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Adduct Influences on (Cyclopentadienyl)lithium

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Abstract: Extensive SCF calculations have been carried out to determine the metal–ring distance in compounds derived from (cyclopentadienyl)lithium by the addition of N-containing ligands coordinated to the Li atom. NH_3 groups have been used to model the ligands. The calculations suggest that the compounds are largely ionic with the N lone pairs coordinating to the positive Li atom, leading to longer and weaker metal–ring bonds. The effect of correlation is discussed on the basis of MP2 calculations for the smaller systems.

I. Introduction

Metal–cyclopentadienyl compounds represent an interesting class of organometallic molecules that have provided challenges for experimentalists as well as theoreticians. The difficulties in a quantitative theoretical description of the bonding in compounds involving the heavier metals are evident in the failure to predict the metal–ring distance for such compounds correctly with even very extensive SCF calculations.[1] This failure is due to the importance of correlation effects involving metal d-orbitals, suggesting that compounds with lighter metals might be better described within the SCF approximation. In fact, a previous study of the bonding and structure of magnesocene—bis(cyclopentadienyl)magnesium—yielded an optimized metal–ring distance only 2 pm longer than that found by gas-phase electron diffraction.[2]

Of particular interest is the very simplest of the metallocenes—(cyclopentadienyl)lithium—which should provide an excellent test case for the theoretical treatment of compounds of cyclopentadiene and light metal atoms. Unfortunately there are no gas-phase structure determinations of (cyclopentadienyl)lithium (CpLi), and the pure compound is assumed to polymerize in the solid state.[3] The best structural information for CpLi compounds derives from X-ray diffraction studies of derivatives involving adducts that coordinate to the Li atom. Lappert et al.[4] carried out one of the earliest of these structure determinations for a compound with one trimethylsilyl substituent on the cyclopentadiene ring and with the two nitrogens of a tetramethylethylenediamine (TMEDA) unit coordinating to a Li atom. The Li atom was found to be in the pentahapto position, i.e. vertically above the center of the Cp ring, with Li–N distances of 212 and 214 pm, and a distance from the Li atom to the ring center of 193 pm. Jutzi and co-workers[5-7] have studied Li–Cp compounds with three $Si(CH_3)_3$ ring substituents and a variety of ligands coordinating to Li, among these chinuclidin (1-azabicyclo[2.2.2]octane), TMEDA, THF (tetrahydrofuran), and PMEDTA (pentamethyldiethylenetriamine), all of which have the pentahapto structure. The monodentate ligand chinuclidin has a Li–N distance of 199 pm and a Li–ring distance of 179 pm, almost equal to the 180 pm found for THF (the other monodentate ligand in the series). For the bidentate TMEDA they find a Li–ring distance of 198 pm, and Li–N distances of 217 pm. The tridentate ligand PMEDTA coordinates only two of the N atoms to Li, and the geometrical parameters of the PMEDTA compound are quite close to those of the TMEDA compound. Finally, Hammel[8] has determined the structure of a TMEDA compound analogous to that investigated by Lappert et al. but with CH_3 replacing the $Si(CH_3)_3$ substituent, yielding a Li–ring distance of 192 pm and Li–N distances of 213.0 and 212.4 pm.

Theoretical investigations have concentrated on the unsubstituted CpLi compound, unhampered by the experimentalist's concern of protecting sensitive compounds by surrounding them with bulky groups. Early ab initio Hartree–Fock calculations carried out by Janoschek et al.[9] using a rather limited basis yielded an optimal Li–ring distance of 168 pm under the assumption of C_{5v} symmetry. Schaefer and co-workers[10] addressed the question of the position of the Li atom with only a C_s symmetry constraint, i.e. moving the Li atom in a plane through the ring center and one of the ring carbons, and perpendicular to the Cp plane. From a fairly exhaustive geometry optimization, they concluded that the molecule had a pentahapto structure with a Li–ring distance of 165 pm using an STO-3G basis set and 182 pm in a double-ζ basis, and with the Li atom in a very shallow potential well. They also found that the CH bonds were bent slightly out of the Cp plane, away from Li. Jemmis and Schleyer[11] optimized the Li–ring distance to 179 pm using a 3-21G basis, and Waterman and Streitweiser[12] reexamined the out-of-plane bending of the CH bonds, supporting Schaefer's interpretation of this as a simple Coulombic effect.

