association of sodium salts, while those of potassium can readily form ion pairs.

The trend of increasing solvation number with increasing heat of solution (as evidenced through more ion pairing with ClO_4^-) follows for the series $Cs^+ > K^+ \simeq Li^+ > Na^+$ with solvation numbers of 5, 4, 4, and 3, respectively. In agreement with this trend Na^+ does not form ion pairs with the ninhydrin anion radical. The lithium ion, however, does not follow this trend, and has a K_{diss} that is much too large when the anion radical of ninhydrin serves as the anion. This may be explained in part by the fact that the Li^+ ion does not have p orbitals available for possible interaction with the conjugated π system of the aromatic anion radical.

From the use of a cation sensitive electrode Nakamura has found that the sodium ion is trisolvated by HMPA when HMPA is added to an ACN solution of sodium perchlorate.[28] These results are in perfect agreement with our results. However, from the addition of HMPA to a lithium perchlorate solution in ACN he could only obtain the lithium cation disolvated by HMPA. This was attributed to the steric effect in the reactions between large HMPA molecules around the small lithium cation.[28] Our results are not in accord with this, but their data might be better explained by the existence of a strong competition for the third and fourth coordination sights between the ACN and HMPA in their system. For the sodium ion HMPA dominates the third site, since it has a stronger affinity for the HMPA than does lithium.

Experimental Section

All of the organic compounds used were purchased from Aldrich Chemical Co. The inorganic salts were purchased from Alfa Inorganics and were stored in a vacuum oven for 48 h at 100 °C prior to use. The method of reduction of neutral molecules to form anion radical and the purification of the HMPA has been previously described.[29]

The g values were measured on a Varian E-9 ESR spectrometer using the dual cavity technique.[30] All values for g were obtained by placing a sample of the free ion in one of the two cavities and a sample containing a known quantity of salt in the other.

The determinations of the gas solubilities and Henry's constants were carried out with the use of a vacuum system connected with a Toepler pump fitted with a gas buret in the same manner as previously described.[15] The methylacetylene was also treated and stored as described previously.[15]

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The Simplest Metallocene: Cyclopentadienyllithium

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Abstract: Calculations were carried out on cyclopentadienyllithium with minimum and double ζ basis sets. The potential curve of the Li over the cyclopentadienyl ring was mapped out with the result that the Li is most stable above the middle of the ring. Geometry optimization of both the cyclopentadienyl ring and the most stable cyclopentadienyllithium complex was carried out and the effect of complexation noted. Optimal scale factors were determined with the minimum basis set. The two basis sets were compared with a view toward establishing the reliability of the minimum basis set for work with larger metallocenes. Using the double ζ basis set, it was determined that the hydrogens do not lie in the plane of the C_5 ring.

The area of metallocene chemistry has proven to be a very fertile one; elucidation of the structure of the metallocenes has occupied the efforts of both experimentalists[1,2] and theoreticians.[3] Ferrocene is the most prominent of the metallocenes and indeed its chemistry and structure have been intensively investigated. The nature of its bonding is most often explained as an interaction between the e_{1g} HOMO orbitals of the cyclopentadienyl ligands and the e_{1g} (d_{xz}, d_{yz}) orbitals of the

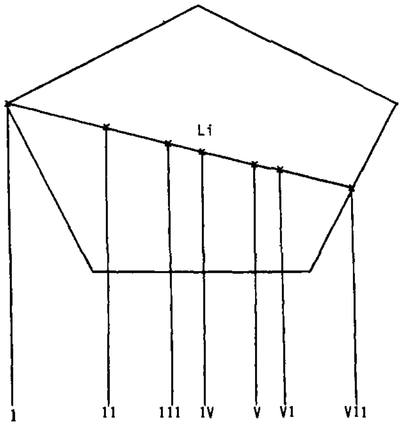

Figure 1. Calculated points on the potential curve over the Cp ring.

metal. The bonding characteristics of other metallocenes have been investigated via ESR and susceptibility measurements.[4] From the theoretical viewpoint, extensive Hartree-Fock studies of the transition metal cyclopentadienyl complexes represent a major theoretical challenge and certain approximations are usually employed[5-7] which still allow an insight into the nature of the structures. However, quite recently Bagus, Wahlgren, and Almlöf[8] have completed an ab initio self-consistent field (SCF) study using a flexible basis set of better than double ζ[9] quality.

