystals of CpLi·donor with donors = PMDETA (1), TMEDA (2), DME (3), and DIGLYME (4) have been selected and mounted for X-ray diffraction in inert oil at cryogenic conditions employing the X-Temp2 device.

Table 1. Li···Cpcentroid and Li–Donor Base Distances of Various (η⁵-Cp)Li Species

<table>
<thead>
<tr>
<th>compound</th>
<th>d(Li···Cpcentroid) [pm]</th>
<th>Li–C range [pm]</th>
<th>d(Li–donor base) [pm] (av)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>208.6</td>
<td>234.5(2) to 245.5(2)</td>
<td>229.5</td>
</tr>
<tr>
<td>2</td>
<td>193.0 (av)</td>
<td>224.8(2) to 229.9(2)</td>
<td>214.0</td>
</tr>
<tr>
<td>3</td>
<td>191.0</td>
<td>222.2(4) to 227.5(4)</td>
<td>199.6</td>
</tr>
<tr>
<td>4</td>
<td>198.8 (av)</td>
<td>230.00(10) to 235.96(10)</td>
<td>211.7</td>
</tr>
<tr>
<td>(η⁵-Cp)Li(12-crown-4) ¹²</td>
<td>206.3</td>
<td>234.5(5) to 241.9(5)</td>
<td>232.7</td>
</tr>
<tr>
<td>(η⁵-CpLi)₂</td>
<td>196.9</td>
<td>227.5(6) to 233.5(9)</td>
<td></td>
</tr>
</tbody>
</table>

av = average.

(η⁵-Cp)Li(PMDETA) (1). 1 crystallizes in the space group P1

Figure 1. Crystal structure of (η⁵-Cp)Li(PMDETA) (1). Disordered moieties (PMDETA is disordered by 57-43%) and hydrogen atom are omitted for clarity. Anisotropic displacement parameters are set to a 50% probability level. Selected bond lengths [pm] and angles [deg] (disordered moiety is labeled with (·)):

Li₁–N₁ 230.4(9), Li₁–N₂ 222.7(6), Li₁–N₃ 231.2(9), Li₁–N' 237.6(9), Li₁–N₂' 212.7(10), Li₁–N₃' 242.4(11), Li₁···Cpcentroid 208.6, N₁–Li₁–N₂ 81.5(2), N₁–Li₁–N₃ 104.6(3), N₂–Li₁–N₃ 80.7(2), N₁'–Li₁–N₂' 80.8(3), N₁'–Li₁–N₃' 105.3(3), N₂'–Li₁–N₃' 81.9(3).

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(η⁵-C₅)Li(TMEDA) (2). Adducts of CpLi derivatives containing TMEDA as a donor base are widely known because of the advantageous crystallization properties of TMEDA. After the first example of [(Me₃Si)₃C₅H₂Li·TMEDA]¹⁵,¹⁶ monomers of CpLi with various substituents such as trimethylsilyl,¹⁷ methyl,¹⁸ tert-butyl,¹⁹ tert-butyl,¹⁹ or 1-methylethylphosphines,²⁰ and isocylopentadienyl²² have been published. The bulky substituents of the Cp derivatives allow a higher solubility in hydrocarbons compared to nearly insoluble parent CpLi. However, the structure of (η⁵-C₅)Li(TMEDA) remains unknown to date. 2 crystallizes in the space group P2₁2₁2 with two molecules in the asymmetric unit (Figure 2). The Li···Cp centroid distance is shortened to an average of 193.0 pm, and the average Li–N distance is only 214.0 pm due to 2-fold coordination. The structural parameters differ slightly from the very similar compound (η⁵-MeC₅H₅)Li(TMEDA)¹⁸ with an average Li–N distance of 212.7 pm and a Li···Cp centroid distance of 191.8 pm. Apparently, the influence of the single methyl substituent at the Cp ring has negligible influence on the bonding situation.

Figure 2. Crystal structure of (η⁵-C₅)Li(TMEDA) (2). The second molecule within the asymmetric, disordered moieties, and hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are set to a 50% probability level. Selected bond lengths [pm] and angles [deg]: Li1–N1 214.9(2), Li1–N2 213.0(2), Li2–N3 214.2(3), Li2–N4 213.7(3), Li1···Cp centroid 192.9, Li2···Cp centroid 193.1, N1–Li1–N2 85.02(8), N3–Li2–N4 84.31(9).