In a general discussion of haptotropic shifts Hoffmann and co-workers[13] analyzed the interaction of cyclopentadienyl with various ligands, based on the interaction between Cp and ligand valence orbitals. The highest occupied molecular orbitals of Cp are π-orbitals which belong to the A and E_1 representations of the C_{5v} group, and in CpLi these interact with the Li 2s and $2p_z$ orbitals and the $2p_x$ and $2p_y$ orbitals, respectively. On this basis they argue that a pentahapto coordination of the ligand should favorably maximize the interaction between the orbitals in the E_1 representation. Some support of this viewpoint may be found in an Xα-SW calculation by Lattman and Cowley.[14]

Thus, the best calculation for CpLi yields a metal–ring distance of 182 pm, but the experimental results range from 179 pm (for a single-N adduct) to 192, 193, and 198 pm (for double-N adducts). The N–Li interaction must affect the bonding between Li and Cp, and so the question as to what is the "real" Li–ring distance in bare, gas-phase CpLi remains. Also, the addition of an increasing number of nitrogen atoms coordinating to Li should lead to successive weakening of the metal–ring bond. To some extent this trend is reflected in the experimental results, but the

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Table I. Basis Sets[a]

primitives	ref	added function	contraction	mnemonic
C				
7s 3p	16	none	4s 2p	C42
9s 5p 1d	18	3d: $\zeta = 0.63$	5s 3p 1d	C531
13s 8p 2d	20	3d: $\zeta = 0.90$ 3d′: $\zeta = 0.45$	9s 5p 2d	C952
Li				
7s 3p	16	2p: $\zeta = 0.97537$ 2p′: $\zeta = 0.19182$ 2p″: $\zeta = 0.04507$	4s 3p	Li43
9s 3p	18	2p's from Li43	5s 3p	Li53
9s 3p 1d	18	2p's from Li43 3d: $\zeta = 0.1332$	5s 3p 1d	Li531
13s 4p	20	2p's in Table II	11s 4p	Li114
N				
7s 3p	16	none	4s 2p	N42
9s 5p 1d	18	3d: $\zeta = 0.63$	5s 3p 1d	N531
H				
3s 1p	17	2p: $\zeta = 0.8$	2s 1p	H21
5s 1p	19	2p: $\zeta = 0.8$	3s 1p	H31
8s 2p	20	2p: $\zeta = 1.14$ 2p′: $\zeta = 0.57$	2s 1p	H42

[a] ζ is the orbital exponent for Gaussian basis function.

data are sparse, the Li potential well is known to be quite shallow, and packing effects may be responsible for some of these displacements, considering the bulky groups involved. Finally, in a covalent picture, a tridenate N-containing ligand might be expected to utilize all of the E_1 contribution from the Li 2p-orbitals and remove the incentive for a pentahapto coordination of Li. In a series of model calculations we have attempted to address these questions. Below we first present the computational details of our calculations and then proceed to discuss the results obtained by us in the light of previous investigations and the above introduction.

II. Computational Details

The bare CpLi system is taken as the starting point for the model systems used in the investigation of the adduct effects, and then an increasing number of NH_3 groups are added to simulate the mono-, bi-, and tridentate ligands. Throughout most of the calculations these NH_3 units have been kept at a local C_{3v} symmetry with an N–H distance of 104 pm and an HNH angle of 107°. (On the basis of pilot calculations this N–H distance has been chosen somewhat longer than the experimental value of 101.2°[15] to achieve a slightly better approximation to the N environment in the experimental structure determinations.) The Cp ring structure has also mostly been fixed at a standard geometry, maintaining D_{5h} symmetry with the C–C distance 142 pm and the C–H distance 108 pm. Further details about the variation of geometrical parameters are presented in the next section.

Hartree–Fock calculations as well as second-order Møller–Plesset perturbation theory (MP2) calculations have been carried out with the program system DISCO.[16] In various parts of this study several Gaussian basis sets have been used. For CpLi we used three different sets: The smallest of these is a standard double-ζ basis derived by Roos and Siegbahn[17] for Li and C. Exponents for Li p-orbitals were derived by scaling down the p-exponents for B given by the same authors. For hydrogen, Huzinaga's[18] (3s) basis scaled by 1.44 and augmented by one p-orbital was used. A medium size basis set was taken from Dunning's[19] contraction of Huzinaga's[18] (9s,5p) basis, but contracted (5s,3p) rather than (4s,2p). Li p-exponents from the Roos–Siegbahn set above were used. Further, one d-orbital was added to the C set—the use of a d-orbital for the Cp carbons has previously been shown to be of importance for the metal–ring distance in magnesocene.[2] We also investigated the effect of using a d-orbital on Li for this medium size basis. For hydrogen Dunning's[20] scaled (5s) set with the same additional p-function as above was used. Finally, we used a large basis set taken from the compilation by van Duijneveldt.[21] The (13s,8p) C basis was taken directly from van Duijneveldt's tables and augmented by two d-orbitals. The Li (13s) basis was reoptimized somewhat, and four p-orbitals were optimized in a separate calculation on the $1s^2 2p^1$ configuration of Li. From our experience with the medium size basis no d-orbitals were used for Li with this set. For H the (8s) basis by van Duijneveldt was used, and 2 p-orbitals were added.

