J. Am. Chem. Soc. **1994,** *116,* 6466–6467

Preparation, X-ray Crystallographic Analysis, and Stereoselective Electrophilic Capture of Coordinatively Isomeric *exo*-Lithium Complexes of Isodicyclopentadiene

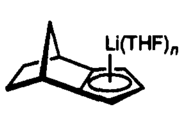
Florence Zaegel,[†] Judith C. Gallucci,[‡] Philippe Meunier,[†]
Bernard Gautheron,[*,†] Mark R. Sivik,[‡] and Leo A. Paquette[*,‡]

Laboratoire de Synthèse et d'Electrosynthèse
Organométalliques Associé au CNRS (URA 1685)
Université de Bourgogne
BP138, 21004 Dijon, Cédex, France
Evans Chemical Laboratories
The Ohio State University
Columbus, Ohio 43210

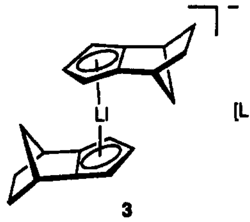
Received February 11, 1994
Revised Manuscript Received June 1, 1994

The structures of organolithium compounds *in solution* have been the subject of attention for four decades because of concerns regarding the mode of solvation, dynamic behavior, and reactivity of ion pairs. Chiefly as a consequence of their synthetic importance, enolates and lithium amide bases have been most heavily scrutinized.[1] Fraenkel and Hallden-Aberton were the first to demonstrate with a (peralkylcyclohexadienyl)lithium that triple ion formation can predominate in solution.[2] More recently, lithium cyclopentadienide was shown to exist as coordination isomers in THF.[3] Structurally similar ate-type complexes have been observed for a ferrocene-bridged cyclopentadienyl system[4] by Eiermann and Hafner and for lithium isodicyclopentadienide (isodiCpLi, **1**)[3] and its analogs[5] by our group in collaboration with Schleyer.

For **1**, the solution structures were determined to be **2** and **3** in which the lithium cation is η^5-coordinated to the exo face in both the contact ion pair and sandwiched states. The conversion of **3** to **2** is endothermic, as indicated by the predominance of **2** in solution at 25 °C. The importance of **2** and **3** is linked to the stereoselectivity with which these structurally distinctive aggregates experience electrophilic capture. The π-facially dissymmetric nature of the isodiCp anion makes the inherent exo reactivity of **2** and endo reactivity of **3** immediately apparent.[5,6]



2



[Li(THF)$_4$]$^+$

3

To achieve further clarification of those factors at play in these processes, we have been actively pursuing the preparation of solvated forms of **2** and **3** as crystalline entities. Herein are reported methods for the isolation of these complexes, their solid-state structures, and some indication of their reaction stereochemistry. The findings confirm the general impression[4] that superior ligands for Li$^+$ favor the triple ion dimer in which the second Li$^+$ is externally solvated.[7] More relevant, the present study establishes the feasibility of securing crystalline forms of cyclopentadienyllithium coordination isomers from an equilibrating system in a selective manner.

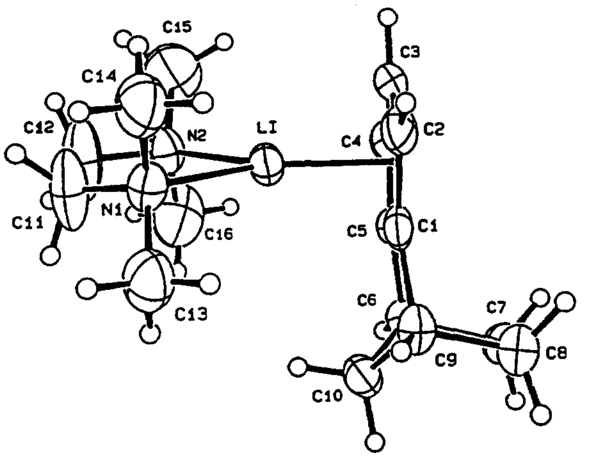


Figure 1. Thermal ellipsoid plot (30% probability) of the molecular structure of **4**.

When a suspension of **1** in dry ether was treated under argon with freshly distilled *N,N,N′,N′*-tetramethylethylenediamine (TMEDA),[8] a clear solution developed. After concentration to half-volume and cooling at −20 °C overnight, (isodiCp)Li(TMEDA) (**4**) was obtained as colorless, air- and moisture-sensitive crystals in 80% yield. The X-ray diffraction data clearly show the Li$^+$ to be positioned on the exo surface of the anion and coordinated to the two nitrogens of the TMEDA (Figure 1).

