I. INTRODUCTION

With their versatile structure, bonding and reactions, organolithium compounds continue to fascinate chemists. Tremendous progress has been made in each of these areas during the last few years. Theoretical studies have played an important role in these developments. Several reviews had appeared on the contribution of theoretical methods in organolithium compounds\(^1\),\(^2\). Wave-function-based quantum mechanical methods at various levels continue to be used in these studies; theoretical studies based on Density Functional Theory
(DFT) have also become popular in recent years. A major review on theoretical studies in organolithium compounds was published in 1995 by Streitwieser, Bachrach and Schleyer. We concentrate here on publications that have appeared since then. During these years considerable progress has been made in the application of theoretical methods to the chemistry of organolithium compounds at various levels of sophistication depending on the problem. Attempts have been made to further delineate the nature of C–Li bonding. Semiempirical calculations with the inclusion of solvent effects through various approximations have been used to study larger systems. Reactions have been modeled in the gas phase. Mechanistic details of several reactions have been studied theoretically. We discuss the developments in the nature of the C–Li bonding first. Theoretical studies on the structure and energetics, reactions and some applications involving NMR parameters are discussed in subsequent sections.

II. THE NATURE OF THE C–Li BOND

The nature of the C–Li bond is still a dilemma for chemists due to the unusual behavior of the bond in different compounds. Although the electronegativity difference suggests the carbon–lithium bond to be essentially ionic, the solubility of some organolithium compounds in nonpolar solvents such as benzene makes the problem more complex. The nature of the C–Li bond is different from those of the heavier analogs of alkali–metal organic complexes; C–Na to C–Cs bonds are acknowledged to be even more ionic than the C–Li bond. It was therefore felt that a certain percentage of covalent character may be associated with the C–Li bond. But recent studies and developments of methodologies for the analysis of wave functions and charge distributions suggest a much higher polarity to the bond. In 1995, Streitwieser, Bachrach and Schleyer suggested: ‘The carbon lithium bond in theory and in chemical properties can be modeled as an essentially ionic bond’. They described a number of examples, which support the ionic behavior of the carbon–lithium bond.

Later, Koizumi and Kikuchi used ab initio calculations of NMR spin–spin coupling constants in monomeric methyllithium, tert-butyllithium and methyllithium oligomers using self-consistent perturbation theory to probe the nature of the C–Li bonding. Their studies suggested that solvation affects the nature of the C–Li bond and reduces the $1J_{\text{CLi}}$ value significantly. The calculations were also carried out using a truncated basis set (the MIDI-4 basis set for lithium which includes only the 1s function and corresponds to lithium cation), which models a purely ionic C–Li bond. The calculated coupling constants were in excellent agreement with experimental data, suggesting the importance of the ionic character of the C–Li bond in alkyllithiums. The calculated $1J_{\text{CLi}}$ value of methyllithium, 44.0 Hz, is found to be very close to that calculated for methyllithium with three solvating ligands. This result, which strongly suggests the ionic nature of the C–Li bond in methyllithium, does not change with the addition of ligands. The difference between the $1J_{\text{CLi}}$ values calculated by two different types of basis set for methyllithium tetramer is much smaller than that in monomeric methyllithium. This trend is in accordance with the observation that the coupling constants in methyllithium tetramer are independent of solvent. Comparing the coupling constants of the ring structures 1a, 1b and 1c (Figure 1) with the tetrahedral structure 1d (staggered and eclipsed form) implies that $1J_{\text{CLi}}$ depends on the state of aggregation rather than on the degree of aggregation. More clearly, $1J_{\text{CLi}}$ in methyllithium varies nearly inversely with the number of lithium atoms, which are bonded directly to the carbon atom. The implications are that the ionic nature of the monomeric MeLi increases on solvation and the tetrameric MeLi has more ionic C–Li bonding. In addition, further solvation is not desirable as the bridging nature of tetramer provides the effect of solvation.
In 1996, Bickelhaupt and coworkers investigated CH₃Li, (CH₃Li)₂ and (CH₃Li)₄ using Density Functional Theory (DFT) and conventional \textit{ab initio} Molecular Orbital Theory (MOT). This study highlighted the important role of a small covalent component in the polar C–Li bond, especially in the methyllithium tetramer. It was suggested that the lithium outer 2p orbital serves only as ‘superposition functions’, helping to describe the carbanion, and does not play any part in covalent interaction. However, there appears to be a small contribution from the inner parts of the Li 2p orbital. Streitwieser and coworkers showed that calculations using a truncated basis set on lithium with only s-type basis functions yield essentially the same result (including the energetic ordering of isomers) as calculated using the full basis sets. They concluded that the bonding is governed by electrostatic interactions. The extended 6-31+G* basis set used in the evaluation of aggregation energies was expected to minimize the basis set superposition error as suggested by Bickelhaupt and coworkers. The result showed that the oligomerization energies (∆\(E_{\text{oligo}} + \Delta ZPE\)) calculated with truncated basis set are up to 20% lower than those obtained using the full 6-31+G* basis. This indicated that the bonding mechanism is more complicated than suggested by the purely electrostatic model.

Charges on lithium calculated using the Voronoi Deformation Density (VDD) decrease from 0.38 via 0.26 to 0.13e along CH₃Li, (CH₃Li)₂ and (CH₃Li)₄ showing that the shift of electron density from lithium to methyl decreases upon oligomerization. Similarly, Hirshfeld lithium charges decrease from +0.49 via 0.42 down to +0.30e along the same series of methyl lithium oligomers (Table 1). The fragment molecular orbital analysis shows (CH₃*)ₙ and (Li*)ₙ fragments to have triplet and quintet electronic structures in (CH₃Li)₂ and (CH₃Li)₄, respectively. Thus the interacting fragments are two singly occupied molecular orbitals (SOMO\textsubscript{low} and SOMO\textsubscript{high}) in each (CH₃*)ₙ and (Li*)ₙ.
TABLE 1. The charges of Li in CH₃Li and its oligomers. Reproduced with permission from Ref. 5

<table>
<thead>
<tr>
<th>Method</th>
<th>CH₃Li</th>
<th>(CH₃Li)₂</th>
<th>(CH₃Li)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voronoi deformation density (VDD)</td>
<td>0.38</td>
<td>0.26</td>
<td>0.13</td>
</tr>
<tr>
<td>Hirshfeld</td>
<td>0.49</td>
<td>0.42</td>
<td>0.30</td>
</tr>
</tbody>
</table>

above trend of decrease in electron density transfer from lithium is in accordance with the increasing population of the (Li*)ₜ(fragment orbitals SOMOₗow and SOMOₗigh from (CH₃Li)₂ [SOMOₗow = 0.57 and SOMOₗigh = 0.63] to (CH₃Li)₄ [SOMOₗow = 0.91 and SOMOₗigh = 0.85]. This is indicative of the increasing importance of a covalent component in the carbon–lithium bond. Also, the carbon–lithium bond is much less ionic according to Hirshfeld⁵ (50–30%) than according to NPA charges (90%). These factors suggest that the degree of ionicity of a bond obtained on the basis of atomic charges should not be regarded as an absolute quantity, rather it will be more meaningful to consider trends in atomic charges across a series of molecules using the same method. Even though Bickelhaupt⁵ emphasized the importance of covalent contributions to the C—Li bonding, the results imply the ‘dual nature’ of the C—Li bond. It can be concluded that the appearance of a covalent or ionic aspect depends strongly on the physical and chemical context.

From their analysis of the conformational energies of pentadienyl anion and the pentadienyl metal compounds, Pratt and Streitwieser⁷ in 2000 pointed out that the stabilization of the planar forms of the organometallic structures results from both conjugation and electrostatic attraction between the negative carbons and the alkali metal cations. To determine the relative magnitude of these effects, the reaction energies were determined for hypothetical reaction, shown in Scheme 1 where M represents any alkali metal.

\[
\begin{align*}
\text{CH₃C=C=CH₂} + M^+ \rightarrow M
\end{align*}
\]

SCHEME 1

The reaction energies for the formation of pentadienyllithium are found to be much greater than those for pentadienyl sodium, which indicate a greater electrostatic attraction for the shorter Li—C bond. The calculated regional charges for the pentadienyllithiums (HF/6-311+G*) indicate that the most positive charge is concentrated on lithium and the most negative charge is concentrated on the carbon atom coordinated to the lithium. These results imply an ionic nature of the C—Li bond in pentadienyllithium. However, the larger magnitude of electrostatic interaction may be due to the shorter distance of the C—Li bond, and not necessarily to a larger charge separation. In other words, it is possible that the charge on lithium may be less than that on sodium in the corresponding sodium derivative and yet the electrostatic interaction may be larger in the former due to the shorter distance.