The CpLi calculation shows negligible changes in expanding the basis set from medium to large. For this reason only the two smallest sets were used for calculations on $CpLiNH_3$. Nitrogen basis sets were taken from Roos and Siegbahn[17] and Dunning[19] for the small and large sets, respectively, and for the larger set, one d-orbital was added. Calculations on $CpLi(NH_3)_2$ and $CpLi(NH_3)_3$ were carried out with the medium size basis, but without the d-orbital on Li, which turned out to be of little importance for the smallest systems. A summary of this basis set information is presented in Table I, and the Li (13s,4p) basis is listed in Table II.

Table II. Lithium (13,4/11,4) Basis Set[a]

s exponents	s exponents	p exponents
0.860574925+004	0.194900567+001	0.153455840+001
0.133317991+004	0.851562846+000	0.274852371+000
0.314066715+003	0.378407525+000	0.735526023–001
0.920748874+002	0.115190097+000	0.240055836–001
0.310930271+002	0.522574174–001	
0.116027231+002	0.228399682–001	
0.464251199+001		

[a] Derived by reoptimizing the 13s basis of van Duijneveldt.[21] Exponents for p-orbitals optimized in calculation on $1s^2 2p^1$ configuration. Only the 3 innermost s orbitals were contracted. Contraction coefficients: 0.833794–004, 0.615330–003, 0.306758–002.

Table III. Theoretical and Experimental Structural Parameters for Pentahapto CpLi Compounds[a]

compd	basis set	R_{Li-Cp}	R_{Li-N}	∠NLiN
CpLi	C42/Li43/H21	179.0		
	C531/Li53/H31	174.1		
	C531/Li531/H31	174.3		
	C952/Li114/H42	174.3		
$CpLiNH_3$	C42/Li43/H21/N42	184.1	202.6	
	C531/Li53/H31/N531	180.1	205.6	
	C531/Li531/H31/N531	180.1	206.0	
	experiment[b]	179	199	
$CpLi(NH_3)_2$	C531/Li53/H31/N531	192.3	215.0[c]	85.0[c]
	C531/Li53/H31/N531	194.2	218.7	95.0
	experiment[b]	198	217	84.1
	experiment[d]	192.8	213.1[e]	84.9
	experiment[f]	192	212.7[e]	
$CpLi(NH_3)_3$	C531/Li53/H31/N531	216	225.0[c]	97.3[c]

[a] The theoretical values are obtained in restricted geometry optimizations with fixed standard Cp and NH_3 geometries. R_{Li-Cp} is the distance from Li to the Cp plane. R_{Li-N} is the Li–N bond distance, assumed to be equal for all Li–N bonds in the same molecule. All distances in pm and angles in deg. [b] Reference 6. [c] Kept fixed during optimization. [d] Reference 4. [e] Average of two Li–N distances. [f] Reference 8.

III. Results

The results of our calculations are summarized in Tables III–V, which also contain some relevant experimental data. Below, we comment on these results in more detail.

A. CpLi. The Li–ring distance was first optimized under the assumption of a rigid, planar ring structure and pentahapto coordination, yielding an overall C_{5v} symmetry. The three different basis sets described in the previous section were used. The smallest basis gave a Li–ring distance of 179 pm, close to the 182 pm obtained by Alexandratos et al.[10] and the 179 pm by Jemmis and Schleyer.[11] Increasing the basis set and adding d-orbitals for polarization reduces the Li–ring distance by 5 pm, in analogy with what was found for magnesocene.[2] The distances from the largest basis sets are virtually identical, indicating that the medium size basis is sufficiently close to a saturation limit at the Hartree–Fock level.