(η⁵-C₅)Li(DIME) (3). DIME as the oxygen analogue of TMEDA has fewer beneficial properties for the crystallization of CpLi. Whereas with compounds 1 and 2 only 1.2 equiv of the donors was used, nearly 6 equiv of DIME was necessary to obtain at least a few crystals under the same crystallization conditions. The crystals are unstable outside the mother liquor. Purification by cooled filtration and washing with hexane (−78 °C) failed under formation of CpLi. The crystals are colorless rhombohedra. (η⁵-C₅)Li(DIME) (3) crystallizes in the space group Pna₂₁ with only one molecule in the asymmetric unit. The molecule is built analogously to 2 (Figure 3). With an average Li–O distance of 199.6 pm these distances of the donor atoms to lithium are significantly shorter than in 2 (214.0 pm). The Li···Cp centroid distance of 191.0 pm is close to that in 2 (193.0 pm). The bond distances are similar to the only other monomeric CpLi derivative coordinated by DIME, a lithiated P-cyclopentadienyl-substituted 1,3,2-diazaphospholene, with an average Li–O bond length of 197.5 pm and a Li···Cp centroid distance of 194.8 pm. The short Li–O distance compared to Li–N results from the higher contraction of the oxygen lone pairs and the higher local dipole moment of the donating region. Free DIME has no dipole moment at all, because the directions of the local dipole moments sum up to zero. The global dipole moment of DIME depends on the coordination to a metal ion and cannot be predicted herein. The local dipole moments of DIME can be compared with the dipole moments of Me₂O and EtOMe of 1.30 [D] and 1.17 [D], respectively. Compared to TMEDA they are twice as high as the dipole moments of trimethylamine (0.61 [D]) and triethylamine (0.66 [D]).²⁰

Figure 3. Crystal structure of (η⁵-C₅)Li(DIME) (3). Hydrogen atoms and disordered moieties have been omitted for clarity. Anisotropic displacement parameters are set to a 50% probability level. Selected bond lengths [pm] and angles [deg]: Li1–O1 202.3(4), Li1–O2 196.9(4), Li1···Cp centroid 191.0, O1–Li1–O2 82.17(15).

Figure 4. Crystal structure of [[DIME]₂Li][[(η⁵-C₅)Li]₁] (4). Hydrogen atoms have been omitted for clarity. Each lithocene moiety is half-occupied. Cp moieties labeled with (’) are symmetry generated. Anisotropic displacement parameters are set to a 50% probability level. Selected bond lengths [pm] and angles [deg]: Li1–Cp centroid 212121 with two molecules in the asymmetric unit. The molecule is built analogously to 2 (Figure 2). The Li···Cp centroid distance is shortened to an average of 193.0 pm, and the average Li–N distance is only 214.0 pm due to 2-fold coordination. The structural parameters differ slightly from the very similar compound (η⁵-MeC₅H₅)Li(TMEDA)¹⁸ with an average Li–N distance of 212.7 pm and a Li···Cp centroid distance of 191.8 pm. Apparently, the influence of the single methyl substituent at the Cp ring has negligible influence on the bonding situation.

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(addictional information)
Table 2. Li···Indenyl plane and Li—Donor Base Distances

<table>
<thead>
<tr>
<th>compound</th>
<th>(d(\text{Li}···\text{Ind})) [pm]</th>
<th>(\text{Li}−\text{C range} ) [pm]</th>
<th>(d_\text{av}(\text{Li}−\text{donor base})) [pm] (\text{av})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>223.0 (av)</td>
<td>232.3 (3), C1; 241.5 (2), C9</td>
<td>215.1</td>
</tr>
<tr>
<td>6</td>
<td>211.1 (2)</td>
<td>236.3 (3) to 251.5 (2)</td>
<td>203.4</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>212.3</td>
</tr>
<tr>
<td>(\eta^5)-IndLi(TMEDA))(^{26})</td>
<td>200.1</td>
<td>227.9 (4) to 237.9 (4)</td>
<td>210.3</td>
</tr>
<tr>
<td>(\eta^5)-1-MeIndLi(THF))(^{27})</td>
<td>229.0</td>
<td>230.9 (6) and 252.6 (6)</td>
<td>196.3</td>
</tr>
<tr>
<td>(\eta^5)-1-n-BuIndLi(sparteine))(^{27})</td>
<td>209.0</td>
<td>229.9 (6) to 243.2 (6)</td>
<td>211.8</td>
</tr>
<tr>
<td>(IndLi))(^{28})</td>
<td>198.2</td>
<td>228.9 (3) to 235.0 (3)</td>
<td></td>
</tr>
</tbody>
</table>

av = average.