Density functional theory calculations on methyllithium, tert-butyllithium and phenyllithium oligomers by Kwon, Sevin and McKee support the ionic character of the C—Li bond⁸. Their calculations of carbon lithium Natural Population Analysis (NPA) charges and dipole moments for CH₃Li, t-BuLi and Ph-Li oligomers (Table 2) indicate the ionic behavior of the C—Li bond. Comparison of the charges of various oligomers suggests that charges of lithium and carbon atoms are almost independent of the size of oligomers. There are minor variations in the charge of the Li on going from CH₃Li via t-BuLi and PhLi, implying that there are changes in the nature of C—Li bonding as a function of the organic group. Thus it is not correct to say that all C—Li bonds are 100% ionic. There are minor variations.
Ponec and coworkers\textsuperscript{9} reconsidered the conventional concept of C–Li bond in CH\textsubscript{3}Li and CLi\textsubscript{6}. Their calculations were based on two recently proposed methodologies: the Atoms in Molecule (AIM) generalized population analysis and Fermi hole analysis. These results support the ionic nature of C–Li bonding in CH\textsubscript{3}Li, but in CLi\textsubscript{6} a different description than the one published earlier\textsuperscript{2} is suggested. The bonding description of CLi\textsubscript{6} proposed by Schleyer and coworkers in 1995 involves a C\textsuperscript{4−} ion surrounded by Li\textsubscript{6}\textsuperscript{4+} in an octahedral fashion (Figure 2). The two electrons in the lithium cluster are placed in an orbital, which is completely symmetric, being a Li–Li bonding orbital among all lithium atoms, with a small contribution from the carbon 2s orbital. This extra electron pair was considered as a part of the Li⋯Li bonding interactions. According to Ponec

\begin{table}
\centering
\begin{tabular}{cccc}
\hline
 & NPA charge\textsuperscript{a} & Dipole moment\textsuperscript{b} \\
Li & C \\
\hline
MeLi (monomer) & 0.83 & -1.48 & 5.51 \\
Me\textsubscript{2}Li\textsubscript{2} & 0.87 & -1.53 & 0 \\
Me\textsubscript{3}Li\textsubscript{3} & 0.84 & -1.51 & 0 \\
Me\textsubscript{4}Li\textsubscript{4} & 0.86 & -1.51 & 0 \\
t-BuLi & 0.81 & -0.59 & 6.23 \\
t-Bu\textsubscript{2}Li\textsubscript{2} & 0.87 & -0.71 & 0 \\
t-Bu\textsubscript{3}Li\textsubscript{3} & 0.82 & -0.69 & 0 \\
t-Bu\textsubscript{4}Li\textsubscript{4} & 0.85 & -0.74 & 0 \\
PhLi (monomer) & 0.87\textsuperscript{c} & -0.64\textsuperscript{c} & 6.61 \\
Ph\textsubscript{2}Li\textsubscript{2} & 0.85\textsuperscript{c} & -0.69\textsuperscript{c} & 0 \\
\hline
\end{tabular}
\caption{The charges on Li and C coordinated to the Li and the dipole moments for a series of MeLi, t-BuLi and PhLi oligomers. Reproduced with permission from Ref. 8}
\end{table}

\textsuperscript{a}At the B3LYP/6-31+G\textsuperscript{*} level where diffuse functions have been omitted from lithium atoms.

\textsuperscript{b}At the B3LYP/6-31+G\textsuperscript{*} level.

\textsuperscript{c}At the B3LYP/6-31+G\textsuperscript{*} level where diffuse functions have been omitted from lithium atoms and carbon atoms not coordinated to the lithium face.
and coworkers the AIM analysis suggests that this electron pair is also shared between the carbon and lithiums and the contributions of C and Li are roughly equal to 1.2 and 0.8\(e\), respectively. Although the oxidation state of the central carbon is indeed close to the NPA estimate (−IV), the interactions between the central atom and the surrounding cage need not be purely ionic as expected so far. This is supported by the result of generalized population analysis, which detects the presence of 3-center bonding interactions in Li−C−Li fragments as seen from the values of the corresponding indices, such as the C···Li cage interactions. The Li···Li bond indices drop from 0.167 (Mulliken-like analysis) to 0.020 (AIM generalized value), correlating the conclusions above.

Thus it is evident from all these studies that the nature of the C−Li bond varies from compound to compound; hence any generalization of the nature of bonding is to be taken cautiously. As Schleyer and Streitwieser have discussed in the past, the C−Li bond is essentially ionic; however, the covalent components cannot be neglected. The unusual behavior of the C−Li bond has been a subject of discussion from the initial years of applying theoretical methods, and the debate continues in an interesting manner due to the developments of new theoretical methodologies. In fact, we support the implications of Bickelhaupt that there is a covalent contribution to the C−Li bonding, however small this turns out to be in specific examples.

### III. STRUCTURE AND ENERGY

Theoretical studies of the structure of organolithium compounds continue to attract much attention for several reasons. Often, it is not possible to obtain detailed structural information from experiments. Experimental realization of a single crystal, which is good enough for X-ray diffraction studies, is not always easy. Even when such detailed information about the structure is available, theoretical studies provide an electronic structural description that helps one proceed further. The theoretical results depend on the level of theory used. This often results in the re-examination of structures studied earlier using lower levels of theory. Many of the structures that were thought to be minima were found to have several imaginary frequencies at more sophisticated levels of theory. Schleyer and coworkers in 1995 discussed a large number of compounds and their optimized structures. We consider here results that have appeared since then. Optimized structures and the factors affecting the stability are discussed below. The last ten years have witnessed a revolution in modeling solvent effects. Several theoretical studies incorporating the effect of solvents are known and we first discuss this aspect of structural studies.

#### A. Effect of Solvation

The structures of organolithium compounds are affected by solvation. For example, Sorger, Schleyer and Stalke have shown that the solid-state cisoid dimeric structure of 3,3-dimethyl-2-(trimethylsilyl)cyclopentenyllithium-tetramethylenediamine does not persist in solution; it is monomeric in THF solution. In 1996, Weiss and coworkers studied the effect of specific and nonspecific solvations by THF on methyl isobutyrate aggregates. This study shows that the solvent influences the stability of the dimer to a higher extent than that of the tetramer. In total disagreement with earlier experimental results, \textit{ab initio} MO calculations (gas-phase studies) at the MP2/SVD//SCF/SVD, SCF/SVD//SCF/SVD and SCF/TZD//SCF/SVD (split valence basis sets augmented with one d-polarization function for carbon and oxygen, for Li augmented with one p-polarization function and a double-\(\zeta\) basis set for hydrogen; this is referred to as SVD; the Karlsruhe TZP basis sets for Li, O and C, and for hydrogen the same DZ basis set as for the structure optimization have been used, is referred to as TZD) levels for the energies of dimer and cubic tetramer,
suggest that the tetramer is more stable than the dimer. But the results of solvent effects, using the semiempirical MNDO and PM3 methods, predict the dimer to be more stable\textsuperscript{11}. Clearly, more careful investigation is required here before definite conclusions can be drawn. The general indication is that the dimers are more strongly affected by solvation than the tetramers.

Since several aspects of the regio- and stereoselectivity of lithium enolates involves the characteristics of their aggregation, the effect of solvation on the structure and aggregation of lithium enolates plays an important role in the mechanistic study. In 1997, Abbotto, Streitwieser and Schleyer investigated theoretically by using \textit{ab initio} and semiempirical MO methods the effect of ether solvent on the aggregation of lithium enolates\textsuperscript{12}. This study shows that solvation has a critical role in determining the relative energies of the aggregated species. $\pi$-Interaction between lithium and the enolate double bond is another factor that helps to determine the relative stabilities of the isomers and the degree of solvation. The cubic tetramer is stable because of the electrostatic stabilization of the aggregation, but the monomeric species is important in the equilibrium owing to its high solvation energies. In contrast, the dimer, and to a greater extent the trimer, is less important. The tendency of lithium cation to reach tetracoordination is shown to be less significant than commonly believed. Jackman and Lange studied the aggregation and reactivity of lithium enolates using $^6$Li and $^{13}$C NMR spectroscopy and suggested that the parent lithium enolate of acetaldehyde exists exclusively as a tetramer in THF solution\textsuperscript{13}. Selection of water as a solvent molecule in the study of the solvation effect is less effective due to the property of water to form hydrogen bonds. In their study Abbotto and coworkers abandoned THF as the solvent due to its large size and took dimethyl ether as a realistic coordinating solvent\textsuperscript{12}.

The effect of solvation in CH\textsubscript{2}=CHOLi was studied in detail. Earlier studies at the B3LYP/6-31+G$^*$ level suggested that the lowest energy minima correspond to isolated bridged lithium enolate $2a$, rather than the open-chain structure $2b$; this is attributed to the interaction of the lithium cation with the enolate anion (Figure 3).

The main consequences of the solvation are found to be the increment in bond lengths between the enolate oxygen atom and the lithium in the mono and the disolvated (3\textit{a}) enolates, together with the increment in the Li–O solvent bond. However, the trend continues up to trisolvated species $3b$ (Figure 4), where the Li–O distance is found to be less than that in isolated species. These characteristics of larger Li–dimethyl ether distance (due to the steric hindrance) and the absence of coordination to the double bonds suggest an ionic interaction of Li with enolate oxygen.

![FIGURE 3. Optimized structures of monomer CH\textsubscript{2}=CHOLi as obtained from B3LYP/6-31+G$^*$ calculations. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society](image-url)
Li-O-C  89.05°
Li-O-C-C  46.07°
O₅-Li-O  111.51, 123.96°
O₅-Li-O₅  107.74°
O₅-Li-O-C  −106.02, 122.66°

**FIGURE 4.** Optimized structures of CH₂=CHO⁻Li(Me₂O)₂ (3a) as obtained from B3LYP/6-31+G* calculations (3b) and CH₂=CHO⁻Li(Me₂O)₃ as obtained from PM3 calculations. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society

The geometries for the dimeric isomers are also optimized at the B3LYP/6-31+G* level. The results were compared with Hartree–Fock and PM3 results. The stable dimers 4a, 4b and 4c are found to have C₁ symmetry (Figure 5).
FIGURE 5. 4a–4c are optimized structures of dimers (CH₂=CHOLi)₂ as obtained from B3LYP/6-31+G* and PM3 calculations. Hydrogen atoms are omitted in PM3. Structure 4d represents the optimized structure of the complex of the dimer (CH₂=CHOLi)₂ with three molecules of Me₂O at the PM3 level. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society.
The relatively high stability of the three isomers 4a, 4b and 4c is attributed to the stabilizing interaction between lithium cation and enolate double bond. Comparison of the energy of monomer, dimer and trimer systems, with and without π-coordination (as in 2a vs 2b in Figure 3) indicated the π-coordination energy to be 0.5–2.6 kcal mol\(^{-1}\). It is found that for the trisolvated monomer 3b (and for other aggregates) π-coordination disappears on solvation (Figure 4). Thus π-coordination is also a decisive factor in determining the most favorable degree of solvation. Abbotto and coworkers concluded that if the negative entropic contribution relative to the third solvation process of monomeric CH\(_2=\text{CHO}Li\) is assumed to be about 5–10 eu, the small negative enthalpy suggests that this step has a positive Δ\(\Gamma\) at room temperature. Thus it is clear that tetracoordination of the lithium center is not necessarily a thermodynamically favored process; less solvated species with coordinated lithium may well be more stable. If we consider the solvation enthalpies and entropies, the most stable solvated species are the disolvated monomer 4a, the trisolvated dimer 4d, the trisolvated trimer 5a and the tetrasolvated tetramer 5b (Figures 5–6). The association energies among these solvated species are monomer/dimer −14.9, monomer/trimer −11.6 and monomer/tetramer −17.2 kcal mol\(^{-1}\) (per mol of monomeric unit). Comparison of these values with the corresponding energies without solvation of −26.0, −33.5 and −35.3 kcal mol\(^{-1}\) (which are increasing in the order monomer/dimer < monomer/trimer < monomer/tetramer) suggests a different order with the monomer/dimer equilibrium being the least favored.