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Table IV. Total Energies for Pentahapto CpLi Compounds Using the Different Approaches Described in Section III[a]

compd	basis set	method	energy
CpLi	C42/Li43/H21	HF/PO	−199.502 747
		HF/TO	−199.504 153
	C531/Li531/H31	HF/PO	−199.749 695
		HF/POH	−199.749 870
		HF/TO	−199.751 202
		MP2/PO	−200.487 743
		MP2/POH	−200.487 839
	C531/Li531/H31	HF/PO	−199.750 315
	C952/Li114/H42	HF/PO	−199.779 721
$CpLiNH_3$	C42/Li43/H21/N42	HF/PO	−255.673 614
	C531/Li53/H31/N531	HF/PO	−255.987 590
		HF/POH	−255.987 616
		HF/TO	−255.992 794
		MP2/PO	−256.932 297
		MP2/POH	−256.932 379
	C531/Li531/H31/N531	HF/PO	−255.988 727
$CpLi(NH_3)_2$	C531/Li53/H31/N531	HF/PO[b]	−312.199615
		HF/PO	−312.201 718
		HF/POH	−312.201 910
$CpLi(NH_3)_3$	C531/Li53/H31/N531	HF/PO	−368.409 465
		HF/POH	−368.409 731

[a] All energies in E_h. HF, Hartree–Fock; PO, partial optimization; POH, partial optimization including out-of-plane CH bend; TO, total optimization. [b] Li–N distance kept fixed.

The size of the larger systems investigated here precludes extensive optimization of all structural degrees of freedom, limiting us to the type of partial optimization described above. However, for CpLi we may also carry out more complete geometry variations, and thus get an indication of possible defects in the restricted approach. The simplest extension is a simultaneous optimization of the Li–ring distance and the out-of-plane bend of the CH bonds, which is the softest distortion mode for Cp. We have also carried out a complete optimization under a C_{5v} symmetry constraint. (This 5-fold symmetry eliminates possible ring puckering, but no such puckering is observed in the total optimization of $CpLiNH_3$ where only C_s symmetry is retained, and we conclude that this relatively hard mode is unimportant for the geometry variations.) As seen from Table V, both these schemes yield out-of-plane CH bends, and our totally optimized results compare favorably with those obtained by Waterman and Streitweiser.[12] Like them, we also find that the bend angle decreases with increasing basis set. Total relaxation reduces the C–C and C–H distances by approximately 1 pm—this may in turn be responsible for and increased out-of-plane CH bend.

Even though the experience with magnesocene suggests that the Hartree–Fock approximation provides a valid description of the structure in CpLi, it is desirable to obtain some indication of the influence of correlation. We have therefore optimized the Li–ring distance (with the other structural parameters fixed at standard values) in an MP2 calculation, using our medium size basis without the d-orbitals on Li. We obtain a reduction of the distance from the Hartree–Fock value of 174.1 to 172.1 pm. Unfortunately, upon closer inspection this entire effect is shown to be due to basis set superposition errors (BSSE). We have estimated this error from counterpoise calculations[22] for Cp^- and Li^+ and find that both MP2 and Hartree–Fock yield BSSE-corrected Li–ring distances of 174.7 pm. We believe that the use of ionic fragments in the counterpoise calculations may overestimate the superposition error somewhat. We are not able to do restricted Hartree–Fock (RHF) open-shell MP2 calculations, but estimates from RHF counterpoise calculations on Cp and Li suggest that the basis set used is reasonably free from superposition errors at the Hartree–Fock level of approximation and that the "real" ring distance is close to 174.3 pm. From our MP2 calculations the effect of correlation on the out-of-plane CH bend appears to be negligible. Thus, these exploratory MP2 calculations serve to strengthen our confidence in Hartree–Fock optimized structures for CpLi.

The calculated force constant for the Li–ring stretch is 1.25 mdyn/Å, corresponding to an IR absorption frequency of 580 cm^{-1}. Garbuzova et al.[3] have measured the IR and Raman spectra of the Li, Na, and K alkali–cyclopentadienyls in the solid phase, and for Li and Na also Raman spectra for solution. They are not able to assign the metal–ring stretch unambiguously, and a medium-strong line in the CpLi IR spectrum at 515 cm^{-1}—which they assign to a translation mode of the alkali atoms in the crystal lattice—is the frequency closest to our calculated value. Considering that CpLi in the solid state is assumed to have a polymer-chain structure, it is unclear what significance to attach to the agreement between our value and that obtained experimentally.

B. $CpLiNH_3$. The NH_3 group was kept at standard geometry throughout the calculations with an N–H distance of 104 pm and an HNH angle of 107°. A pentahapto coordination with a linear ring-center–Li–N configuration was assumed, and the Li–ring and Li–N distances were optimized simultaneously. Two basis sets were used, the smallest of these produced a Li–ring distance of 184 pm and a Li–N distance of 203 pm. Increasing the basis produced the same type of reduction of the Li–ring distance as seen for CpLi. However, the Li–N distance increases by a corresponding amount, and the net effect is just a shift of the Li atom toward the ring in an almost rigid $Cp–NH_3$ framework. A simple analysis of the two stretching motions predicts vibrational frequencies of 511 and 292 cm^{-1}, respectively.