In order to help build a sound foundation for a systematic study of the metallocenes, we decided to perform a careful study of what might be considered the simplest metallocene: cyclopentadienyllithium (CpLi), which may be considered to be a cyclopentadienyl anion (Cp^-) complexed with a lithium cation. Our effort was directed at determining the most stable position of the Li over the ring, with geometry optimization of both the Cp^- and the CpLi species. To our knowledge, only solution chemistry has been done on the CpLi complex. Although experimental investigations of this complex are difficult due to complications arising from solvent dependencies[10] and the entire question of what type of ion pairing is involved,[11] some conclusive work seems to have been carried out by an investigation of its ^{7}Li NMR spectrum by Cox and co-workers.[12] From studies on the effect of solvent, cation, and temperature on the proton chemical shifts of CpLi, it was concluded that this species exists in solution as a contact ion pair.[11] Furthermore, the ^{7}Li chemical shift in CpLi is completely compatible with the suggestion that the Li cation is located directly above the π cloud of the Cp^-, in the shielding region of the induced diamagnetic ring current. Other experimental work has been done by Wagner and Ebel,[13] who measured the absorption spectrum of CpLi in diethyl ether as well as doing Pariser-Parr-Pople Configuration Interaction (PPP-CI) calculations on the molecular states of Cp^-.

Knowledge of how the Cp^- ring is perturbed upon complexation with Li^+ is important in understanding the bonding of the complex. There have been several theoretical studies in this regard. Preuss and co-workers[14] did a floating spherical Gaussian orbital[15] (FSGO) calculation on the Cp^- ring; it should also be noted that they did an FSGO calculation on the CpLi complex,[16] wherein they optimized the distance of the Li over the middle of the ring. CNDO/2 calculations done on Cp^- determined[17] that the anion is most stable in the symmetrical D_{5h} geometry with C-C bond lengths of 1.401 Å (the C-H bond lengths were fixed at 1.08 Å). MINDO/3 calculations by Dewar and Haddon[18] also showed the planar D_{5h} structure to be most stable with optimum C-C bond lengths of 1.417 Å and optimum C-H bond lengths of 1.110 Å. Gallup and Norbeck[19] carried out valence-bond calculations on the Cp^- species and found the symmetrical structure to be most stable; eight valence-bond structures were used to give the total wave function. Most recently, Lichtenberger and Fenske[20] calculated the energy and wave function of the Cp^- species using a minimum basis set of contracted Gaussian functions, while assuming a D_{5h} geometry. The most extensive ab initio work other than ours on CpLi to date is a STO-3G study of Schleyer et al.[21]

Theoretical Details

Calculations were done using single determinant self-consistent field (SCF) theory. Two basis sets of contracted Gaussian functions[9] were employed. The first and more extensive basis used was a double ζ (DZ) basis set, including two basis functions per atomic orbital. For carbon and hydrogen, the Dunning-Huzinaga set was used[22,23] with the basis on carbon being (9s5p/4s2p) and that on hydrogen being (4s/2s). The Li basis was that used by Pearson, Hunt, Bender, and Schaefer[24] and involved a Dunning-Huzinaga (9s/4s) set as well as a 4p set obtained by Williams[25] contracted to 2p using Dunning's rules;[22] the set on Li was thus (9s4p/4s2p). Since it was of interest to see how the results of a double ζ calculation coincide with those from a minimum basis set, which seems to be a more practical set for the larger metallocenes, the second basis set used was the STO-3G set.[26] Standard orbital exponents were used, though the effect of exponent optimization was also investigated.