The calculations of the natural charge populations of selected B3LYP/6-31+G* optimized structures, using the two different basis sets 6-31+G* and 6-311+G**, reveal the increase of negative charge on the oxygen, and a decrease on the carbons on aggregation (Table 3). The results are rationalized as follows. Compared to the monomer, each oxygen of the dimer is close to two positively charged lithium centers and, as a consequence of its higher effective electronegativity, it removes more charge from the double bond. The increase in the charge on oxygen is about the same as the decrease in C\(_\beta\) charge. In the dimer in which the π-coordination is absent, the lithium atom carries more positive charge. Hence the oxygen of the bridged unit is effectively less electronegative and less charge is withdrawn from the α-carbon. This fact suggests that the π-coordination between the enolate double bond and the lithium cation increases the negative charge by about 0.1 electron at the β-position. The lack of significant difference observed between the carbon of the bridged unit in 4a in Figure 5 and the corresponding position of the C\(_{2h}\) isomer (Figure 7) suggests that the π-delocalization from oxygen to the double bond is not important and that the polarization mechanism controls charge redistribution in lithium enolates. This is also reflected in the identical distances of O−C and C−C bonds\(^{12}\) in the unbridged enolate unit of C\(_1\) isomer (Figure 5) and in the C\(_{2h}\) isomer 6 (Figure 7).

The decrease in the negative charge on C\(_\beta\) on going from monomer to higher aggregates implies the opposite behavior in the solvated monomers. The reverse behavior is due to the bonding of lithium to more oxygens on solvation. Thus the solvation limits its effect on charge redistribution primarily to the lithium cation, and the populations on the enolate moiety are relatively unaffected by solvent contribution.

**B. Stability due to Sulfur**

The high nucleophilicity of heterosubstituted allyllithium compounds makes them attractive reagents in synthetic organic chemistry. Structural studies of these compounds give a fundamental understanding about the control of the regioselectivity. Often, these studies are difficult due to the tendency of the compounds to form complex fluxional aggregates in solution. Piffl and coworkers have studied the dependency of the oxidation state of sulfur on the structure and electronic properties of the heterosubstituted
1. Theoretical studies in organolithium chemistry

Li₁-O₂-C₃  121.04°
O₂-Li₁-O₁  115.44°
O₁-Li₁-O₁  116.63°
O₁-Li₁-O₂  127.70°
Li₁-O₂-C₃-C₇  38.67°
O₂-Li₁-O₁-Li₂  3.15°
O₂-Li₁-O₂-O₁  174.24°

(C₃) (PM3)

Li₃-O₂-C₃  131.14°; O₂-Li₃-O₃  90.54°
O₁-Li₃-O₂  88.96°; O₂-Li₃-O₂  119.91°
O₂-Li₃-O₃  124.45°; O₈-Li₃-O₈  131.43°
Li₃-O₂-C₃-C₇  3.81°; O₁-Li₁-O₂-Li₃  1.63°;
O₂-Li₂-O₃-Li₃  6.10°; C₇-O₃-Li₂-Li₃  −128.28°
O₈-Li₃-O₈-O₄  −142.20°; O₈-Li₂-O₂-Li₃  −129.75°

(S₄) (PM3)

FIGURE 6. Optimized structures of trimer (CH₂=CHOLi) (5a) complex with three molecules of Me₂O from PM3 computations and of the Cubic tetrasolvated tetramer (CH₂=CHOLi)₄(Me₂O)₄ (5b) obtained at the PM3 level. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society
TABLE 3. The natural charge population in monomeric and aggregated structures of \( \text{CH}_2=\text{CHOLi} \) and corresponding solvated forms using method A (B3LYP/6-31+G*/6-31+G*) and method B (B3LYP/6-311+G**//6-31+G*) calculations

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>( \text{Li} )</th>
<th>( \text{O} )</th>
<th>( C_\alpha ) (CH)</th>
<th>( C_\beta ) (CH(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2=\text{CHOLi} ) (( C_1 ))</td>
<td>A</td>
<td>+0.926</td>
<td>−0.887</td>
<td>+0.158 (0.036)</td>
<td>−0.820 (−0.375)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>+0.923</td>
<td>−0.884</td>
<td>+0.912 (0.330)</td>
<td>−0.758 (−0.369)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi(Me}_2\text{O}) ) ( C_1 )</td>
<td>A</td>
<td>+0.889</td>
<td>−0.882</td>
<td>+0.161 (0.331)</td>
<td>−0.803 (−0.367)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>+0.888</td>
<td>−0.881</td>
<td>+0.194 (0.324)</td>
<td>−0.742 (−0.360)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi(Me}_2\text{O})_2 ) (( C_1 ))</td>
<td>A</td>
<td>+0.873</td>
<td>−0.891</td>
<td>+0.159 (0.318)</td>
<td>−0.765 (−0.346)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>+0.868</td>
<td>−0.891</td>
<td>+0.192 (0.313)</td>
<td>−0.706 (−0.340)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi} ) ( C_1 ) ( \text{unit 1}^a )</td>
<td>A</td>
<td>+0.913</td>
<td>−0.998</td>
<td>+0.160 (0.348)</td>
<td>−0.725 (−0.273)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>+0.913</td>
<td>−1.002</td>
<td>+0.195 (0.343)</td>
<td>−0.660 (−0.267)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi} ) ( C_1 ) ( \text{unit 2}^a )</td>
<td>A</td>
<td>+0.943</td>
<td>−1.059</td>
<td>+0.160 (0.350)</td>
<td>−0.625 (−0.203)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>+0.950</td>
<td>−1.068</td>
<td>+0.196 (0.327)</td>
<td>−0.564 (−0.199)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi} ) ( C_2h )^c</td>
<td>A</td>
<td>+0.948</td>
<td>−1.087</td>
<td>+0.148 (0.322)</td>
<td>−0.615 (−0.182)</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHOLi} ) ( C_1 ) ( \text{unit 2}^b )</td>
<td>A</td>
<td>+0.921</td>
<td>−1.015</td>
<td>+0.145 (0.332)</td>
<td>−0.688 (−0.238)</td>
</tr>
</tbody>
</table>

\(^a\) Bridged (Li-\( \pi \)-interaction) unit of the dimer.
\(^b\) Non-bridged unit of the dimer.
\(^c\) Plane corresponding to the moiety Li–O–Li–O is perpendicular to the plane of the carbon atoms.

allyllithium compounds\(^1\)\(^4\). They combined \textit{ab initio} calculations with experimental NMR and cryoscopic investigations, which gave insight to the structural assignments as suggested by Weston and Ahlbrecht in 1999\(^1\)\(^5\). The stability of the \textit{endo} conformation over the \textit{exo} (called the ‘\textit{cis}-effect’) is observed both experimentally and theoretically for all lithiated compounds during the studies. Successive coordination of THF molecules to lithium and re-optimization of the two nearly isoenergetic \textit{endo} conformers for 1-\textit{thiophenylallyllithium} 7\( a \) and 7\( b \) (Figure 8) shows that specific solvation has a strong influence on the structure and electronic properties of the anionic substrate.

Increasing the solvation causes the \( C_\gamma \)–Li contact to be gradually given up whereas the electrostatic contact of the lithium to the \( \alpha \)-carbon is maintained. However, the estimation of the solvation number in the solid state shows the presence of two THF molecules per lithium. This study suggests that specific solvation increases the ability of the sulfur group to localize the negative charge on the \( \alpha \)-carbon atom (\( \alpha \)-heteroatom stabilization).
Close examination of various B3LYP/6-31+G* optimized geometries of all the three isomers of sulfoxyl-substituted allyllithium suggests the minimum energy structures as 8a and 8b (Figure 9). The relative stabilities of these structures are attributed to the additional electrostatic interaction due to the presence of extra Li–O contact.

Although in structure 8c the allyl system is decoupled, the structure shows surprising stability (only 2.2 kcal mol$^{-1}$ above global minimum) due to the presence of Li–O contact. The calculations on the solvated structure lead to the conclusion that the presence of Li–O contact reduces the number of THF molecules bound to lithium as compared to the thiophenyl compound. This is supported by experimental results, which suggests the presence of two THF molecules per allyllithium unit in the solid state. The cation decoupled solvated allyl system 9a is only 1.7 kcal mol$^{-1}$ less stable than 9b (Figure 10) even though specific solvation stabilizes conformer 8c more than 8a. The calculated solvation energies indicate that conformer 8a is only 0.5 kcal mol$^{-1}$ more stable than 8c, indicating the presence of both conformers in the solution. The conformational equilibrium

![Diagram of structures](image-url)
FIGURE 10. Energetically stable solvated conformers found for sulfoxides of 1-thiophenylallyl-lithium at the B3LYP/6-31+G* computations. Energy difference in kcal mol$^{-1}$. Reprinted with permission from Reference 14. Copyright 2000 American Chemical Society

was not found in the NMR timescale since warming the solution caused a slight broadening of the signals observed in the $^1$H and $^{13}$C NMR spectra; the solution decomposes, however, before coalescence is observed.