$CpLiNH_3$ is still small enough to permit more complete geometry optimization. Again we have varied the CH bend angle, this time keeping the Li–ring and Li–N distances fixed at the optimum values found above. We have also done a total optimization using gradient methods. The CH bend angle is close to that found for CpLi, and the reduction of this angle upon total optimization may partly be a consequence of the increase in Li–ring and Li–N distances. As expected, the NH bond is considerably reduced by total optimization and comes out somewhat shorter than the experimental value of 101.2 pm. MP2 calculations yield a similar distance reduction for Li–ring (4 pm) and Li–N (3 pm) as seen for CpLi, but again we find this to be due mostly to superposition errors and choose to regard the Hartree–Fock values as quite reliable.

C. $CpLi(NH_3)_2$. The standard geometry of the NH_3 group described above was maintained and the $Li(NH_3)_2$ unit was kept at local C_{2v} symmetry, with the H atoms in the HNLiNH plane furthest away from the C_2 axis. Assuming pentahapto Cp–Li coordination with the Cp ring perpendicular to the local C_2 axis, this yields an overall C_s symmetry with three degrees of freedom for structure optimization: the Li–ring distance, the Li–N distance, and the NLiN angle. Optimization was initially performed only for the Li–ring distance with the remaining two parameters fixed at 215 pm and 85°, respectively (close to the values from Jutzi et al.[6]). Under these conditions the optimum Li–ring distance was found to be 192 pm.

However, the TMEDA unit used in the experiment places constraints on the relative position of the N atoms, and in order to elucidate the influence of this on the other structural parameters, the two NH_3 groups were released in a further simultaneous optimization of all three degrees of freedom. The overall estimated minimum is found for a Li–ring distance of 194 pm, a Li–N distance of 219 pm, and a NLiN angle of 95°. thus, the net result from releasing the NH_3 groups is a 10° opening of the NLiN angle, a lengthening of the Li–N bonds, and a slight increase in the Li–ring distance. Fixing the geometry at this optimized structure and optimizing the CH out-of-plane band separately yields an angle of 1.63°.

D. $CpLi(NH_3)_3$. This is a system with a total of 258 basis functions in our standard basis set, and our present computational resources preclude any extensive structure optimization. We have therefore maintained a local C_{3v} symmetry for the $Li(NH_3)_3$ units, again with the H atoms in the vertical mirror planes furthest from the C_3 axis. Li–N distances were kept at 225 pm and NLiN angles at 97° (estimated from trends in the previous calculations). Two

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Table V. The Effects of Total Geometry Relaxation in Hartree–Fock Calculations for Pentahapto CpLi and $CpLiNH_3$[a]

method	R_{Li-Cp}	R_{C-Cp}	R_{C-H}	∠CpH	R_{Li-N}	R_{N-H}	∠HNH
			CpLi C42/Li43/H21				
PO	179.0	(142.0)	(108.0)	(0.0)			
TO	179.5	141.5	106.9	3.05			
			CpLi C531/Li53/H31/N531				
PO	180.0	(142.0)	(108.0)	(0.0)			
POH	174.5	(142.0)	(108.0)	1.21			
TO	174.7	140.9	107.2	1.46			
			$CpLiNH_3$ C531/Li53/H31/N531				
PO	180.1	(142.0)	(108.0)	(0.0)	205.6	(104.0)	(107.3)
POH	(180.1)	(142.0)	(108.0)	1.31	(205.6)	(104.0)	(107.3)
TO	181.5	140.8	107.3	1.23	206.8	100.2	107.1

[a] R_{Li-Cp} is the distance from Li to the Cp plane, R_{C-C} is the Cp C–C distance, and ∠CpH is the out-of-plane CH bend. R_{Li-N} is the Li–N bond distance, ∠HNH and R_{N-H} are the NH_3 bond angle and bond length. PO, partial optimization; POH, partial optimization including out-of-plane CH bend; TO, total optimization. Numbers in parentheses indicate that the parameter was kept fixed at this value during optimization. All distances in pm and angles in deg.

