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Solid-State Structural Analysis of the "Naked" Isodicyclopentadienide Anion

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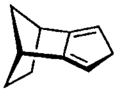
The crystallographically determined structural features of Na(isodiCp)(15-crown-5) and $[\text{K-cryptand}(2.2.2)]^+(\text{isodiCp})^-$ are compared to those of the corresponding Li(TMEDA) complex and the sandwich dimer involving Li^+ (cocrystallized with $Li(12\text{-crown-}4)_2$). The features of the potassium salt are distinctively different from those of its congeners. As a consequence of the encapsulation of the K^+ ion by the cryptand, no interaction occurs with the isodiCp anion, which is "naked". Notwithstanding the complete dissociation that exists, the stand-alone isodiCp anion exhibits appreciable folding about the bond that it shares with the norbornyl framework. The dihedral angle is 8.3(1)° in a downward direction away from the exo surface. This unrivaled opportunity to observe the free isodicyclopentadienide anion is shown to be in agreement with the results of HF−SCF calculations.

The remarkable contrasteric below-plane π-facial stereoselectivity[1] exhibited by isodicyclopentadiene (**1**) toward all but the most highly reactive dienophiles[2] has been rationalized at different times in terms of σ/π interaction,[3] pyramidal distortion,[4] torsional angle decompression,[5] and adduct thermodynamics.[6] Since experimental tests have since demonstrated the latter two interpretations not to be tenable,[7] the concept that disrotatory orbital tilting within ψ_1, induced by admixing of the high-lying norbornyl σ-orbitals with the proximal π orbitals of the fused diene (see the end-on view **2**), persists as the likely means by which destabilizing antibonding interactions are minimized during dienophile capture from the bottom. This issue gains increased significance in light of theoretical calcula-



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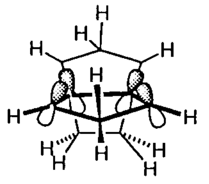

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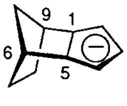

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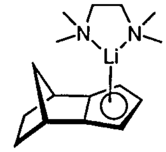

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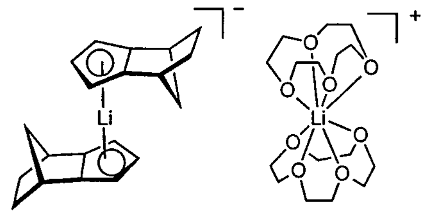

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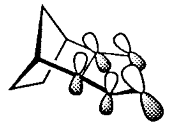

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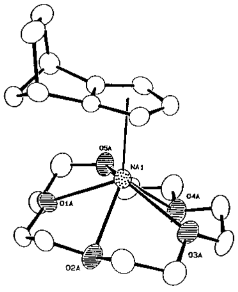
tions,[3] wide-ranging experiments,[8] and spectroscopic evidence[9] that suggest the stereoselection exhibited by the related isodicyclopentadienide anion (**3**) to be comparably governed. In this instance, the effect of the fused norbornane ring is to guide electrophilic attack cleanly to the endo surface of the more distal cyclopentadienide carbon. When titanium and zirconium halides are involved, variations in reaction temperature can lead to crossover in diastereoselection.[10] Detailed NMR studies of the lithium salt of **3** have shown a monomer−dimer equilibrium to be responsible for this reversal in stereocontrol.[11]

The question of the actual structure of **3** has more recently been probed by X-ray diffraction methods. Initially, the lithium aggregation isomers **4** and **5** were secured in crystalline form from the equilibrating system in a selective manner.[12] Both the TMEDA complex and the sandwich dimer (cocrystallized with Li(12-crown-4)$_2$) have their lithium atoms positioned *exo* with respect to the isodiCp ligand and strongly coordinated to the five-membered rings in essentially an η^5 fashion. The Li−ring centroid distances are 1.906(7) and 1.987(3)/2.008(3) Å for the two independent anions of **5**, respectively. Since the aim of our investigations was to produce alkali-metal complexes possessing an isodiCp ligand anion as “naked” as possible, the acquisition of suitably crystalline sodium and potassium salts was pursued, and the distinctively different structural features of Na(isodiCp)(15-crown-5) (**6**)[13] and [K-cryptand-(2.2.2)]$^+$(isodiCp)$^-$ (**7**)[14] are detailed herein.