The presence of two chelating oxygen atoms in 1-(phenyl)sulfonylallyllithium enables the lithium to form a very stable intramolecular O─Li─O scissor contact ion pair, at least in the solid state. Thus, among all the heteroatom-substituted allyllithium compounds, the lithium is bonded not only to the heteroatom but also to the allylic backbone. Recent investigations of the structure of lithiated allylic norbornyl sulfones showed that, in addition to the exo–endo equilibrium, there is also a monomer–dimer aggregational equilibrium present in THF solution, which occur rapidly on the NMR timescale. Knowledge of the solution structure of these three types of lithiated compounds enabled Piffl and coworkers to develop a reliable model system for the calculation of heterocumulene fixation. New developments in this area will help direct experimental investigations$^{14}$.

C. Lithium Amides

Though many lithium amides have no formal Li─C bonds, they are included here as honorary organolithium compounds because the lithium amides are used extensively in organic synthesis. The interest in aminolithium complexes is in their use as non-nucleophilic Brønsted–Lowry bases in organic synthesis and in their applications as anionic transfer reagents for the preparation of other main group and transition metal amides. In addition to the $ab$ initio molecular orbital calculations on the association of solvent-free and solvated LiNH$_2$, the theories concerning autocomplexation of these species have considerable interest. In 1995, Gardiner and Raston reported a model $ab$ initio theoretical study of (E)-4-lithio-1,4-diazabut-1-ene focusing on the energetics of association to the possible diastereomers arising from amido nitrogen bridging$^{16}$. The $ab$ initio theoretical studies dealt with the aggregation of Lewis base functionalized derivatives, which are very few in number. Their study used a 3-21G* basis set. The fully
1. Theoretical studies in organolithium chemistry

Figure 11. Optimized geometries for minima located using the 3-21G* basis set for [LiN(H)CH2CHNH] (10), [cis-\{Li[\mu-N(H)CH2CHNH]\}]2 (11) and [trans-\{Li[\mu-N(H)CH2CHNH]\}]2 (12). Reprinted with permission from Reference 16a. Copyright 1995 American Chemical Society.

Optimized structures of [LiN(H)CH2CHNH], [cis-\{Li[\mu-N(H)CH2CHNH]\}]2 and [trans-\{Li[\mu-N(H)CH2CHNH]\}]2 with Cs symmetry for monomer 10, C1 for centrosymmetric dimer 11 and C2 for symmetric dimer 12 are represented in Figure 11.

The minimum energy structure corresponding to the monomer 10 has Cs symmetry. The Li–N bond distance in this highly electron-deficient complex, as expected, is much shorter than typically observed. The calculations suggest the dimeric species to have structures with Ci and C2 symmetry (11 and 12). The amido nitrogen atoms in the dimers are sp3 hybridized16a, which introduce stepped and concaved secondary structures into the three edge-fused rings of the Ci and C2 symmetric dimers. The formation of Ci and C2 dimers gives stabilization energies of 31.9 and 32.0 kcal mol\(^{-1}\), respectively.

Even though ab initio molecular orbital calculations on unsolvated and solvated model compounds of lithium amides suggest the formation of polymeric/cyclic oligomeric aggregates featuring Li\(_n\)N\(_n\) ladder core, a shortage of direct experimental evidence makes the evaluation of the reliability of the study difficult. The only structurally characterized polymeric lithium amide in the solid state, \{Li(\mu-N(Pr-i))\}\(_n\) has a coiled linear Li\(_n\)N\(_n\) framework. Gardiner and Raston also reported the synthesis of the lithium amides 14–16 by lithiation of N,N’-di-tert-butylethylenediamine 13 by alkyllithium species (Figure 12) together with ab initio molecular orbital calculations, in order to monitor the energetics of

The calculations indeed proved the polymeric ladders \(16a\) as energetically favored over stacked dimers. The aggregates of various oligomeric/polymeric form in \(N,N'\)-dilithium ethylenediamide complexes were optimized using basis sets ranging from STO-3G, 3-21G\(^*\), to 6-31G\(^*\). The association energies and optimized structures (Figure 13) are discussed below.

The above data indicate that the association energy for dimerization of stacked dimeric species \(G\) is \(-26.3\) (\(-29.2\)) kcal mol\(^{-1}\) (energies at the 6-31G\(^*\) and 3-21G\(^*\) level of theory). The energies for the polymerization of the species \(C\) and \(F\) are \(-40.4\) (\(-47.0\)) kcal mol\(^{-1}\) and \(-40.6\) (\(-46.1\)) kcal mol\(^{-1}\), respectively. This calculated energy of aggregation suggests the formation of a polymeric ladder as more favorable than the stacked dimer. In the experiment, it is seen that the stacked dimer crystallizes only on rapid cooling.
FIGURE 13. The aggregates of various oligomeric/polymeric form in \(N,N'\)-dilithiummethylenediamide complexes were optimized using minimal basis sets ranging from STO-3G, 3-21G\(^*\), to 6-31G\(^*\). Reprinted with permission from Reference 16b. Copyright 1996 American Chemical Society
of solutions but the polymeric ladder form precipitates from solution over time as the most stable form. This was found to be in good agreement with theoretical calculations.

The centrosymmetric four-ring ethylene edge-bridged ladder structure of \([\text{Li}_2\text{N}(2,6-i-\text{Pr}_2\text{C}_6\text{H}_3)\text{CH}_2]_2\) is 16.7 (19.8) kcal mol\(^{-1}\) higher in energy than the polymeric ethylene face-bridging ladder. This energy difference, close to that of the ladder and stacked dimer difference, can be attributed to the influence of the steric effect due to the highly hindered aryl group. Comparison of the unsolvated ladders E and H with ladders bearing a single molecule of water on each terminal lithium atom, J and K, shows an energy difference of 5.0 (4.6) and 3.8(3.1) kcal mol\(^{-1}\), which favors the ethylene edge-bridged ladders (per monomeric unit), \((\text{H-E})/2\) and \((\text{K-J})/2\). According to the authors this preference is due to the relief of steric strain in the ‘Li\(_2\)N\(_2\) double bridged’ butterfly shaped Li\(_2\)N\(_2\) ring.

D. Oligomerization and Aggregation

The questions of oligomerization and aggregation of organolithium compounds appear wherever these reagents are discussed. We have already given several examples in the context of solvation. In view of the great insights it provides to the structure and energies, we give here definite examples not discussed earlier. While the literature in this area is not as extensive as those of lithium amides, there are several interesting theoretical studies.

An \textit{ab initio} study on the ‘superbasic reagents’ formed by transmetalation reaction is performed using mixed alkali–metal dimers\(^{17}\). Comparison of the structure and energies of the resulting dimeric aggregates suggests that mixed aggregates are more stable than other possible combinations (Figure 14a). The stability of mixed metal dimers is attributed to a combination of high LiX/LiO bond strengths and the decrease of the metal–metal repulsions, even though the latter is considered to be a main factor in mixed dimers involving heavier alkali metals (Rb, Cs). The relative energies for dimethyl ether solvated mixtures compared to the uncomplexed species and computational results on the intermolecular exchange reactions are illustrated in Figure 14b. The final energies are obtained by single point calculations using B3LYP density functional theory on RHF optimized geometries. Although mixed aggregates may well exist in superbasic mixtures, their enhanced reactivity is yet to be explained.

E. Examples of Other Organolithium Compounds

Goldfuss, Schleyer and Hampel studied in 1996 the interactions of alkali–metal ions with cyclopropyl groups and correlated them with experimental results from X-ray crystal structure of \([\text{Li}–\text{O}–\text{C(Me)}–(c-\text{Pr})_2]_6\) \(^{17a}\) (Figure 15). This work explained the bonding in terms of edge-coordinated cyclopropyllithium arrangements. The geometries of the lithium-bonded cyclopropyl groups obtained from the X-ray crystal structure studies and from theoretical studies at the B3LYP/6-311+G\(^*\)* level are comparable. The geometries \(17b–f\) obtained from the calculations are given in Figure 15. The coordination energies and natural charges of protonated lithium-complexed hydrocarbons are listed in Table 4. The results indicate the exceptional stability of edge complex \(17d\) in comparison to corner transition structure \(17c\) and face isomer \(17e\). The C–C bent bonds of cyclopropane \(17b\) give rise to areas of negative electrostatic potential outside the ring; this favors the Li\(^+\) edge coordination of \(17b\) over \(17c\) (corner coordination). Above the ring plane the positively charged H atoms provide three electrostatic potential minima, surrounding a lower positive area. This explains the ‘meta’-stable Li\(^+\) position in \(17e\).