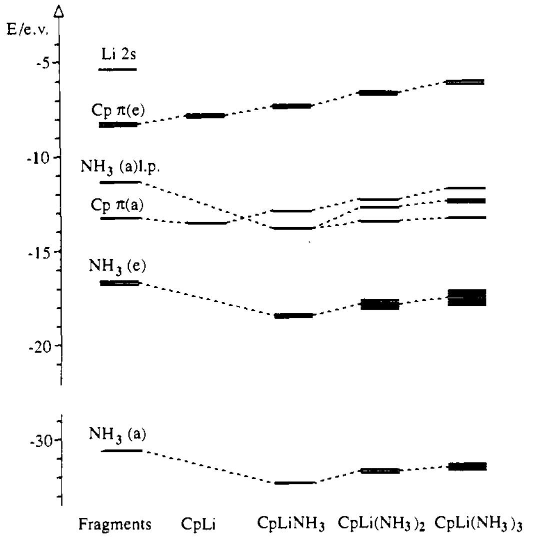

Figure 1. Variation in orbital energies for CpLi compounds.

Table VI. Calculated Orbital Energies (eV) for CpLi and Various Fragment Configurations[a]

	Cp^-/Li^+ sep	Cp^-/H^+ froz	Cp^-/H^+ rel	CpLi	Cp/Li sep	
					-5.33	Li 2s
e_1	-1.61	-8.53	-7.81	-7.89	-8.11	e_1
a_1	-7.24	-14.86	-14.07	-13.47	-13.12	a_1
e_2	-7.89	-14.10	-13.58	-13.55	-14.39	e_2
e_1	-8.60	-14.75	-14.29	-14.26	-14.99	e_1
a_1	-12.87	-18.83	-18.56	-18.50	-19.21	a_1
e_2	-13.82	-19.76	-19.40	-19.40	-19.43	e_2
e_1	-19.40	-26.04	-25.33	-25.28	-25.90	e_1
a_1	-24.71	-32.14	-31.07	-30.91	-31.46	a_1

[a] sep, separated fragments; froz, frozen orbitals; rel, relaxed orbitals. See text for further explanation.

series of optimizations were performed, one with the Li atom in a pentahapto position and one with Li vertically above one of the ring carbons in a monohapto configuration corresponding to that discussed by Anh et al.[13] in their analysis of sigmatropic shifts. The pentahapto configuration yields a minimum at a Li–ring distance of 216 pm, while the monohapto minimum is found at 225 pm and at 6 kcal/mol higher energy. Separate optimization of the CH bend angle yields 1.95°.

IV. Discussion

As pointed out in the introduction, the chemical bonding in CpLi may be described in a simple MO-interaction picture. In the C_{5v} symmetry of the pentahapto complex, the occupied Cp π-orbitals span the A_1 and E_1 representations, while Li 2s transforms according to A_1, and the (empty) Li 2p orbitals split into A_1 and E_1. The bonding in the complex is effected by placing the 6 valence electrons of the system in what is essentially the Cp π-a_1 and π-e_1 orbitals.

Our main tools in analyzing the bonding situation in CpLi and the N adducts are the orbital energies and a population analysis. Orbital energies are presented in Figure 1 for the orbitals supposedly involved in the bonding—the Cp π-a_1 and π-e_1 and the valence orbitals of the NH_3 groups. Starting with the orbital energies of the fragments, we trace the development from bare CpLi through increasing degrees of NH_3 addition. The combination of Li and Cp to make CpLi is accompanied by a lowering of the Cp π-a_1 orbital energy; however, the Cp π-e_1 orbitals are not lowered correspondingly. In fact, this orbital energy increases, and the increase is almost identical with that observed for the highest lying Cp σ-orbital (σ-e_1), suggesting that these energy changes are due to charge transferred from Li to provide a significant ionic contribution to the bonding. Thus, the Cp–Li bond appears to be due almost exclusively to interaction between orbitals with A_1 symmetry.

It is difficult to ascertain the degree of ionicity in the CpLi bond. A comparison of orbital energies for CpLi with those of the separated systems Cp^-/Li^+ and Cp/Li (Table VI) shows great dissimilarity between the separated ions and the two other systems. However, this comparison is hardly realistic as these ionic fragments would be quite close in CpLi, with a concomitant stabilization of the Cp^- orbitals by the proximity of a positive charge. The effect of this stabilization may be gauged by calculating the orbital energies of Cp^- in the presence of a positive charge. We have done this at two levels—first with a proton 174 pm above a Cp^- ion with frozen orbitals and second with a fully relaxed electron distribution for the same Cp^-/H^+ system. The frozen orbital model yields a dramatic orbital stabilization, but some of this is undone by the subsequent relaxation. Even the relaxed model may overestimate the stabilization, due to the use of H^+ instead of Li^+. This primarily affects the highest a_1 orbital and manifests itself as a significant shift of electrons into the most diffuse p_z orbitals on C. (A more rigorous way to treat this stabilization problem would be to carry out a constrained space orbital variation in the manner of Bagus et al.[23]). Disregarding this highest a_1 orbital, the electronic environment of Cp in CpLi as reflected in the orbital energies is considerably closer to the relaxed Cp^- ion in the presence of a positive charge than to a separate neutral Cp. We conclude from this that there is a sizable ionic contribution to the CpLi bond, at least of the magnitude suggested by the 0.6 electron charge transfer obtained in the Mulliken population analysis.