The Li–C distances for the "Cp" ring range from 2.216 to 2.267(12) Å so that the Li-to-Cp interaction clearly qualifies as η^5. The Li distance from the ring centroid (1.91 Å) is comparable to that observed in Li(C$_5$H$_4$CH$_3$)TMEDA (1.92 Å)[9] and Li[C$_5$H$_4$-Si(CH$_3$)$_3$]TMEDA (1.93 Å).[10] Atoms C(6) and C(9) are each 0.21 Å from the least-squares plane through C(1)–C(2)–C(3)–C(4)–C(5) and on the opposite side of this plane from the Li atom. This gives rise to a slight endo bending in the complex as is evident in the ORTEP drawing. The N(1)–Li–N(2) angle of 83.5(4)° is as expected for TMEDA bound to Li$^+$.

In a similar experiment, **1** was dissolved in dry THF under argon, treated dropwise with an excess of 12-crown-4 (predistilled from K), concentrated to approximately the 25% level, and cooled to −20 °C for 48 h.[11] By this means, [(isodiCp)Li(12-crown-4)]$_2$ (**5**) was isolated as pale yellow crystals (75%), which became green when exposed to air or light. The crystal structure of **5** determined at 203 K reveals the unit cell to be composed of two Li$^+$(12-crown-4)$_2$ ions and two independent [(isodiCp)$_2$Li]$^-$ complexes (Figure 2). Of the latter, the Li–C distances for the "Cp" ring are in a smaller range for molecule B [2.300–2.341(3) Å] than for molecule A [2.292–2.389(3) Å]. The respective Li to ring centroid distances are 1.987 and 2.008 Å. All of these

---

[†] Université de Bourgogne.

[‡] Ohio State University.

(1) (a) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988,** *110,* 3546. (b) Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987,** *109,* 6524.

(2) Fraenkel, G.; Hallden-Aberton, M. P. *J. Am. Chem. Soc.* **1981,** *103,* 5657.

(3) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1990,** *112,* 8776.

(4) Eiermann, M.; Hafner, K. *J. Am. Chem. Soc.* **1992,** *114,* 135.

(5) (a) Bauer, W.; O'Doherty, G. A.; Schleyer, P. von R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991,** *113,* 7093. (b) Bauer, W.; Sivik, M. R.; Friedrich, D.; Schleyer, P. von R.; Paquette, L. A. *Organometallics* **1992,** *11,* 4178. (c) Paquette, L. A.; Sivik, M. R; Bauer, W.; Schleyer, P. von R., submitted for publication.

(6) Sornay, C.; Meunier, P.; Gautheron, B.; O'Doherty, G. A.; Paquette, L. A. *Organometallics* **1991,** *10,* 2082 and relevant references cited therein.

(7) X-ray crystallographic analysis of a more complex structure having two interstitial lithium ions has been reported: Bladauski, D.; Broser, D.; Hecht, H.-J.; Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979,** *112,* 1380. See also: Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993,** *12,* 1266.

(8) Sendlinger, S. C.; Hagerty, B. S.; Rheingold, A. L.; Theopold, K. H. *Chem. Ber.* **1991,** *124,* 2453.

(9) Hammel, A.; Schwarz, W.; Weidlein, J. *Acta Crystallogr.* **1990,** *C46,* 2337.

(10) Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1984,** *262,* 271.

(11) Chen, H.; Jutzi, P.; Leffers, W.; Olmstead, M. M.; Power, P. P. *Organometallics* **1991,** *10,* 1282.

0002-7863/94/1516-6466$04.50/0

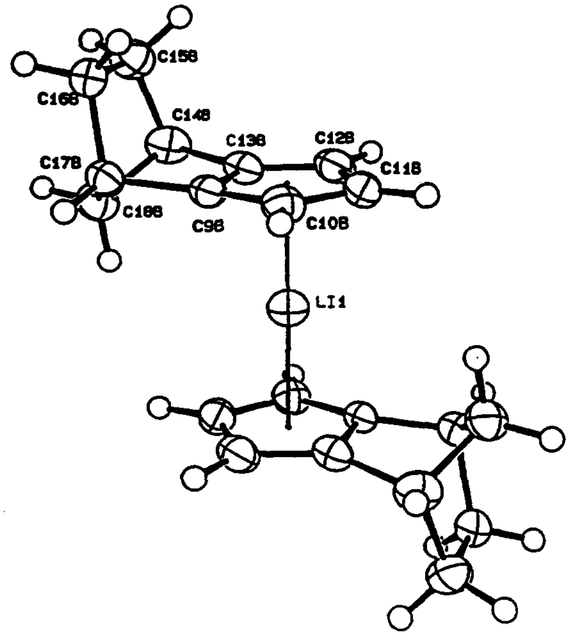


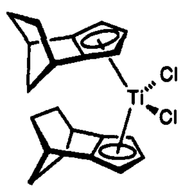
Figure 2. Thermal ellipsoid plot (50% probability) of one of the independent (isodiCp)$_2$Li molecules of **5**.

values are significantly longer than the analogous distances in **4**. However, other related complexes with comparable dimensions are known.[11,12] The isodiCp ligands in **5** are bent away from the Li at levels comparable to those found in **4**. Also, because each Li is on an inversion center, the Cp rings are in a staggered arrangement and the two isodiCp ligands are oriented in opposite directions.