In 1997, Jemmis, Schleyer and coworkers studied the structure and energetics of lithiated cyclopropenyl cation and their acyclic isomers using \textit{ab initio} MO (HF/6-31G\(^*\)) and density functional theory (DFT, B3LYP/6-31G\(^*\)) methods\(^{19}\). Successive lithiation results in
Starting compounds | Mixed aggregate | Transmetalated compounds

<table>
<thead>
<tr>
<th>Solvated</th>
<th>Unsolvated</th>
<th>Solvated</th>
<th>Unsolvated</th>
<th>Solvated</th>
<th>Unsolvated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>-5.3</td>
<td>-8.7 (-9.1)</td>
<td>-10.1</td>
<td>-12.4 (-10.1)</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>-8.1</td>
<td>-13.7 (-13.9)</td>
<td>-9.1</td>
<td>-10.4 (-7.1)</td>
</tr>
</tbody>
</table>

FIGURE 14a. Relative energies for dimethyl ether solvated mixtures [(MOH)₂/(LiCH₃)₂; M = Na, K] compared to the uncomplexed species at B3LYP basis D //RHF basis A. (D //MP2(full) basis B energies for the unsolvated equilibria are given in parentheses.) Basis A: Li, Na, H, C, N, O, F (6-31+G*) K, Rb, Cs: 9VE-ECP MWB 6s6p1d/4s4p1d; basis B: Li, Na, H, C, N, O, F (6-31++G**), K, Rb, Cs: 9VE-ECP MWB 6s6p2d/5s5p2d; basis D: Li, Na, H, C, O (6-311+G*), K: 9VE-ECP MWB 6s6p2d/5s5p2d. Reprinted with permission from Reference 17. Copyright 1996 American Chemical Society.
Starting compounds  Cation exchange  Anion exchange  Mixed aggregates  Transmetalated compounds

\[ E_{rel} = 0.0 \]

<table>
<thead>
<tr>
<th></th>
<th>X Li</th>
<th>X Li</th>
<th>X Li</th>
<th>X Li</th>
<th>X Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>M= Li</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X= H</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>X= CH₃</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>X= NH₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>X= OH</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>X= F</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

| M= Na  |       |       |       |       |       |
| X= H  | -10.2 | -10.5 | -11.9 | -16.8 |
| X= CH₃ | -6.3  | -7.3  | -9.1  | -10.1 |
| X= NH₂ | -2.9  | -2.6  | -4.3  | -2.6  |
| X= OH  | -2.0  | 0.0   | -2.0  | 0.0   |
| X= F   | -4.0  | -1.8  | -4.8  | -2.6  |

| M= K   |       |       |       |       |       |
| X= H  | -14.4 | -9.5  | -16.0 | -14.1 |
| X= CH₃ | -11.8 | -5.8  | -13.9 | -7.1  |
| X= NH₂ | -6.5  | -0.9  | -8.2  | 0.6   |
| X= OH  | -6.8  | 0.0   | -6.8  | 0.0   |
| X= F   | -11.2 | -3.8  | -12.2 | -6.5  |

| M= Rb  |       |       |       |       |       |
| X= H  | -17.6 | -10.6 | -19.0 | -16.9 |
| X= CH₃ | -15.1 | -6.8  | -17.2 | -9.3  |
| X= NH₂ | -8.1  | -0.7  | -9.8  | 1.0   |
| X= OH  | -8.6  | 0.0   | -8.6  | 0.0   |
| X= F   | -13.6 | -4.2  | -14.5 | -7.4  |

| M= Cs  |       |       |       |       |       |
| X= H  | -18.7 | -10.0 | -19.8 | -16.4 |
| X= CH₃ | -16.9 | -6.7  | -18.9 | -9.4  |
| X= NH₂ | -8.5  | 0.1   | -9.9  | 2.5   |
| X= OH  | -9.5  | 0.0   | -9.5  | 0.0   |
| X= F   | -14.7 | -4.6  | -15.6 | -8.2  |

FIGURE 14b. Summary of computational results on intermolecular exchange reactions at MP2(full) (+ΔZPE) (kcal mol⁻¹). Reprinted with permission from Reference 17. Copyright 1996 American Chemical Society
FIGURE 15. Asymmetric unit in the X-ray crystal structure of [Li−O−C(Me)-(c-Pr)2]$_6$ 17a, cyclopropane 17b ($D_{3h}$); 17c–f are optimized geometries of Li$^+$ and LiOH cyclopropane complexes ($C_{2v}$, $C_{2v}$, $C_{3v}$, $C_{2v}$ respectively) at RB3LYP/6-311+G** (C, H, O), /6-31G* (Li) level. Bond distances are given in angstroms. Reprinted with permission from Reference 18. Copyright 1996 American Chemical Society
TABLE 4. Coordination energies and natural charges of protonated lithium-complexed hydrocarbons illustrated in Figure 15. Reproduced with permission from Reference 18. Copyright 1996 American Chemical Society

<table>
<thead>
<tr>
<th>PG(NIMAG)b</th>
<th>E coord (kcal mol⁻¹)c</th>
<th>qH⁺ or qLi⁺ (au)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>17c</td>
<td>C₂v (1)</td>
<td>13.18</td>
</tr>
<tr>
<td>17d</td>
<td>C₂v (0)</td>
<td>22.91</td>
</tr>
<tr>
<td>17e</td>
<td>C₃v (0)</td>
<td>11.63</td>
</tr>
<tr>
<td>17f</td>
<td>C₂v (0)</td>
<td>8.86</td>
</tr>
</tbody>
</table>

a B3LYP/6-311++G**(C,H,O),/6-31G** (Li) optimized geometries.
b Point group and number of imaginary frequencies, obtained from B3LYP frequency calculations.
c H⁺ or Li⁺ coordination energies E coord (ZPE corrected) of the protonated or Li⁺-complexed species.
d Natural charges of coordinated H⁺ or Li⁺.

C₃H₂Li⁺, C₃H₂Li₂⁺ and C₃Li₃⁺ with lithiation energy of 67.0, 48.2 and 40.5 kcal mol⁻¹, respectively (equations 1, 2 and 3). The fall-off in this lithium-substituted cyclopropane ion is somewhat less than that along CH₂Li⁺, CHL₂⁺, and CLi₃⁺ series. This study showed the elongation of adjacent C–C bonds when both Li and NH₂ substituents are used; this is attributed to hyperconjugation and π-delocalization. The results suggest that one NH₂ and two Li substituents should be more stabilizing than two NH₂ and one Li substituents.

\[
\begin{align*}
c\cdot C₃H₃⁺ + CH₃Li & \rightarrow c\cdot C₃H₂Li⁺ + CH₄ \quad \Delta H = -67.0 \text{ kcal mol}^{-1} \quad (1) \\
c\cdot C₃H₂Li⁺ + CH₃Li & \rightarrow c\cdot C₃HLi₂⁺ + CH₄ \quad \Delta H = -48.2 \text{ kcal mol}^{-1} \quad (2) \\
c\cdot C₃HLi₂⁺ + CH₃Li & \rightarrow c\cdot C₃Li₃⁺ + CH₄ \quad \Delta H = -40.5 \text{ kcal mol}^{-1} \quad (3)
\end{align*}
\]

Improvements of the theoretical methodologies during the past few years have resulted in valuable corrections in the proposed structures. The availability of accurate structural and energetic data has encouraged detailed mechanistic studies of the reactions of organolithium compounds. These are discussed in the next section.

IV. THEORETICAL STUDIES INVOLVING REACTIONS OF ORGANOLITHIUM COMPOUNDS

Many reactions exhibited by organolithium compounds are studied theoretically. The structure, energy and bonding discussed above have direct consequences in determining the reaction paths. The large variety of the reactions of organolithium compounds studied theoretically are discussed below.

A. Regioselectivity in Addition

Regioselectivity of a reaction is important in synthetic organic chemistry. Although experimental results suggest an overview concerning the regioselectivity of the lithium metallation reaction, detailed theoretical studies were unavailable until recently. Application of the theoretical methodologies to various regioselectivity problems will be useful in predicting the result of a reaction. In 1995, Opitz and coworkers conducted a theoretical survey on the lithiation reaction of lithium methyl-1-naphthylcarbamate·2H₂O,
lithium methyl-2-naphthylcarbamate·2H₂O and lithium 1,2,3,4-tetrahydroisoquinoline carbamate·2H₂O based on MO theory²⁰. The theoretical results using PM3 and MNDO approximations correlate well with experiments. Comparison of the calculated energy of various transition state structures indicates the favored reaction path. The usefulness of semiempirical calculations for the investigation of the regioselectivity of lithiation reaction for molecules in which the carbon center has the same type of hybridization is very clear from this study.

Canepa and Tonachini investigated the addition reaction of formaldehyde with (1,1-difluoroallyl)lithium and (1,1-dichloro)allyllithium and -potassium (and the corresponding free anions) at HF and MP2 levels of theory²¹. It is found that the α-attack pathway (Scheme 2) is sharply preferred in 1,1-difluoroallyllithium, in the free anion and in 1,1-dichloroallylpotassium. In contrast, for (1,1-dichloroallyl)lithium the transition state energies for both the α- and γ-pathways are nearly the same, and the γ-attack pathway (Figure 16 and Table 5) is slightly preferred. Their calculations indicate that varying substituents on the electrophilic carbon could modulate the regioselectivity. These results are in good agreement with experiments.

Canepa and Tonachini investigated the addition reaction of formaldehyde with (1,1-difluoroallyl)lithium and (1,1-dichloro)allyllithium and -potassium (and the corresponding free anions) at HF and MP2 levels of theory. It is found that the α-attack pathway (Scheme 2) is sharply preferred in 1,1-difluoroallyllithium, in the free anion and in 1,1-dichloroallylpotassium. In contrast, for (1,1-dichloroallyl)lithium the transition state energies for both the α- and γ-pathways are nearly the same, and the γ-attack pathway (Figure 16 and Table 5) is slightly preferred. Their calculations indicate that varying substituents on the electrophilic carbon could modulate the regioselectivity. These results are in good agreement with experiments.

The theoretical study of Saa and coworkers on the stereochemical puzzle of Birch and vinylogous Birch reductive cleavage (BICLE and VIBICLE) of unsaturated benzyl ethers throws some light on the mechanistic path. Their work, involving the theoretical analysis of these complex reactions using a simplified model for contact, solvent separated and isolated ion pairs, is the first one in which calculations predict the existence of haptomers in anion radicals. Alternative routes for the vinylogous Birch reductive cleavage of cinnamyl ether (18) and Birch reductive cleavage of methyl phenylpropenyl ether (19) promoted by lithium naphthalenide is examined (Figures 17a and 17b) in order to understand the mechanistic details.