The addition of one NH_3 group leads to a red-shift of the Cp orbital energies. For the entire $CpLiNH_3$ complex this is compensated by a lowering of all valence NH_3 orbitals and particularly the N lone pair orbital which is pointing toward the electron depleted Li atom. Successive addition of NH_3 groups further

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(23) Bagus, P. S.; Herrman, K.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *80*, 4378–4386.

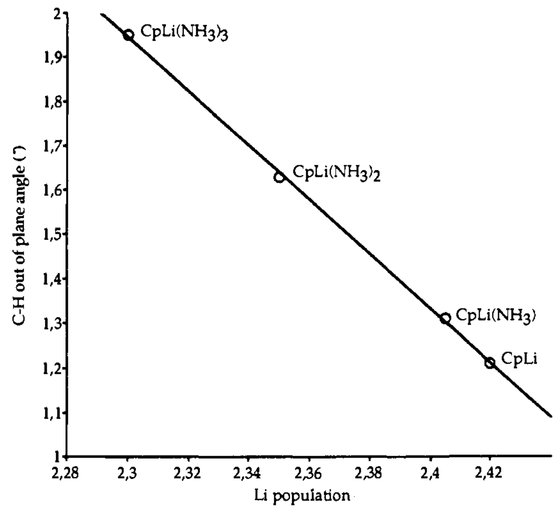

Figure 2. Variation in CH bend angle and Li population for CpLi compounds. The bend angle is calculated from partial geometry optimization (POH).

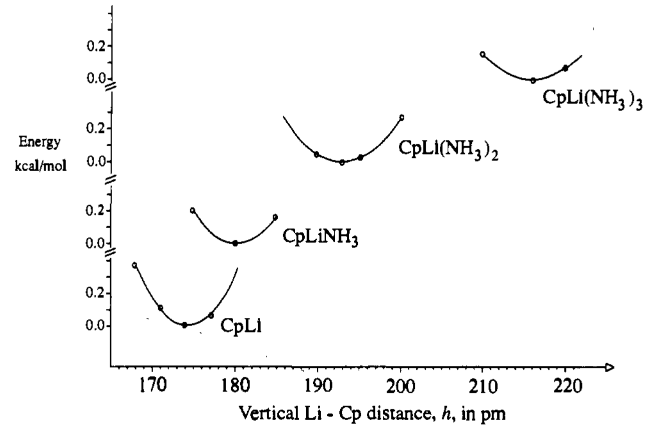

Figure 3. Change in potential and Li–ring distance with increasing N-substitution for CpLi compounds.

Table VII. Fragment Energies (E_h) and Energies of Formation from Fragments (kcal/mol)[a]

Fragment Energies	
Li^+	−7.236
Li	−7.432
Cp	−192.203
Cp^-	−192.233
NH_3	−56.196
Formation Energies	
Cp + Li → CpLi	−72.2
$Cp^- + Li^+ \rightarrow CpLi$	−176.3
	−172.6[b]
	−163.2[c]
$Cp + Li + NH_3 \rightarrow CpLiNH_3$	−98.5
$Cp + Li + 2NH_3 \rightarrow CpLi(NH_3)_2$	−109.8
$Cp + Li + 3NH_3 \rightarrow CpLi(NH_3)_3$	−116.7

[a] Hartree–Fock values unless otherwise indicated. [b] Hartree–Fock value corrected for superposition error. [c] MP2 value corrected for superposition error.

red-shifts the Cp orbitals, and with more NH_3 units to share the complexation energy, also ligand orbitals shift to higher energies with increasing substitution. The Mulliken population analysis indicates that a negative charge of 0.6–0.7 is transferred from Li to Cp while the NH_3 fragments remain neutral. The populations are virtually constant throughout the series, but they are sensitive to the inclusion of d-orbitals on Li, which reduces the transferred charge to 0.4.

In summary, our calculations depict the bonding in these compounds as a largely ionic bond between Cp and Li, created by a transfer of charge from Li to Cp. The NH_3 units successively added are stabilized by an interaction between the N lone pair and the positive Li atom. No evidence is found of significant Cp π-e_1 orbital participation anywhere in these complexes. Our conclusions are in agreement with the analysis by Waterman and Streitweiser[12] that the out-of-plane bending of the C–H bonds in CpLi is due to electrostatic interaction rather than distortions to facilitate overlap between Cp π-e_1 and Li 2p orbitals. Accepting this premise, the out-of-plane CH bend may also be taken as an indicator of the positive charge on Li. In Figure 2 we show how the calculated bend angle increases with increasing NH_3 addition. We note the almost linear relation between the bend angle and the Li atom population. The increase in bend angle with increasing CpLi distance supports our view of this as a mainly ionic system where the charge polarization increases with increasing Li–ring distance.

