

## Structure, Bonding, and Solvation of Lithium Vinylcarbenoids

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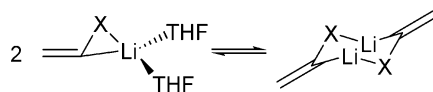
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X = F, Cl, Br, OMe, NMe<sub>2</sub>

Molecular modeling was used to determine the structure of lithium vinylcarbenoids in the gas phase and in THF solution. Solvent effects were modeled by microsolvation with explicit THF ligands on each of the lithium atoms. The carbenoid geometries are dependent on the heteroatom and on solvation. The calculations predict 1-chlorovinyl lithium and 1-bromovinyl lithium to be a mixture of monomer and dimer at 200 K and mostly monomer at higher temperatures, whereas the 1-fluoro-, 1-methoxy-, and 1-dimethylaminovinyl lithium are predicted to be dimeric in solution.

### Introduction

Carbenes are reactive divalent carbon compounds that undergo a variety of reactions, including double bond insertion to form cyclopropanes and insertion into a variety of single bonds. A large number of organometallic compounds undergo reactions typical of carbenes and are known collectively as carbenoids. Of particular importance are lithium, zinc, and transition metal carbenoids.

Numerous dihalogenated organic compounds undergo a lithium–halogen exchange reaction with alkyllithiums to form lithioalkyl halides.<sup>1–4</sup> These compounds display both electrophilic and nucleophilic properties and undergo the characteristic carbene-like reactions and are therefore referred to as lithium carbenoids. Many lithium carbenoid reactions are synthetically useful, including cyclopropane formation from alkenes, carbon–hydrogen, carbon–carbon, and carbon–heteroatom bond insertion, alkyne formation, and reaction with aldehydes and ketones. In addition to lithiated alkyl and vinyl halides, lithio derivatives of ethers, amines, and sulfur compounds also have carbenoid properties.

The simplest lithium carbenoids are the lithium halomethanes, which are prepared from an alkyllithium and a di- or polyhalomethane. Seebach and co-workers observed several lithium carbenoids of alkyl halides by NMR at temperatures below –100 °C. Two spectral features were noteworthy. The first was a large deshielding effect in the <sup>13</sup>C spectrum upon replacing a hydrogen or halogen with lithium. The second was a large <sup>6</sup>Li–<sup>13</sup>C coupling constant of about 17 Hz that was independent of the lithium haloalkane. The large coupling constants indicated a greater s-orbital character in the carbon orbitals bonding to the lithium atom.<sup>1–4</sup>

The structure and bonding in these lithium halomethanes has been the subject of several computational investigations at different levels of theory. The most stable geometry for the gas-phase monomer of lithiofluoromethane and lithiochloromethane has the halogen bridging the carbon–lithium bond. (Scheme 1, **a**)<sup>5–12</sup>

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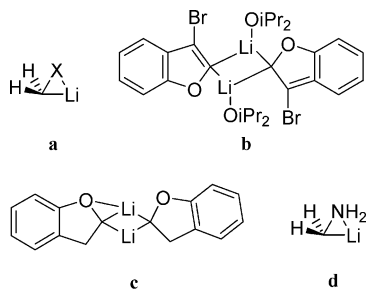
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## SCHEME 1. Representative Lithiocarbenoid Structures



Calculations were performed on monomeric and dimeric lithiohalomethanes in the gas phase, microsolvated by THF ligands, solvated by a continuum solvent model, and with both microsolvation and continuum solvation. The calculations predict these carbenoids to be dimeric in the gas phase, but the calculated dimerization energies decreased with solvation by ethereal solvents. Both microsolvation and continuum solvation resulted in increased lithium–carbon and lithium–halogen bond distances.