The MNDO structures of intermediates and transition states for the cleavage of benzyl and cinnamyl ethers through anion-radical routes and dianion routes involving CIPs (contact ion pairs) and IIPs (isolated nonsolvated ion pairs) are given in Figure 18.
Based on their study, Saa and coworkers\textsuperscript{22} suggested the lower energy cleavage routes as those involving contact ion pair, in which an important role is played by the lithium counterion, by assisting the leaving group through a spin $\beta$-elimination pathway. Transition states TS A and TS B in Figure 18a clearly illustrate this assertion. The lithium-promoted cleavage of phenylpropenyl derivatives (BICLE) is a stepwise process involving transient radical anion/cation species (Figure 18a). But the lowest energy route for cleavage of cinnamyl derivatives (VIBICLE), also stepwise, is that of the dianion/dication.
TABLE 5. (1,1-Dichloroallyl)lithium and (1,1-difluoroallyl)lithium. Total$^a$ and relative$^b$ energies of the important structures. Reproduced with permission from Reference 21. Copyright 1996 American Chemical Society

<table>
<thead>
<tr>
<th>Structure in Figure 16</th>
<th>MP2/3-21G$^c$</th>
<th>RHF/3-21G$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ (hartee)</td>
<td>$ΔE$ (hartee)</td>
</tr>
<tr>
<td>(1,1-Dichloroallyl)lithium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$σ$-Complex A(i)</td>
<td>-1150.94546</td>
<td>0.0</td>
</tr>
<tr>
<td>$α$ T.S A(ii)</td>
<td>-1150.93094</td>
<td>9.1</td>
</tr>
<tr>
<td>$γ$ T.S A(iii)</td>
<td>-1150.93765</td>
<td>4.9</td>
</tr>
<tr>
<td>$σ$ Product</td>
<td>—</td>
<td>-22.7</td>
</tr>
<tr>
<td>$γ$ Product</td>
<td>—</td>
<td>-18.9</td>
</tr>
<tr>
<td>(1,1-Difluoroallyl)lithium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$σ$-Complex B(i)</td>
<td>-433.91239</td>
<td>0.0</td>
</tr>
<tr>
<td>$α$ T.S B(ii)</td>
<td>-433.90641</td>
<td>3.8</td>
</tr>
<tr>
<td>$γ$ T.S B(iii)</td>
<td>-433.88817</td>
<td>15.2</td>
</tr>
<tr>
<td>$σ$ Product</td>
<td>—</td>
<td>-26.8</td>
</tr>
<tr>
<td>$γ$ Product</td>
<td>—</td>
<td>-20.6</td>
</tr>
</tbody>
</table>

$^a$In hartees.
$^b$In kcal mol$^{-1}$.
$^c$Level of theory at which the geometries of the critical points are optimized.

species as seen in transition structures TSC and TSD (Figure 18b). There are two competing diastereomeric transition states for the latter due to the existence of a chiral plane, but only one for the former, which does not have a chiral plane. This is responsible for the puzzling stereochemistry observed for BICLE and VIBICLE reactions.

In 1998, Kubota, Nakamura and coworkers studied the addition of substituted (alkoxy)allyllithium and zinc reagents to cyclopropenone acetal$^{23}$. They found that the regioselectivity of the (alkoxy)allylithiation is dependent on the substituent, while the diastereoselectivity remains constantly high (>97%). This is supported by their theoretical study (at the B3LYP/6-31G* level, Scheme 3) which reveals that a (hydroxy)allyllithium species of $π$-allylmetal nature can react with cyclopropane via two [2 + 2]-type four-centered transition states of similar energies leading to $α$- and $γ$-adducts.

Tomioka and coworkers studied recently the effect of the electronic and steric factors in $α$,$β$-unsaturated imines required for high 1,2- and 1,4-regioselectivity$^{24}$ (Figure 19). The 1,4- and 1,2-addition reactions of organolithium reagents with enaldimines depend on the nature of imines. Besides experimental investigation, they found that calculations using MOPAC (PM3, precise mode) and ab initio calculations at the HF/STO-3G level are comparable. The study reveals that the relative magnitude of the LUMO coefficient is one of the essential factors governing the substituent-dependent regioselectivity of the ambident enimines. An electron-withdrawing aryl group can increase the C2 LUMO coefficient and direct the 1,2-selective addition reaction. Hence, the LUMO coefficient as well as steric control would become an essential methodology for designing a selective reaction.

B. Self-condensation Reaction

Self-condensations are another set of important reactions of organolithium compounds. Tamao and Kawachi had reported that [(tert-butoxy diphenyl)silyl]lithium (20) exhibited ambiphilic character, and underwent a self-condensation reaction to give a [2-(tert-butoxy)disilylnyl]lithium derivative in THF as shown in Scheme 4, and also a nucleophilic substitution reaction with $n$-butyllithium$^{25}$. 


Li(NH$_3$)$_2$Naph stands for Li(NH$_3$)$_2$Naph, which stands for lithium naphthalenide. The diagram illustrates two alternative routes for vinylogous birch reductive cleavage of cinnamyl ether promoted by lithium naphthalenide. The anion-radical route involves the formation of a radical species, while the dianion route involves the formation of a dianion species. The reagents and products are shown in the diagram, with the reaction pathways indicated by arrows. Reprinted with permission from Reference 22. Copyright 1996 American Chemical Society.
1. Theoretical studies in organolithium chemistry

Li(NH₃)₂Naph stands for Li(NH₃)₂Naphthalene.

FIGURE 17b. Alternative routes for Birch reductive cleavage of methyl phenylpropenyl ether promoted by lithium naphthalenide. Reprinted with permission from Reference 22. Copyright 1996 American Chemical Society
FIGURE 18a. MNDO-determined structures of intermediates and transition states for the cleavage of cinnamyl and phenylpropenyl ethers 18 and 19, through anion-radical routes involving contact ion pairs (CIP) and isolated ion pairs (IIP). All energies are in kcal mol\(^{-1}\). Geometrical features relevant to haptomeric activation are shown: (1) C—OMe bond length and bond order (in brackets), (2) Li—OMe distance and (3) enthalpy of formation. Reprinted with permission from Reference 22. Copyright 1996 American Chemical Society.
FIGURE 18b. MNDO-determined structures of intermediates and transition states for the cleavage of cinnamyl and phenylpropenyl ethers 18 and 19, through dianion-radical routes involving contact ion pairs (CIP) and isolated ion pairs (IIP). All energies are in kcal mol\(^{-1}\). Geometrical features relevant to haptomeric activation are shown: (1) C—OMe bond length and bond order (in brackets), (2) Li—OMe distance and (3) enthalpy of formation. Reprinted with permission from Reference 22. Copyright 1996 American Chemical Society.
SCHEME 3. (Alkoxy)allylmetalation of cyclopropene, the four-centered transition states leading to both $\alpha$-adduct and $\gamma$-adduct are shown.
1. Theoretical studies in organolithium chemistry

FIGURE 19. Scheme showing 1,2- and 1,4-selective addition reactions of NuLi (Nu = Ph, Bu) followed by work-up. Reprinted with permission from Reference 24. Copyright 2001 American Chemical Society

SCHEME 4. Self-condensation reaction of [(tert-butoxydiphenyl)silyl]lithium (20) to give [2-(tert-butoxy)disilanyl]lithium derivative 21

In this case the self-condensation product undergoes no β-elimination, perhaps due to the low stability of the corresponding elimination product, disilene. Tanaka and coworkers studied theoretically the self-condensation reaction of lithium (alkoxy)silylenoid26 and provided a new reaction mode of silicon–silicon bond formation. A possible mechanism for this reaction involves the direct condensation of two molecules in which one functions as a nucleophile and the other as an electrophile. Although (t-BuO)Ph₂SiLi was used experimentally, (MeO)H₂SiLi was used as a model to make the calculation feasible. Various geometries are optimized at HF/6-31G* level of theory and single-point energies at the optimized stationary points were calculated at the MP2/6-31G** level. Stable geometries of (MeO)H₂SiLi 22 (I–VI) and its bis (23) and tris (24) solvated compounds are reproduced in Figure 20.

In order to undergo self-condensation, the two reactant molecules should approach each other to form a Si–Si bond. The geometries of the intermediate, the transition structure and the product are shown in Figure 21.

The potential-energy profile of the self-condensation reaction is given in Figure 22. The small activation energy of 0.9 kcal mol⁻¹ agrees with the experimental result that the compound undergoes a self-condensation reaction at low temperatures. The product is 24.8 kcal mol⁻¹ more favorable than the reactants. The transition state is formed at the Si–Si distance of 2.62 Å in which one silicon center has become nucleophilic and the other electrophilic. The lithium-assisted ionization of the Si–O bond lowers the energy of the σ*(Si–O) in the electrophilic part. The interaction between the HOMO in the nucleophilic part and the backside lobe of the σ*(Si–O) orbital in the electrophilic part leads to the formation of the Si–Si bond and breaking of the Si–O bond (Figure 23).
The study also suggests that the reaction proceeds via $S_N 2$-type displacement with retention of configuration of the silicon in the nucleophilic part but with inversion of configuration of the silicon in the electrophilic part. However, the final products, [2-(alkoxy)disilanyl]lithium and lithium methoxide, were in good agreement with experimental results. The verification of the stereochemistry is of future interest.

C. Lithium Organocuprate Clusters

The reactions of organocuprate reagents are of great importance owing to their synthetic utilities. The nature of the reacting species and their mechanism was a mystery until 1960. It was after the work of House in 1960, who demonstrated that the reactive species in organocopper reactions is a species having $R_2CuLi$ stoichiometry, that the study emerged in new directions.