Experimental structural information is available only for compounds differing significantly from our simple model systems, and then only in the solid phase. The potential for the Li atom is quite flat for Cp and becomes even flatter as the NH_3 groups are added, as demonstrated in Figure 3. Possible distortions due to packing effects and bulky substituent groups must therefore be kept in mind when comparing the present calculations to experimental data. Comparing our $CpLiNH_3$ results to the structural data by Jutzi et al.[6] for the chinuclidine complex, we find excellent agreement for the Li–ring distance, whereas the Li–N distance is off by 7 pm conceivably due to the considerable difference between chinuclidin and NH_3. For $CpLi(NH_3)_2$ it is natural to compare with the TMEDA complexes studied by Lappert et al.,[4] Jutzi et al.,[6] and Hammel.[8] Two of these complexes differ only in the number of trimethylsilyl groups attached to the Cp ring—1 (Lappert) and 3 (Jutzi), respectively. Unfortunately the Li–ring distances from the two structures differ by 5 pm, and the Li–N distances differ by 4 pm. Comparison of the calculated parameters for $CpLi(NH_3)_2$ with the experimental data for the monotrimethylsilyl TMEDA complex reveals differences very similar to what is observed between $CpLiNH_3$ and the chinuclidin complex. This is somewhat puzzling, because the chinuclidin complex has the same ring substituents as the other TMEDA complex with three trimethylsilyl groups. This difference in behavior may be due to the weaker potential of the complexes with two nitrogens, making these more susceptible to repulsion between the ring substituents and the TMEDA units. We conclude that the longer Li–ring and Li–N distances in the mono-methyl and mono-trimethylsilyl Cp-TMEDA compounds as compared to the chinuclidin complex are a result of adding more nitrogens rather than packing and steric repulsion, and that the additional Li–ring lengthening observed for the trimethylsilyl compound is due to steric repulsion between bulky substituents.

We know of no structural data on compounds where CpLi coordinates three N atoms. With the lack of e_1 orbital participation in the bonding observed for all members of this series, there is no a priori reason why $CpLi(NH_3)_3$ should be less prone to pentahapto coordination than the smaller compounds. Our calculation indicates that a monohapto coordination directly above the Cp plane is improbable, but we have not been able to investigate possible end-on configurations with a tilted $Li(NH_3)_3$ group and the Li no longer constrained to be directly above the Cp plane. However, for this compound the ring-$Li(NH_3)_3$ stretching potential is extremely flat and packing as well as steric repulsions may have a decisive effect on the molecular structure.

The possibility of coordinating three N atoms to Li in CpLi may also be discussed in light of the calculated formation energies of these compounds from their fragments. In Table VII we list the fragment energies and the formation energies of the various molecules. While Hartree–Fock reaction energies in general cannot be regarded as accurate, we expect the trends exhibited in Table VII to be quite realistic. The simplest reaction is that of the neutral fragments yielding CpLi. The energy of this reaction is much smaller than that obtained with ionic fragments, due to the unfavorable separation of charges in the dissociated limit. The superposition error is small at this level, while correlation changes the ionic fragment reaction energy by 15 mhartrees. This is due mainly to the importance of correlation in describing the electronically crowded Cp^- ion. The effect of correlation should be smaller for the reaction of the neutral fragments, and it might well be reversed, favoring the final product more than do the Hartree–Fock calculations.

The successive additions of NH_3 groups are all exothermic, but decreasingly so. With increased crowding around the Li atom, correlation may improve results for the larger systems, but the LiN bond is mostly electrostatic, and the effect should not be dramatic. There is certainly nothing in these results precluding the coordination of three N atoms by a CpLi compound, but the low reaction energy of the last N addition will probably make it vulnerable to competing reactions which may keep one N atom away from the two that coordinate to Li.

We feel that the present calculations provide a satisfactory understanding of the bonding and electronic structure in these CpLi compounds. However, some further improvements readily suggest themselves. The simple model systems we have employed are quite far from the compounds investigated experimentally, and this excludes effects like strain and substituent repulsion from our calculations. Although our MP2 calculations show correlation effects to be of minor importance for the structural features of CpLi, a more complete treatment should provide definitive conclusions on this point.

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