All calculations were done on the Harris Corporation Slash Four minicomputer using the GAUSSIAN-70 computer program.[27]

The calculations were done as follows: the C-C and C-H bond lengths in the Cp^- ring were first optimized assuming D_{5h} symmetry. Then, the position of the Li over the ring (using the previously optimized Cp^- parameters) was optimized. This was accomplished by moving the Li from directly over one carbon (position I) to one-half the distance from the carbon to the middle of the ring (II), then two-thirds of that distance (III), then over the middle (IV), then one-third of the distance from the middle to the midpoint of the opposite bond (V), then one-half of that distance (VI), and finally over the midpoint of that bond (VII). The positions are marked in Figure 1. At *each* position over the ring, the Li-ring distance was optimized. Then, once the optimum Li position was determined, the Cp^- ring was reoptimized to note the effect of complexation. These calculations were done with both the DZ and STO-3G basis sets. Also, to note the effect of constraining the orbital exponents to a standard value in the STO-3G basis set, the exponents were optimized in both the Cp^- and the CpLi species.

Results and Discussion

The first exploration of the CpLi potential energy surface was carried out with the STO-3G basis set. Geometry optimization of the Cp^- species yielded the following optimum values: r(CC) 1.393, r(CH) 1.080 Å, $E = -189.73142$ hartrees. The C-C and C-H bonds were held to these values as the Li^+ was moved across the ring (see Figure 1). The optimum distance over the ring at each point, as well as the optimum energy, is given in Table I. Note that the most stable position of the Li is over the middle of the ring, in agreement with the solution chemistry of this species. The potential well is a rather deep one, as there is a 54.1-kcal destabilization in moving the Li from the middle of the ring to its optimum position over a carbon atom and a 41.3-kcal destabilization in moving it from the middle to its optimum position over the midpoint of a C-C bond.

Given now the most stable position of the Li over the Cp ring, it was decided to optimize this CpLi complex as a whole. The following optimum values were obtained: r(CC) 1.417, r(CH) 1.079, r(ring-Li) 1.644 Å, and $E = -197.28975$

Table I. Optimized Values for STO-3G and Double ζ Basis Sets[a]

Position	r(ring-Li), Å STO-3G	r(ring-Li), Å DZ	Δr, Å DZ-3G	E(STO-3G), hartrees	E(DZ), hartrees	ΔE(3G-DZ), hartrees	E(CpLi-[Cp^- + Li^+]) STO-3G, kcal	E(CpLi-[Cp^- + Li^+] DZ, kcal
I	1.909	2.040	0.131	−197.20037	−199.61556	2.41519	−209.3	−146.4
II	1.771	1.939	0.168	−197.25273	−199.63549	2.38276	−242.1	−158.9
III	1.715	1.885	0.170	−197.26960	−199.64193	2.37233	−252.7	−162.9
IV	1.649	1.820	0.171	−197.28661	−199.64867	2.36206	−263.4	−167.2
V	1.696	1.867	0.171	−197.27507	−199.64407	2.36900	−256.2	−164.3
VI	1.736	1.903	0.167	−197.26292	−199.63937	2.37645	−248.5	−161.3
VII	1.849	2.000	0.151	−197.22085	−199.62372	2.40287	−222.1	−151.5

[a] The optimized Cp rings are different for the STO-3G and DZ sets.

Table II. Scale Factor Optimization in Cp^- (r(CC) 1.393, r(CH) 1.080 Å) and CpLi (r(CC) 1.417, r(CH) 1.079, r(ring-Li) 1.644 Å)

	Cp^-		CpLi	
	STD	OPT	STD	OPT
C_{2sp}	1.72	1.6764	1.72	1.7176
H_{1s}	1.24	1.1709	1.24	1.2177
Li_{2sp}			0.80	0.8310
E	−189.73142	−189.75322	−197.28975	−197.29114