Experimental evidence indicates that cuprates in solution exist largely as dimer ($R_2CuLi)_2$ (25), which is found as the reactive species in conjugate addition. The kinetic results were consistent with the participation of the dimer ($R_2CuLi)_2$/enone complex 26 (Figure 24) in the C−C bond-forming process of the conjugate addition. Relatively unreactive $\alpha, \beta$-unsaturated ketones, esters and nitriles were also found to form complexes represented by 26 in Figure 24.

Since NMR studies suggest a $C_\alpha−C_\beta$ double bond in 26 to be significantly weak, a better representation of the cuprate/enone complex is as a cupriocyclopropene 27, which is represented in the reaction shown in Figure 25. However, the indispensability of the dimeric cluster in the crucial C−C bond-forming step is not clearly understood.

In 1997, the work of Nakamura, Mon and Morokuma demonstrated the important roles of the cluster structure and the cooperation of different metals therein. They determined

![FIGURE 20. Optimized geometries and relative energies (kcal mol$^{-1}$) for (MeO)H$\text{SiLi}$ (22), (MeO)H$\text{SiLi}$($\text{H}_2\text{O}$)$_2$ (23) at MP2//HF/6-31G** and optimized geometry for (MeO)H$\text{SiLi}$($\text{H}_2\text{O}$)$_3$ (24) at HF/6-31G**. Bond lengths are in angstroms, bond angles in degrees. Reprinted with permission from Reference 26. Copyright 1998 American Chemical Society]
FIGURE 21. Optimized geometries for reactive intermediate (Int), transition state (TS) and product (P) at MP2//HF/6-31G** for the self-condensation reaction of lithium(alkoxy)silylenoid. Bond lengths are in angstroms, and bond angles in degrees. Reprinted with permission from Reference 26. Copyright 1998 American Chemical Society
FIGURE 22. Potential-energy profile for the self-condensation reaction of lithium(alkoxy)silylenoid 23, VII (see Figure 20) at MP2/HF/6-31G**. Reprinted with permission from Reference 26. Copyright 1998 American Chemical Society

the structures of the intermediates and the transition states on the potential-energy surface of the reaction pathway for transfer of a methyl group of a cuprate cluster (Me2CuLi)2 to acrolein in the conjugate addition, using DFT calculations. At the stage of crucial C—C bond formation, intrinsic reaction coordinate (IRC) analysis was also performed. The study demonstrated a rotational pathway for the dimer which undergoes the conjugate addition, and cooperation of lithium and copper atoms in order to facilitate the reaction. A number of complexes that exist before the transition state of irreversible C—C bond formation as well as a series of structural rearrangements involved in the conjugate addition are shown in Figure 26. The two Lewis acidic lithium atoms in the cluster cooperatively assist the electron transfer process. Electron transfer from the cuprate moiety to the substrate triggers the cluster opening. This study reveals the important role of the cations in organocuprate clusters for the C—C bond-forming reaction. These theoretical calculations also suggest the importance of solvation in the C—C bond-forming stage of carbocupration and the conjugate addition.

Nakamura and coworkers extended their work on organocuprate clusters by studying its effects on acetylene. In 1997, they illustrated the 1,2-addition of cuprates to acetylene and discussed computational studies on the conjugate addition of bis-, tris- and tetrametallic cuprate clusters to acrolein. In the cluster reaction of Me2CuLi.LiCl, the lithium atom in the cluster stabilizes the developing negative charge on the acetylene moiety and assists the electron flow from the copper atom. Experimental results imply that the solvation of lithium atom with a crown ether, which separates the lithium cation from the cluster, affects the carbocupration reaction. Excellent correlation between the theoretical and experimental results suggests the cooperative functions of lithium and copper atoms in the cuprate reactions.
D. Organolithium Compounds Involving Aldehydes and Ketones

Though lithium enolates are important reagents in their versatile synthetic utility, the property of aggregation makes it difficult to understand the mechanism of their reactions. The carbonyl carbon kinetic isotope effect (KIE) and the substituent effect were measured in 1997 for the reaction of lithium pinacolone enolate (CH$_2$=C(OLi)C(CH$_3$)$_3$) with benzaldehyde by Yamataka, Tsuno and coworkers$^{28}$. The results were compared with those for other lithium reagents such as MeLi, PhLi and CH$_2$=CHCH$_2$Li. 

Ab initio MO calculations at HF/6-31+G$^*$ were carried out to estimate the equilibrium isotopic effect (IE) on the addition to benzaldehyde. Two general mechanisms were analyzed for carbonyl addition reaction using model compounds: the polar addition mechanism (PL) and the electron transfer (ET)–radical coupling (RC) sequence (Figure 27).
In this study, benzaldehyde and benzaldehyde-methyllithium adduct were fully optimized at HF/6-31G* and their vibrational frequencies were calculated. The authors used MeLi instead of lithium pinacolone enolate, since it was assumed that the equilibrium IEs are not much different for the MeLi addition and lithium enolate addition. Dehalogenation and enone-isomerization probe experiments detected no evidence of a single electron transfer to occur during the course of the reaction. The primary carbonyl carbon kinetic isotope effects and chemical probe experiments led them to conclude that the reaction of lithium pinacolone enolate with benzaldehyde proceeds via a polar mechanism.
FIGURE 26. The reaction pathway of the conjugate addition of (Me₂CuLi)₂ to acrolein. Approximate stereochemistry is implied by the use of bold lines. Dative bonds are depicted by a thick dotted line and forming/cleaving forming bonds by a broken line. Note, however, that this distinction could be oversimplified and may be misleading. RT₁—(Me₂CuLi)₂; RT₂—acrolein; CPli—lithium complex formed by coordination of RT₂ to Li atom of RT₁; CPel—complex formed by isomerization of CPli via transition state TSiso₁; CPop—Copper π-complex which is in equilibrium with CPel via transition state TSiso₂; PD—product complex formed from CPop via transition state TS by following intrinsic reaction pathway. The energy changes are in kcal mol⁻¹ at the B3LYP/631A//B3LYP/631A (which consists of the Ahlrichs all-electron SVP basis set for Cu and 6-31G(d) for the rest) and are given above the arrows. Reprinted with permission from Reference 27. Copyright 1997 American Chemical Society
In 1998, Hasanayn and Streitwieser reported the kinetics and isotope effects of the Aldol–Tishchenko reaction\textsuperscript{29}. They studied the reaction between lithium enolates of isobutyrophenone and two molecule of benzaldehyde, which results in the formation of a 1,3-diol monoester after protonation (Figure 28). They analyzed several aspects of this mechanism experimentally. \textit{Ab initio} molecular orbital calculations on models are used to study the equilibrium and transition state structures. The spectroscopic properties of the lithium enolate of \textit{p}-(phenylsulfonyl) isobutyrophenone (LiSIBP) have allowed kinetic study of the reaction. The computed equilibrium and transition state structures for the compounds in the sequence of reactions in Figure 28 are given along with the computed reaction barriers and energy in Figure 29 and Table 6.

The excellent agreement with the experimental and calculated isotope effect (calculated for formaldehyde, 3.22, and for acetaldehyde, 3.3; experimental value 2.9) supports the computational approach. This suggests that the computed transition structure for hydride transfer in the reaction of the lithium enolate of acetone with acetaldehyde (Figure 30) is realistic.
FIGURE 29. Optimized geometries for the reactants, transition structures and products in the sequence of reactions between the lithium enolate (LiEn) derived from acetaldehyde and formaldehyde. The total reaction sequence is: LiEn + CH₂O → complex-1 → TS1 → P1 → complex-2 → TS2 → P2 (Figure 28) → TS3 (Figure 30) → P3 (Figure 28). Theoretical calculations were carried out at the HF/6-311++G* level. Reprinted with permission from Reference 29. Copyright 1998 American Chemical Society.
TABLE 6. Computed reaction and activation energies and corresponding isotope effects for the sequence of reactions between lithium vinylxide (LiEn) and formaldehyde and between the lithium enolate of acetone (LiAc) and acetaldehyde. Reproduced with permission from Reference 29. Copyright 1998 American Chemical Society

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (^a)</th>
<th>ΔZPE (^b)</th>
<th>ΔΔZPE (^c)</th>
<th>MMI (^d)</th>
<th>EXC (^d)</th>
<th>EXP (^d)</th>
<th>Isotope effect (^e,f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiEn + CH(_2)O → complex-1</td>
<td>−18.4</td>
<td>1.625</td>
<td>0.122</td>
<td>1.35</td>
<td>0.83</td>
<td>0.82</td>
<td>EIE (_{\text{com}-1}) = 0.92</td>
</tr>
<tr>
<td>LiEn + CH(_2)O → TS1</td>
<td>−12.2</td>
<td>2.379</td>
<td>0.225</td>
<td>1.35</td>
<td>0.91</td>
<td>0.68</td>
<td>KIE(_{1}) = 0.84</td>
</tr>
<tr>
<td>LiEn + CH(_2)O → P1</td>
<td>−26.8</td>
<td>4.135</td>
<td>0.256</td>
<td>1.34</td>
<td>0.94</td>
<td>0.65</td>
<td>EIE(_{1}) = 0.82</td>
</tr>
<tr>
<td>P1 + CH(_2)O → complex-2</td>
<td>−13.8</td>
<td>1.280</td>
<td>0.085</td>
<td>1.36</td>
<td>0.80</td>
<td>0.87</td>
<td>EIE(_{\text{com}-2}) = 0.95</td>
</tr>
<tr>
<td>P1 + CH(_2)O → P2</td>
<td>−11.1</td>
<td>2.205</td>
<td>0.225</td>
<td>1.37</td>
<td>0.85</td>
<td>0.68</td>
<td>KIE(_{2}) = 0.79</td>
</tr>
<tr>
<td>P1 → P3</td>
<td>−14.1</td>
<td>4.070</td>
<td>0.293</td>
<td>1.37</td>
<td>0.92</td>
<td>0.61</td>
<td>EIE(_{2}) = 0.77</td>
</tr>
<tr>
<td>LiAC + MeCHO → TS1-Me</td>
<td>−3.0</td>
<td>0.315</td>
<td>−0.033</td>
<td>0.99</td>
<td>1.00</td>
<td>1.06</td>
<td>EIE(_{3}) = 1.05</td>
</tr>
<tr>
<td>LiAC + MeCHO → TS1-Me</td>
<td>−9.0</td>
<td>1.872</td>
<td>0.175</td>
<td>1.15</td>
<td>0.98</td>
<td>0.74</td>
<td>KIE(_{1-Me}) = 0.84</td>
</tr>
<tr>
<td>LiAC + MeCHO → P1-Me</td>
<td>−24.5</td>
<td>3.654</td>
<td>0.187</td>
<td>1.15</td>
<td>1.00</td>
<td>0.73</td>
<td>EIE(_{1-Me}) = 0.84</td>
</tr>
<tr>
<td>P1-Me + MeCHO → P2-Me</td>
<td>−10.2</td>
<td>3.348</td>
<td>0.240</td>
<td>1.16</td>
<td>1.00</td>
<td>0.67</td>
<td>EIE(_{2-Me}) = 0.78</td>
</tr>
<tr>
<td>P2Me → TS3-Me</td>
<td>27.9</td>
<td>−1.584</td>
<td>−0.702</td>
<td>1.00</td>
<td>1.02</td>
<td>3.27</td>
<td>KIE(_{3-Me}) = 3.33</td>
</tr>
</tbody>
</table>