Several carbenoid structures have been observed or calculated for lithioethers and C-lithioamines. The carbenoid-like crystal structure (Scheme 1, **b**) has been obtained as the bis-diisopropyl etherate and is stable to elimination of LiBr.<sup>13</sup> A similar crystal structure was observed in the TMEDA solvate of structure **c** of Scheme 1.<sup>14</sup> Calculated structures of lithiomethylamine (Scheme 1, **d**) showed that it also adopts a carbenoid-like bridged structure similar to fluoromethyl lithium and chloromethyl lithium and that lithium bridges the carbon and heteroatom more effectively than sodium. The bridged structures were 5–10 kcal/mol more stable than the corresponding anions at the HF/6-31G\*/3-21G level and up to 20 kcal/mol more stable than unbridged isomers.<sup>8,15</sup> A carbenoid-like isomer of the lithium enolate of acetaldehyde has also been reported as a local minimum on the potential energy surface.<sup>16</sup>

Carbene-like properties and copper-mediated coupling reactions have been reported for lithiovinylhalides.<sup>17</sup> Similar coupling reactions have been observed with lithiated vinyl ethers.<sup>18</sup> An NMR study revealed that a TMEDA solvate of 2-lithiobenzofuran is dimeric in toluene,<sup>14</sup> similar to the calculated dimeric structures for fluoromethyl lithium and chloromethyl lithium. Although X-ray studies have provided some detail of the solid-state structures of lithium vinylcarbenoids, details of the solution structures of lithium vinylcarbenoids remain unknown. In this paper we investigate the geometries, dimerization energies, and solvation state of lithium vinylhalide, vinyl ether, and vinylamine carbenoids.

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## Computational Methods

All geometry optimizations and frequency calculations were performed using Gaussian 98 or Gaussian 03<sup>19</sup> Solvation was modeled by microsolvation with explicit THF ligands on the lithium atoms. Although the use of continuum solvent models in combination with microsolvation sometimes generates slightly better energies than microsolvation alone, the continuum solvent models have proven inconsistent with lithium compounds and were not used in this study. The free energies of each species were obtained by adding the thermal correction to the free energy, obtained from the frequency calculations, to the calculated internal energies. Geometry optimizations were performed with the MIDIX<sup>20</sup> and 6-31+G(d) basis sets, and single point energy calculations were performed with the 6-311+G(2df, 2pd) basis set. Free energies were obtained by adding the thermal correction to the free energy, obtained at the B3LYP/MIDIX level, to the internal energy at either the B3LYP/6-31+G(d) or B3LYP/6-311+G(2df, 2pd) level. Basis set superposition errors (BSSE) from the smaller basis set were estimated using counterpoise corrections. Atomic charges were calculated using the Natural Bond Order (NBO) analysis.<sup>21</sup>

All frequency calculations in this paper were carried out for temperatures of 200 and 298 K. The standard-state molar free energy of a solute in the liquid phase at these temperatures is given by  $G^\circ_T(l) = G^\circ_T(\text{gas}) + \Delta G^\circ_s$  ( $T = 200$  or  $298$  K), where  $l$  denotes a solute in the liquid phase and  $\Delta G^\circ_s$  is the standard-state free energy of solvation. The microsolvation model assumes that  $\Delta G^\circ_s$  is adequately represented by the coordinated ethereal ligands, so that  $G^\circ_T(l) \approx G^\circ_T(g)$  of the “supermolecule” composed of the organolithium compound plus its coordinated ethereal ligands. Furthermore,  $G^\circ_T(g) = E_{\text{en}} + E_{\text{vib}_0} + G^{\text{trans},o_T} + G^{\text{rot},T} + G^{\text{vib},T} + RT$  where  $R$  is the gas constant. The individual terms were calculated as follows:  $E_{\text{en}}$ , the electronic energy plus nuclear repulsion, by the B3LYP hybrid density functional method<sup>22,23</sup> with the 6-31+G(d) basis set;  $E_{\text{vib}_0}$ , the  $y = \text{unscaled}$  zero point energy, by B3LYP calculations with the MIDIX basis set;  $G^{\text{trans},o_T}$ , the standard-state thermal translational energy for a standard state of 1 mol/L (not 1 atm) from the masses;  $G^{\text{rot},T}$ , the thermal rotational free energy, from

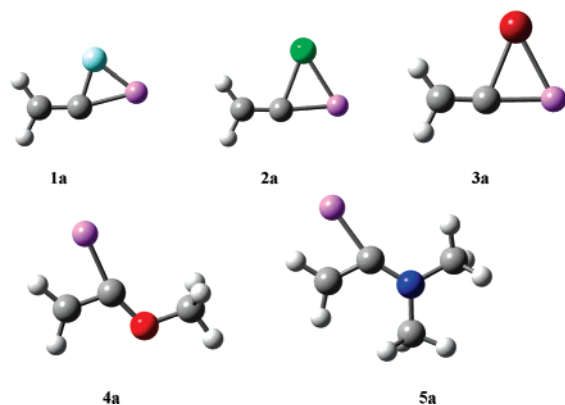
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**FIGURE 1.** Optimized gas-phase geometries of  $\text{H}_2\text{C}=\text{CLiX}$  carbene monomers. Grey, carbon; white, hydrogen; violet, lithium; light blue, fluorine; green, chlorine; dark red, bromine; light red, oxygen; dark blue, nitrogen.