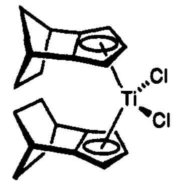
The discovery that reaction of **1** with different chelating agents results in coordination to different aggregation states corroborates the existence of an equilibrium between **2** and **3**, although less direct ways of arriving at **4** and **5** cannot be ruled out.

Modest stereocontrol in favor of the endo isomer was noted upon exposure of lithium reagents **1**, **4**, and **5** to methyl iodide (average 77%) and chlorotrimethylsilane (average 75%) in the temperature range −78 to 25 °C.[13] Virtually no stereoselectivity was observed with D_2O except for **1** at low temperature. In contrast, higher stereoselectivity is the rule with organometallic electrophiles such as $TiCl_3{\cdot}3THF$ and *exo*-(isodiCp)$TiCl_3$. The endo,exo (**6**), endo,endo (**7**), and exo,exo (**8**) complexes were produced to varying degrees[6,14] depending upon temperature and the nature of the lithium reagent. For example, condensations involving $TiCl_3{\cdot}3THF$ led to the following ratios for **6**:**7**:**8**. At 25 °C: **1** = 2, 3, 95%; **4** = 40, 20, 40%; **5** = 25, 15, 60%. At −64 °C: **1** = 5, 95, 0%; **4** = 35, 55, 10%; **5** = no reaction. The 12-crown-4 complex **5** is less stable and less reactive than that containing TMEDA. The highest stereoselectivity was observed with *exo*-(isodiCp)$TiCl_3$: (25 °C) **1** = 100% exo; **4** = 95% endo; **5** = 85% endo; (−78 °C) **1** = 95% endo.

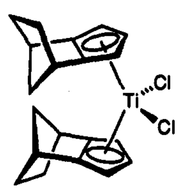
In light of these results, it becomes possible to refine the existing mechanistic model for these processes.[3] At first glance, it is not obvious that the lithium controls the facial selectivity. In the presence of CH_3I, Me_3SiCl, or D_2O, the similar product ratios realized with **1**, **4**, and **5** suggest that equilibrium between coordination isomers might be rapidly reestablished upon dissolution of all three complexes in THF at 25 °C[15] and that product formation is dictated by the more reactive of these two organometallics.



6

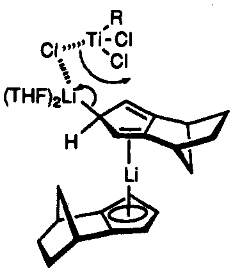


7

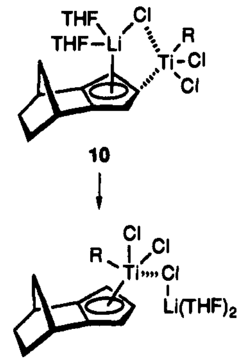


8

Complex **3** should be the inherently more associatable reagent if the peripheral lithium first becomes covalently linked because of the heightened Lewis-acidic character of this center.[16] As depicted in **9**, the electrophile would consequently be attracted to the endo surface and ultimately be converted to endo product.



9



10

11

Facial selectivity erodes when D_2O is involved because of the acid–base nature of the deuteron transfer and its appreciable exothermicity. As a consequence, **2** has the opportunity to compete and, by a related process, ultimately to position isotopic label on the exo surface in nearly comparable amounts.

The temperature dependence exhibited by **1** toward $TiCl_3{\cdot}3THF$ (endo/exo = 0:100 at 25 °C; 95:5 at −78 °C) is dramatic. At 25 °C where **2** predominates, the appreciable electrophilicity of this reagent promotes virtually exclusive reaction with this complex to deliver exo,exo product via **10** and **11**. In experiments involving **1** at −78 °C, associations with isomer **3**, which is highly favored in the concentration gradient, eventuate in stereochemical crossover. For **4**, the lithium remains sequestered by TMEDA. The less robust **5** might be expected to lend itself more than **4** to the production of exo,exo product **8**, and this is indeed observed. The stereoselection observed with (isodiCp)$TiCl_3$ as reaction partner is still more impressive.[17]

Supplementary Material Available: Crystallographic details, bond lengths, bond angles, positional parameters, anisotropic thermal (displacement) parameters, and calculated positional parameters for the hydrogen atoms of **4** and **5** (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(12) (a) Jutzi, P.; Schlüter, E.; Krüger, C.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 994. (b) Jutzi, P.; Schlüter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959. (c) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 737.

(13) (a) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105*, 3126. (b) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 7364.

(14) (a) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2159. (b) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873.

(15) TMEDA is well-known to be inferior to THF as a ligand for the lithium cation in LDA: Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448.

(16) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* (N.Y.) **1979**, *26*, 1.

(17) The Ohio State group thanks the National Science Foundation for financial support.