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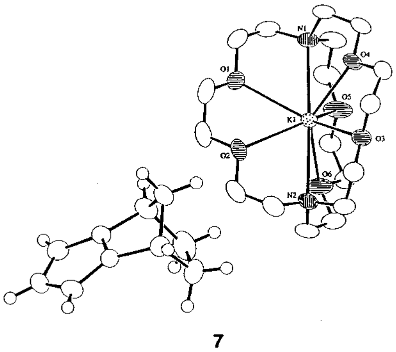

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The preparation of **6** was realized by deprotonation of **1** with NaNH$_2$ in THF under argon at 0 °C[15] and treatment of the resulting beige powder with dry 15-crown-5 in a manner adapted from Jutzi et al.[16] The pale green crystals (82% after crystallization from THF at −20 °C) are very air sensitive. (IsodiCp)K was obtained by deprotonation with KH[17] followed by admixing with cryptand(2.2.2) in THF. Crystallization from the concentrated blue-colored THF solution at −20 °C furnished purple-tinted crystals of **7** (79%). The relevant spectral data are compiled in Table 1.

Table 1. ^{1}H (200 MHz) and ^{13}C (50 MHz) Data (Values in ppm)

^{1}H NMR	isodiCpNa^a	**6**^{b}	isodiCpK^a	**7**^{a}
central	5.53 (t)	6.20 (t)	5.60 (t)	5.22 (t)
peripheral	5.31 (d)	6.02 (d)	5.17 (d)	5.04 (d)
bridgehead	3.06 (s)	3.67 (s)	3.02 (s)	2.97 (s)
exo-ethano	1.54 (d)	2.11 (d)	1.70 (d)	1.53 (m)
endo-ethano	0.72 (d)	1.45 (d)	0.74 (d)	0.74 (dd)
syn-methano	1.24 (d)	1.85 (d)	1.45 (d)	1.31 (d)
anti-methano		1.50 (d)	1.29 (d)	
^{13}C NMR				
central		105.0	103.8	104.3
peripheral		94.1	94.5	92.8
quaternary		129.1	130.0	127.7
bridgehead		42.4	42.0	43.0
ethano bridge		32.0	31.2	32.3
methano bridge		49.9	53.2	51.5

^{a} In THF-d_8 solution. ^{b} In C$_6$D$_6$ solution.

The Na(isodiCp) (15-crown-5) structure exhibits a Na−ring centroid distance of 2.535(4) and 2.502(4) Å for the two independent molecules in the asymmetric unit. This distance is significantly longer than that of 2.329 Å in [Na(Cp)$_2$]$^-$ [(TAS)Cp(TAS)]$^+$.[18]

The main feature of **7**, which sets it apart from **4**−**6**, is the fact that the K$^+$ is encapsulated by the cryptand and has no interaction with the isodiCp anion, which stands alone. Structural studies of naked cyclopentadienide complexes have been reported previously.[19]

A structural feature common to these complexes appears in the bend about the C(1)−C(5) bond, which is shared by the norbornane framework and the Cp ring. As a measure of this bend, the dihedral angle between the best planes through C(1)−C(2)−C(3)−C(4)−C(5) (Cp ring) and C(6)−C(5)−C(1)−C(9) is used. These angles are 8.4(1)° for **4**, 6.9(2)° and 8.1(2)° for **5**, 9.5(2)° and 11.1(2)° for **6**, and 8.3(1)° for **7**. Consequently, substan-

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(13) C$_{20}$H$_{31}$NaO$_5$; fw = 374.45; triclinic, $P1$; $a = 11.309(2)$ Å, $b = 13.628(2)$ Å, $c = 14.297(2)$ Å; $\alpha = 102.72(1)°$, $\beta = 109.73(1)°$, $\gamma = 92.99(1)°$; $V = 2003.8$ Å^3, $Z = 4$; $\rho_{calcd} = 1.24$ g/cm^3; I = 203 K. A clear 0.15 × 0.31 × 0.38 mm^3 crystal covered with Paratone N was placed in a cooled N$_2$ gas stream for data collection. A total of 9279 unique reflections were measured with Mo Kα radiation from 4° to 55° in 2θ. For the 4999 reflections with $F_o^2 > 1\sigma(F_o^2)$ and 469 variables, $R(F) = 0.060$ and $R_w(F) = 0.040$.