\(^a\)Energies are given in kcal mol\(^{-1}\) and corrected for ΔZPE (scaled by a factor of 0.9).

\(^b\)ΔZPE = ZPE\(_{\text{product}}\) − Σ (ZPE\(_{\text{reactants}}\)); or ZPE\(_{\text{TS}}\) − Σ (ZPE\(_{\text{reactants}}\)) (protio species).

\(^c\)ΔΔZPE = ΔZPE\(_{\text{Me}}\) − ΔZPE\(_{\text{H}}\); ΔZPE\(_{\text{Me}}\) corresponds to the terms for the reactions of monodeuteriated aldehydes.

\(^d\)Terms defined by IE = MMI x EXC x EXP (IE is the Isotopic exchange equilibrium, MMI is the mass moment of inertia term representing the rotational and translational partition function ratios, EXC is the vibrational excitation term and EXP is the exponential zero point energy).

\(^e\)Isotope effects were computed at 25°C. The symmetry term due to CH\(_2\)O/CHDO has not been accounted for in the calculation, since this is unique to formaldehyde. EIE is the equilibrium isotope effect and KIE is the Kinetic isotope effect.

\(^f\)The two hydrogens of formaldehyde become inequivalent in their action products. Similar isotope effects are obtained when either of the two hydrogens is deuteriated.

The computed transition state also rationalizes the observed stereochemistry. For the current reactions, a transition structure represented in Figure 31 appears to be appropriate. This structure indicates that the three substituents R and R’ are all equatorial and give rise to the anti product. The corresponding syn product would require a highly strained structure in which one R’ group is axial.
E. Other Reactions

Besides the reactions discussed earlier for organolithium compounds, there are several specific reactions which have been studied theoretically. A brief description of some of them is given below.

Romesberg and Collum studied the lithium-amide-mediated metallations of ketones and the corresponding N-alkylimines, through semiempirical MNDO calculations. The study suggests that the relative stabilities of the transition state structures for two or more competing reaction pathways are not regulated by their geometries, but depend more precisely on the effect of substituents and solvents. In 1998, Johansson, Tegenfeldt and Lindgren attempted to model the lithium ion transport along a polyethyleneoxide (PEO) chain. They used the PEO oligomer diglyme (CH3(CH2CH2O)2CH3) as the model system. The results obtained using HF/6-31G* and MP2/6-311+G** were compared with the NMR data for the activation energies of conformational transformations in complexed PEO. A transport path of Li+ along a single PEO chain involving tetradeutate and tridentate coordination with small energy difference has been calculated.

In the same year, Schleyer and coworkers came up with a revolutionary observation regarding the anionic (3 + 2) cycloaddition of allyl, 2-borylallyl- and 2-azaallyllithium to ethylene. Their study used B3LYP/6-311+G** and MP2(fc)6-31+G* computations. The study revealed that the concerted 4π + 2π mechanism as expected from the Woodward–Hoffmann rules is less favorable than the two-step pathway for the cycloadditions of ethylene to the allyl, 2-borylallyl and 2-azaallyl anion and their lithiated counterparts. The work was also in excellent agreement with that of Sauers in 1996. A suggestion for the unfavorability of the concerted cycloaddition mechanism has been made in terms of molecular polarizability anisotropy of the reactants, which is illustrated in Figure 32 and Table 7. The diagonal elements of the polarizability tensors (αxx, αyy and αzz) define the molecular polarizabilities along the x, y and z axes and measure the ease and direction in which the electrons in a molecule are shifted by an external magnetic field. Experimental data are only available for ethylene.

The electrostatic interaction of ethylene and the allylic compounds is more favorable energetically for the stepwise than for the concerted cycloaddition mechanism.

Campos, Sampedro and Rodriguez studied theoretically in 1998 the competition of the concerted and stepwise mechanism of hydrogen migration and lithium iodide α-elimination in the trihydrate 1-iodo-1-lithioethene. Since the lithiated derivative of 1-iodoethane readily decomposes to ethylene, experimental techniques are found to be of less use. Their ab initio theoretical calculations indicate that the preferred mechanism is the concerted rather than stepwise pathway as illustrated in Figure 33. Their studies also suggest that 1-iodo-1-thioethene prefers to be a monomer in THF and the activation barriers for the cis and trans hydrogen migration are nearly the same.
Table 7. The polarizability tensors of ethylene, allyl anions and allyl lithiums. Reproduced with permission from Reference 32. Copyright 1998 American Chemical Society

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha_{xx}$</th>
<th>$\alpha_{yy}$</th>
<th>$\alpha_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>24.91</td>
<td>22.68</td>
<td>36.22</td>
</tr>
<tr>
<td>Allyl anion</td>
<td>48.65</td>
<td>89.51</td>
<td>111.42</td>
</tr>
<tr>
<td>Allyllithium</td>
<td>50.73</td>
<td>50.31</td>
<td>81.56</td>
</tr>
<tr>
<td>2-Borylallyl anion</td>
<td>80.26</td>
<td>86.12</td>
<td>134.73</td>
</tr>
<tr>
<td>2-Borylallyllithium</td>
<td>71.44</td>
<td>59.22</td>
<td>95.69</td>
</tr>
<tr>
<td>2-Azaallyl anion</td>
<td>51.35</td>
<td>75.06</td>
<td>113.26</td>
</tr>
<tr>
<td>2-Azaallyllithium</td>
<td>42.53</td>
<td>49.77</td>
<td>83.34</td>
</tr>
</tbody>
</table>

V. APPLICATIONS IN SPECTROSCOPY

In addition to the structural characterization, several dynamic processes involving organolithium reagents are monitored by various spectroscopic methods. Theoretical studies have helped enormously in these studies. Many of these applications have already been discussed. A few additional results are added here. Experimentally observed and theoretically calculated $^{13}$C and $^1$H NMR shifts suggest some insights into the mechanism of the reactions. Wave functions obtained at the RHF/6-31+G* level of theory were used with the new method IGAIM (Individual Gauges for Atoms In Molecules) developed by Keith and Bader in the calculation of $^{13}$C and $^1$H NMR chemical shifts. Werstiuk and Ma supported the usefulness of this method in 1996 during their study of $^{13}$C and $^1$H chemical shift calculations on unsaturated hydrocarbons and organolithium compounds. The ionic nature of the C–Li bond is supported by theoretical calculation of the NMR spin–spin coupling constant by Koizumi and Kikuchi in 1995. The implications of their study and conclusion on the mostly ionic nature of the C–Li bond in alkylolithiums are supported by experiment. The usefulness of HOESY experiment in the description of initial state geometries of organolithium complexes is also supported by crystallographic and computational results of Hilmersson and coworkers. This study suggests the importance of theory in extracting maximum information from an experimental technique.
FIGURE 33. Hydrogen migration and lithium iodide α-elimination in 1-iodo-1-lithioethene trihydrate.

(a): The concerted pathway involving migration of the hydrogen with a cis relationship to the lithium atom together with a simultaneous loss of lithium iodide through transition state TS1 to yield acetylene.

(b): The concerted pathway involving the migration of the hydrogen with a trans relationship to the lithium atom through transition state TS2 giving the acetylene.

(c): The stepwise route involving the formation of carbene through transition state TS3 and finally giving acetylene via TS4. Reprinted with permission from Reference 34. Copyright 1998 American Chemical Society.
VI. CONCLUSIONS

It is clear from the above survey that theoretical approaches contribute enormously in the study of structure, bonding, energetics and reactions of organolithium compounds. Major advances have been made in understanding the nature of the C−Li bond during the last six years. A predominantly ionic bond with a definite, though small and varying covalent contribution is perhaps a description that reflects the emerging trends. Theoretical studies of various reactions gave a clear answer to many questions, which were unanswered in the past. The developments in software and hardware have enabled theoretical studies on systems that were considered beyond reach just a few years ago. Theoretical calculations in conjunction with spectroscopic measurements are of great importance in many applications. Further developments of sophisticated methodologies and more powerful computers will lead to yet deeper understanding of the chemistry of organolithium compounds through theoretical studies.

VII. REFERENCES

1. Theoretical studies in organolithium chemistry