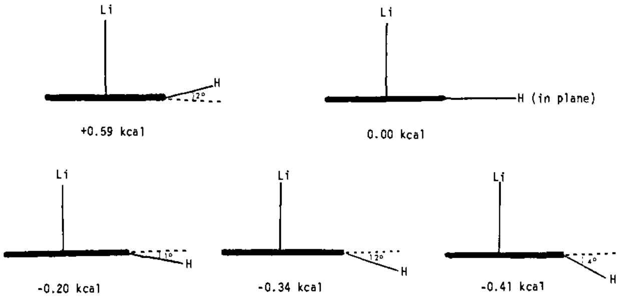

Figure 2. End view of CpLi with hydrogens bent out of plane (only one of the five equivalent hydrogens shown). Energies relative to planar Cp complex.

hartrees. Complexation of the Li to the ring thus results in an expansion of the C-C bonds by 0.024 Å and a contraction of the C-H bonds by 0.001 Å; the ring-Li distance changes by 0.005 Å, but it is to be noted that all of the stabilization energy (1.9 kcal) comes from optimization of the Cp ring; optimization of the Li distance brings no additional lowering of the energy (to five decimal places).

Use of the STO-3G basis set is most often constrained to the standard scale factor values determined by Pople.[26] To determine how serious a constraint this is in our case, calculations were done in which the C_{2sp} and H_{1s} scale factors were optimized in the Cp^- and the C_{2sp}, H_{1s}, and Li_{2sp} scale factors were optimized in the optimum CpLi structure. The results are shown in Table II; the standard values are shown for comparison purposes. Note that scale factor optimization yields a 13.7-kcal stabilization in the Cp anion; as expected, both the C and H valence orbitals expand to accommodate the negative charge. The change in CpLi is much less dramatic, with scale factor optimization resulting in a 0.9-kcal stabilization; this, too, is as expected because the standard values were derived from neutral molecules and thus yield a good description of the uncharged CpLi.

We then proceeded to the DZ basis set. Geometry optimization of the Cp anion yielded r(CC) 1.416, r(CH) 1.076 Å, $E = -192.14628$ hartrees. Using these geometrical parameters for the Cp ring, Li^+ was then moved across the ring as before; the optimized distances above the ring as well as the corresponding optimum energies are shown in Table I. The shape of the potential well is qualitatively the same as with the STO-3G basis, though not as steep; there is a destabilization of 20.8 kcal in going from the middle of the ring to the optimum position over a carbon atom and a destabilization of 15.7 kcal in going from the middle to the optimum position over the midpoint of a C-C bond.

As may be seen in Table I, the STO-3G results parallel the DZ results. The ring-Li bonds are all longer in the DZ basis set by 0.15 ± 0.02 Å; that the 3G results are shorter is to be expected because of an overweighting of the basis set towards Li in such minimum basis calculations.[28] Of course, the double ζ energies are lower, but all by a relatively uniform value of 2.39 ± 0.03 hartrees. The small deviations from an average value in both the bond length and energy results indicate the reliability of STO-3G calculations in future metallocene work.

The most stable CpLi species was then optimized as a whole. The following optimum values were obtained: r(CC) 1.422, r(CH) 1.070, r(ring-Li) 1.820 Å, $E = -199.64895$ hartrees. There was an expansion of the C-C bonds by 0.006 Å, a contraction of the C-H bonds by 0.006 Å, and a stabilization of 0.2 kcal. The ring-Li bond length is in a very shallow well and may be considered optimal at 1.820 Å; decreasing that distance by 0.004 Å resulted in an energy change of less than 1×10^{-6} hartree. While optimization of the whole CpLi species is somewhat more important with the STO-3G basis set than the DZ basis set, both results indicate that full optimization of the entire metallocene species is not necessary if qualitative results are desired.