Figure 5. Crystal structure of \(\eta^5\)-IndLi(PMDETA) (5). The second molecule within the asymmetric unit disordered moieties and hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are set to a 50% probability level. Selected bond lengths [pm] and angles [deg]: Li1−N1 218.9 (2), Li1−N2 214.2 (2), Li1−N3 212.6 (2), Li2−N4 219.8 (2), Li2−N5 213.8 (2), Li2−N6 211.5 (2), Li1−C9 214.5 (2), Li1−C12 232.3 (3), Li2−C12 239.5 (2), Li2−C19 231.5 (2), N1−Li1−N2 84.88 (9), N1−Li1−N3 118.64 (11), N2−Li1−N3 85.54 (9), N4−Li2−N5 84.96 (8), N4−Li2−N6 118.88 (9), N5−Li2−N6 86.39 (8), Li1−Ind 224.1 (2), Li2−Ind 221.8 (2).

\([\eta^5\text{Cp}]\text{Li}_{1}\] [TAS]. Recently Wheatley, Wright, et al. isolated a \(
\text{Cp}_2\text{Li}_3\) triple-decker anion accompanying a complex mixed vanadium—lithium cation.\(^{25}\)

\(\text{IndLi}−\text{PMDETA} (5), \text{DME} (6), \text{and DIGLYME} (7).\) Compared to \(
\text{Cp}\) the negative charge in the indenyl anion might additionally be distributed in an adjacent aromatic six-membered ring. Therefore, indenyl is a softer Lewis base and less attractive to hard metal ions compared to the cyclopentadienyl anion. Additionally, the negative charge in indenyl seems not to be as delocalized as in \(
\text{Cp}\) as in \(\eta^5\)-IndLi(TMEDA) the lithium ion coordinates in a \(\eta^5\)-position over the five-membered ring, but it is significantly shifted to the carbon atom C2 (Figure 6).\(^{26}\) In \(\eta^5\)-1-MeIndLi(THF) it coordinates in a \(\eta^1/\eta^3\)-position above C3.\(^{27}\) Stucky et al. already predicted a higher gross atomic charge at the donating solvent (Table 2). To vary the amount of donating electron density, indenyllithium (IndLi) has been treated \(\text{with the same donor base selection to give the Cp complexes.}\n
\(\eta^2\)-IndLi(PMDETA) (5). S was synthesized by adding PMDETA to a solution of IndLi in THF. It crystallizes in the space group \(P2_1/c\) with two molecules in the asymmetric unit. Due to the increased donor capacity compared to TMEDA, we anticipated the lithium ion in the new complex to be shifted to a position of higher charge concentration like in \((\eta^2\)-1-MeIndLi)(THF). However, in S the lithium atom coordinates in a \(\eta^1/\eta^5\) fashion over the C1/C2 bond, but significantly shifted to C2 (average distances: \(\text{Li}−\text{C1} 240.9\) pm; \(\text{Li}−\text{C2} 231.8\) pm). This at first sight counterintuitive slippage is triggered by the formation of an additional weak C−H···Ar hydrogen bond, reminiscent of the benzylithium coordination observed recently\(^{29}\) (Figure 6).
The hydrogen atom H17C (H5 in Figure 6) of the methyl group C17 (C3S) is pointing to the center of the six-membered ring with a distance to the aromatic plane of 252.7 pm (253.6 pm). This is a strong indication of a C–H···π interaction with the six-membered ring, giving the organometallic complex additional energy.30 The fixation of the Li(PMDETA) moiety in this six-membered ring, giving the organometallic complex additional action alone but also by hydrogen bonding. We revealed that (η5-1-MeInd)Li(TMEDA)26 show a similar interaction of a H atom with the π-system of the six-membered ring, although this was not noticed by the authors. In (η5-1-MeInd)Li(TMEDA)28 show a similar interaction of a H atom with the π-system of the six-membered ring, although this was not noticed by the authors. In (η5-1-MeCp)Li(TMEDA) the distance of the bonded H atom to the indenyl plane is 259.5 pm, in (η5-1-MeCp)Li(sparteine)27 and (η5-Ind)-Li(TMEDA)26 show a similar interaction of a H atom with the π-system of the six-membered ring, although this was not noticed by the authors. In (η5-1-MeInd)Li(TMEDA), the distance of the bonded H atom to the indenyl plane is 259.5 pm, in (η5-1-MeCp)Li(sparteine) 258.9 pm, and in (η5-Ind)Li(TMEDA) 268.0 pm. We are convinced that these interactions play a significant role in the arrangement of the cationic fragment relative to the anion. The position of the highest charge density is not chosen, but the Ind···H interaction operates as an additional anchor for the Li(donor base) moiety and represents a significant structure-determining factor. Especially in the 2-fold-coordinated (η5-Ind)Li(TMEDA) the Li(TMEDA) moiety seems to be rotated about 90° from the position of least steric hindrance. The lithium ions of the indenyllithium derivatives mentioned above have very different positions above the ring planes, which mostly depends on the supplied electron density from the donor base. The more density supplied, in this case by THF and PMDETA, the more the Ind···Li distance increases (227.4 pm and 221.7 pm) and the lithium ion shifts to the ring periphery. The influence of the Ind···H interaction then seems to prearrange the position toward the ring periphery and plays the leading role above the charge distribution in the indenyl plane. The spatial distance of the lithium ion and the hydrogen atom in 5, (η5-Ind)Li(TMEDA), (η5-1-MeInd)Li(TMEDA), and (η5-1-MeCp)Li-sparteine) is remarkably constant in the range 301.6 to 321.2 pm due to the comparable Li–O–C–H and Li–N–C–H connection along three similar bonds. In the superposition plot in Figure 6 it is clearly visible that this structural motif is displaced over the indenyl plane.