**TABLE 1.** C=C Bond Lengths and Natural Atomic Charges of  $\text{H}_2\text{C}(2)=\text{C}(1)\text{LiX}$  Monomers

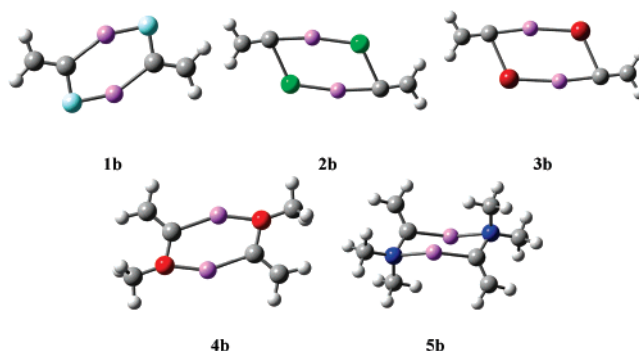
X	C=C (Å)	charge C1	charge C2	charge Li	charge X
F	1.326	-0.188	-0.632	0.926	-0.587
Cl	1.323	-0.363	-0.601	0.920	-0.461
Br	1.324	-0.422	-0.596	0.916	-0.398
OMe	1.363	-0.259	-0.711	0.880	-0.606
NMe <sub>2</sub>	1.377	-0.350	-0.779	0.903	-0.536

B3LYP/MIDIX geometries;  $G^{\text{vib}}_T$ , the thermal vibrational free energy, from unscaled B3LYP/MIDIX vibrational frequencies;  $\Delta G^{\circ}_S$ , from B3LYP/6-31+G(d) microsolvated calculations, with a gas-phase standard state as specified above and a liquid-phase standard state of 1 mol/L.

## Results and Discussion

The gas-phase optimized geometries of the lithium vinylcarbenoid monomers are shown in Figure 1. The fluoro- (**1a**), chloro- (**2a**), and bromocarbenoids (**3a**) had geometries similar to those reported for fluoro- and chloromethylithium, with the carbon, lithium, and halogen forming a three-membered ring.<sup>12</sup> The corresponding methoxy- (**4a**) and dimethylaminocarbenoids (**5a**) optimized to different structures, with the lithium atom coordinating to a vinylic hydrogen rather than the oxygen or nitrogen atom. In both cases, the vinylic hydrogen nearest the lithium made a  $\text{H}-\text{C}=\text{C}$  angle of  $121^\circ$ , compared to the other  $\text{H}-\text{C}=\text{C}$  angles of  $126^\circ$  and  $128^\circ$  in **4a** and **5a**, respectively. The  $\text{Li}-\text{H}$  contacts were 2.006 Å in **4a** and 1.880 Å in **5a**.

The calculated natural atomic charges from a NBO analysis differed significantly from the halide carbenoids to the methoxy- and dimethylaminocarbenoids, as did the C=C bond lengths. The results are shown in Table 1. The C=C bond length in the methoxy- and dimethylaminocarbenoids was longer than the corresponding halocarbenoids by about 0.04–0.05 Å. The NBO analysis also showed the lithium atom to have a larger positive charge in the halogen carbenoids compared to the methoxy and dimethylamino analogues, suggesting more ionic character of the bonds. However, the charge distribution on the two carbon atoms and the heteroatom varied considerably in the five compounds, making a quantitative assignment of ionic character difficult.