(14) C$_{28}$H$_{47}$KN$_2$O$_6$; fw = 546.79; triclinic, $P1$; $a = 10.380(1)$ Å, $b = 10.948(1)$ Å, $c = 13.678(2)$ Å; $\alpha = 85.86(1)°$, $\beta = 76.46(1)°$, $\gamma = 75.00(1)°$; $V = 1459.6$ Å^3, $Z = 2$; $\rho_{calcd} = 1.24$ g/cm^3; I = 208K. A clear 0.38 × 0.38 × 0.38 mm^3 crystal covered with Paratone N was placed in a cooled N$_2$ gas stream data collection. A total of 6746 unique reflections were measured with Mo Kα radiation from 4° to 55° in 2θ. For the 4714 reflections with $F_o^2 > 1\sigma(F_o^2)$ and 387 variables, $R(F) = 0.048$ and $R_w(F) = 0.039$. One of the ethyl fragments of the cryptand ligand is disordered and is modeled with two orientations.

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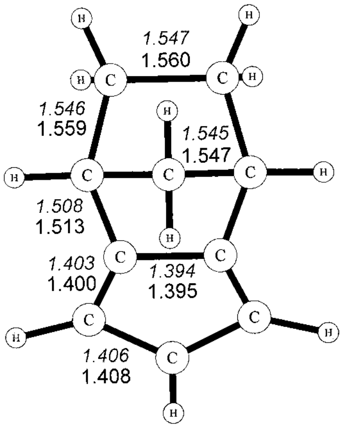

Figure 1. Comparison between the measured (*italics*) and calculated parameters for the isodicyclopentadienide anion.

tive downward folding of the Cp ring persists in the isodiCp anion, even when direct complexation to a metal is absent. The unit cell for **7** further reveals that the [K-cryptand(2.2.2)]$^+$ and [isodiCp]$^-$ are sandwiched in the solid state, with the anion alternating between an *exo* and *endo* disposition throughout its domain.

The structural determination of **7** provides an unrivaled opportunity to observe the isodiCp anion free of any ionic interaction from either π-surface. The *endo* tilting intrinsic to the naked species conforms to expectations based on INDO calculations.[3,8,20] According to this model, the substantial σ/π mixing causes tilting deformations within the peripheral p lobes of ψ_1 as in **8**. Presently, HF−SCF[21] calculations have been performed on anion **7**. The geometrical parameters obtained by X-ray methods (italics) and by making recourse to a 6-31G[22] basis set are compared in Figure 1.

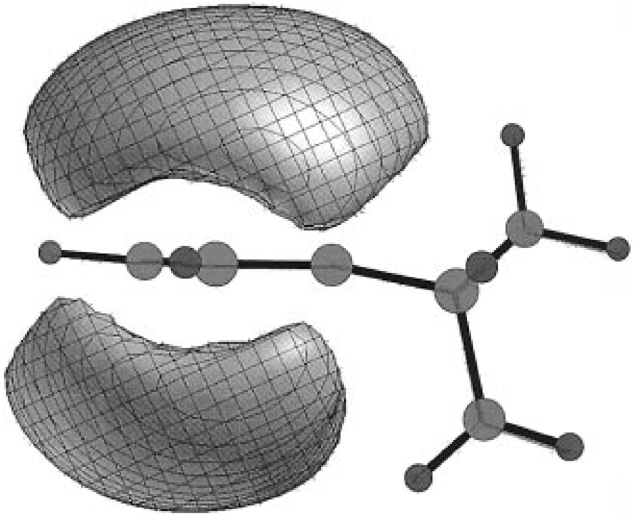

Figure 2. Electrostatic potential surface (−0.17) for the isodicyclopentadienide anion.

The very satisfactory agreement between these data provides suitable indication that the chosen basis is reliable. Examination of the highest occupied MOs provides no useful insight into the orbital tilting phenomenon. However, a plot of the electrostatic *iso*-surface reveals the existence of a higher potential on the *exo* surface syn to the methano bridge (Figure 2). These findings are an indication that electrophilic attack from the above-plane direction should be preferred.[23]

Supporting Information Available: Tables listing experimental details of the X-ray structure determinations, atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles for **6** and **7** (43 pages). Ordering information is given on any current masthead page.

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