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The DME molecule (O2)3-chelates the same lithium ion, and a second bridges both metals of the dimer. The molecule crystallizes in the space group P21/n, and the asymmetric unit consists of half the dimer with an inversion center at the central C15–C15′ bond of the bridging DME molecule (Figure 7). The average distance of the oxygen atoms to the lithium ion is 203.4 pm, and the average O–Li–O angle is 93.2°. The Li–O distance of 199.5(2) pm is slightly shorter than Li–O1, at 204.2(2) pm, and Li–O2, at 206.6(2) pm. The steric constraint of the ethylene bridge leads to a less ideal coordination compared to the free arm of the bridging DME, resulting in a longer Li–O distance. The average Li–O distance in (η5-1-MeInd)Li(TMEDA)29 is 196.3 pm, and the average O–Li–O angle is 101.1°. Compared to DME, the higher dipole moment of THF (1.75 D) and the unconstrained arrangement of the molecules in (η5-1-MeInd)Li(TMEDA)29 give shorter Li–O distances and an even distribution of the donor molecules in the coordinative sphere of the metal. The consequence is a more pronounced transfer of electron density to the lithium ion, causing a weaker affinity to the π-system of the indenyl anion. The lithium ions shifts from the η5-position in 6 to a η3/η5-position in (η5-1-MeInd)Li(TMEDA)29. The shift occurs from a delocalized position to a position of higher localized charge concentration. This also matches with the distances of the lithium ion to the aromatic ring system. In 6 the Li–plane distance is 211.2(2) pm and the metal is slightly shifted to C1 and C2 (Li1–C9 244.5(2) pm; Li1–C1 236.3(2) pm; Li1–C2 236.7(2) pm; Li1–C3 246.4(2) pm; Li2–C8 251.5(2) pm). In (η5-1-MeInd)Li(TMEDA)29 this distance is 227 pm due to the reduced attraction of the lithium ion to the aromatic π-density. Short Ind···H interactions like in 5 were not detected in 6.