A final set of calculations with CpLi was undertaken when it was found that Haaland and co-workers[29] had determined by gas-phase electron diffraction that the C-H bonds in Cp_2Cr are bent 2.9° out of the plane of the C_5 ring (toward the metal atom), with similar findings for Cp_2Fe.[30] We thus decided to explore whether the H's are most stable in the plane of the C_5 ring in CpLi; for a higher degree of accuracy, we used our DZ basis set and our optimum CpLi geometry (r(CC) 1.422, r(CH) 1.070, r(ring-Li) 1.820 Å). All H's were moved simultaneously from the C_5 plane, maintaining the stated bond length parameters, in the following manner: 1° out of the plane away from Li, 2° away from Li, 4° away from Li, and 2° towards the Li. The results are seen in Figure 2. The optimum value is 3.56° out of the plane *away* from the Li with an energy of −199.64962 hartrees; this represents a 0.42-kcal stabilization with respect to the complex with the H's in the C_5 plane. This result probably arises because the ring-metal bonding in CpLi is almost wholly ionic and Coulombic attraction is enhanced by shifting more ring negative charge to the side facing the lithium cation. That is, in an isolated Cp anion the π charge is evenly divided between the two faces of the molecule; rehybridization at each carbon shifts charge to the side from which the hydrogen bends. Alternatively, this effect can be regarded as a polarization of π electrons by the lithium cation that gives partial lone-pair character to each carbon with concomitant bending away of C–H bonding electrons. This interpretation implies that, in those organometallic ring compounds in which hydrogens bend towards a central metal, bonding is predominantly covalent rather than ionic; that is, the corresponding rehybridization at each carbon is such to improve the directional character of orbitals used for ring-metal covalency. If this interpretation is correct, it has the important corollary of providing an operational approach to the determination of ionic and covalent character of ring-metal bonding in organometallic ring compounds. By this criterion, for example, the bending of methyl groups[31] toward the central uranium atom in bis(η-1,3,5,7-tetramethylcyclooctatetraene)uranium(IV) is indicative of covalent bonding in the uranocene ring system.

Finally we note the predicted dissociation energy of CpLi. Using the double ζ basis, we find CpLi to lie 167.2 kcal[32] below infinitely separated Cp$^-$ + Li$^+$. By subtracting the experimental ionization potential (124.3 kcal) of Li atom and adding the electron affinity of Cp (42.4 kcal)[33] we find a dissociation energy of 85.3 kcal for the process

$$\mathrm{Li(C_5H_5)} \rightarrow \mathrm{Li} + \mathrm{C_5H_5}$$

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Model Organometallic Systems. The Interaction of ^{2}S Be$^+$, ^{1}S Be, and ^{3}P Be with Acetylene and Ethylene[1]

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Abstract: To model the interaction between metal atoms and unsaturated hydrocarbons, several electronic states of the Be–$\mathrm{C_2H_2}$ and Be–$\mathrm{C_2H_4}$ systems have been investigated using ab initio electronic structure theory. Double ζ basis sets have been used (after some experimentation with polarization functions) at the self-consistent-field level of theory. For ten different electronic arrangements, potential energy curves have been predicted for the perpendicular approach of the Be nucleus to the midpoint of the carbon–carbon bond. The interaction of Be$^+$ ion (ground ^{2}S state) with both acetylene and ethylene is attractive, yielding equilibrium Be midpoint separations of 2.03 and 2.09 Å and binding energies of 30 and 33 kcal/mol. In contrast the ^{1}S ground state of the neutral Be atom has an essentially repulsive interaction. The threefold degenerate excited ^{3}P state splits into ^{3}A$_1$, ^{3}B$_1$, and ^{3}B$_2$ components as it approaches the ethylene molecule. The ^{3}B$_2$ state is rather strongly bound, 19 kcal for Be–$\mathrm{C_2H_2}$ and 25 kcal for Be–$\mathrm{C_2H_4}$. The ^{3}A$_1$ state is strongly repulsive, while the ^{3}B$_1$ state assumes an intermediate role. These trends are readily explained by qualitative molecular orbital concepts.

During the past five years some of the most spectacular advances in chemical research have occurred in the areas of organometallic[2-5] and surface[6-10] chemistry. Much of the research in both these fields has as its goal a fundamental understanding of catalysis. Actually, neither type of research is precisely relevant to the understanding of the type of catalysts used most commonly in industrial processes. Such catalysts typically consist of finely divided metal particles[11-14] (containing perhaps 50 metal atoms) distributed on a support material, e.g., silica or alumina. Thus, it is apparent that catalytic organometallic cluster compounds[15,16] (with two, three, or four metal atoms) contain a smaller number of metal atoms,