The treatment of IndLi with DIGLYME gives aSSIP. Like in 4, the Li1 ion is complexed by two molecules of DIGLYME. The counterion is a naked indenyl anion. Compound 7 crystallizes in the space group C2/c. The asymmetric unit consists of one octahedrally coordinated lithium ion and two indenyl anions with half-occupancy. The formation of a SSIP like in 7 has previously also been reported for fluorenyllithium.34

### CONCLUSION

In this work we have presented new unprecedented complexes of CpLi and IndLi. The Li···Cp center distance scales to the...
electron-releasing capacity of the donor base. The better the density supply from the base, the longer the Li···Cp_center distance. The donor capacity decreases in the order PMDETA > TMEDA > DME. Along this line the number of donor atoms decreases from three to two, and additionally the increasing steric demand of the Li(donor) moiety is also mirrored in the increasing Li···Cp_center distance. The position of the metal cation is not fully dictated by the electron density distribution in the indenyl rings and electrostatics. Interestingly, a strong C−H···π interaction of a PMDETA methyl group with the center of the Cp perimeter causes a shift of the lithium toward the C1 position. This sort of bonding has never been taken into account in these organometallic species before but clearly impacts the adjustment of the cationic fragment toward the delocalized electron density in the planar carbamions.

**Experimental Section**

**General Data.** All preparations were performed in a dry and O2-free N2 atmosphere using Schlenk techniques. Solvents were dried under reflux with appropriate drying agents in a N2 atmosphere. Organic substrates were purchased from Sigma Aldrich; lithium organic substrates, from Chemetall. CpLi has been prepared by lithiation of freshly distilled Cphp with n-Buli in Et2O at −15 °C.

**Synthesis of (η5-C5Me5)Li(PMDETA) (1).** C5Li (0.50 g, 6.94 mmol) was suspended in pentane (20 mL), and the mixture was cooled to −15 °C. PMDETA (1.45 mL, 9.94 mmol, 1.4 equiv) and THF (1.5 mL) were added dropwise until the white suspension turned into a clear and colorless solution. The mixture was purified by filtration and stored for crystallization at −23 °C. For isolation the clear and colorless block-shaped crystals and the mother liquor were cooled to −78 °C, filtrated, washed with cooled (−78 °C) pentane, and dried under reduced pressure. The product was obtained as a white solid, which converts into a crystalline solid (0.7 g, 35%). 1H NMR (500 MHz, THF-d8) 8.62. Found: C 72.12, H 8.70.

**Synthesis of (η5-C5Me5)Li(TMEDA) (2).** The synthesis of 2 is analogous to that for 1 [C5Li (0.50 g, 6.94 mmol), TMEDA (2.20 mL, 14.67 mmol), THF (8.0)]. The clear and colorless block-shaped crystals were filtered and washed with pentane at room temperature and dried under reduced pressure. The product was obtained as a white solid (0.57 g, 43%). 1H NMR (500 MHz, THF-d8) 7.47. Anal. (%) Calcd for C22H38O6Li2: C 75.60, H 9.73. Found: C 77.84, H 10.96.

**Synthesis of (η5-C5Me5)Li(DIGLYME) Li (3).** The synthesis of 3 is analogous to that for 1 [C5Li (0.61 g, 8.47 mmol), DME (5.50 mL, 52.92 mmol), THF (7.0)]. Crystallization was accomplished at −45 °C. The clear and colorless rhombuses were filtered and washed with cold hexane at −78 °C. Under reduced pressure compound 3 converts to CpLi and free DME donor base. No product could be isolated for characterization.

**Synthesis of (η5-C5Me5)Li(DIGLYME2) (4).** The synthesis of 4 is analogous to that for 1 [C5Li (0.50 g, 6.94 mmol), DIGLYME (2.00 mL, 14.06 mmol), THF (15.0)]. The clear and colorless needle-shaped crystals were filtrated, washed with pentane, and dried under reduced pressure. The product was obtained as white needles (0.89 g, 39%). 1H NMR (500 MHz, THF-d8) 7.38. Found: C 73.09, H 11.24, N 14.30.

**Crystal Structure Determination.** Crystals were selected in inert oil cooled by a N2 cooling flow generated by a XTEM2 device. The
data for 1, 3, and 4 were collected with an INCOATEC Mo microfocus source, and those of 5, 6, and 7 were measured with an Mo rotating anode, each equipped with INCOATEC mirror optics. The data for 2 were collected with a fine-focused sealed tube with a graphite monochromator. Each X-ray diffractometer was equipped with an APEX II detector on a D8-goniometer and a low-temperature device. The data were collected at 100(2) K with λ = 71.073 pm and integrated with SAINT, and an empirical absorption correction with SADABS. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using atoms giving crystal data for C46H58Cl2Sn. This can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

**REFERENCES**


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**NOTE ADDED IN PROOF**

A most interesting paper by Klett et al. was just published to elucidate the co-complexation of CpLi/IndLi and lithium amides.36