**FIGURE 2.** Optimized gas-phase geometries of  $\text{H}_2\text{C}=\text{CLiX}$  carbene dimers.

**TABLE 2.** C=C Bond Lengths and Natural Atomic Charges of  $\text{H}_2\text{C}(2)=\text{C}(1)\text{LiX}$  Dimers

X	C=C (Å)	charge C1	charge C2	charge Li	charge X
F	1.332	-0.218	-0.596	0.870	-0.520
Cl	1.313	-0.171	-0.639	0.868	-0.608
Br	1.317	-0.273	-0.618	0.853	-0.494
OMe	1.348	-0.265	-0.647	0.859	-0.689
NMe <sub>2</sub>	1.356	-0.433	-0.593	0.864	-0.644

**TABLE 3.** Gas-Phase Dimerization Free Energies of  $\text{H}_2\text{C}=\text{CLiX}$  Carbenoids at 200 K

X	B3LYP/6-31+G(d)	B3LYP/6-311+G(2df,2pd)	BSSE
F	-36.09	-34.45	2.17
Cl	-24.01	-21.22	2.22
Br	-28.56	-21.39	8.29
OMe	-50.41	-46.21	2.85
NMe <sub>2</sub>	-36.33	-30.66	2.62

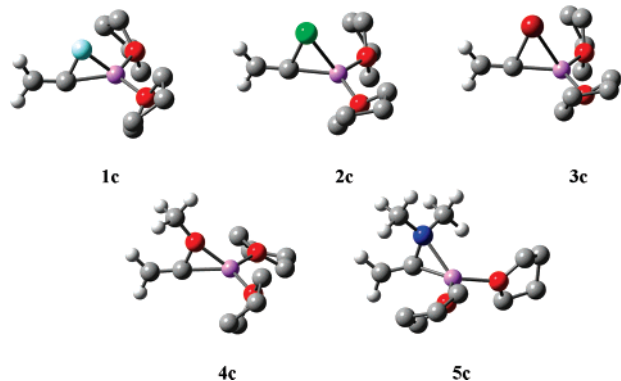
The gas-phase optimized geometries of the lithium vinylcarbenoid dimers are shown in Figure 2. In structures **1b–4b**, the lithium and halogen or oxygen atoms were essentially coplanar with the vinyl group, whereas **5b** adopted a chairlike geometry. The calculated C=C bond lengths and natural atomic charges are shown in Table 2. The trend in C=C bond lengths was comparable to that of the monomer, except that this bond was lengthened in the fluorocarbenoid dimer compared to those of the chloro- and bromocarbenoids. The atomic charges on the lithium atoms suggest that the bonding is more covalent in the dimer than in the monomer, and there is less variation in the covalent character of the dimer as the heteroatom is changed, although the negative charge distribution between the two carbon atoms and the heteroatom still varied with structure. Except for the dimethylaminocarbenoid, the charge on C<sub>1</sub> of the dimer is relatively constant compared to that of the monomer. The slightly nonlinear C=C–Li bond angle in the halocarbenoids **2b** and **3b** is suggestive of the structure reported for the singlet vinylolithium radical, whereas the corresponding bond angles in **1b**, **4b**, and **5b** are similar to the calculated geometry of vinyl-lithium.<sup>24</sup>

The gas-phase dimerization energies of lithium vinylcarbenoids at 200 and 298 K are listed in Tables 3 and 4, respectively, along with the basis set superposition errors (BSSE) resulting from the use of the 6-31+G(d)

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**TABLE 4.** Gas-Phase Dimerization Free Energies of  $\text{H}_2\text{C}=\text{CLiX}$  Carbenoids at 298 K

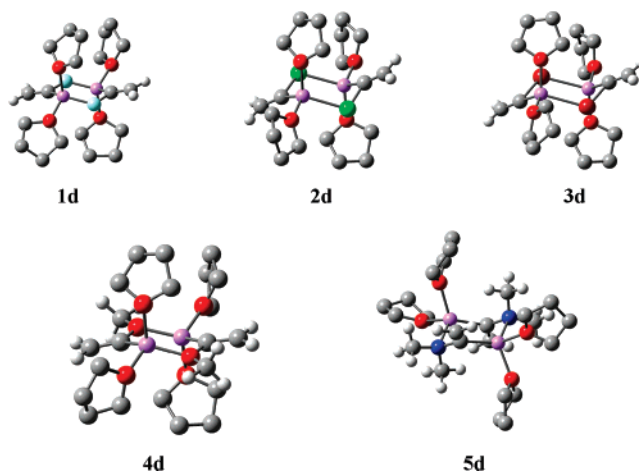
X	B3LYP/6-31+G(d)	B3LYP/6-311+G(2df,2pd)	BSSE
F	-32.73	-31.10	2.17
Cl	-20.44	-17.65	2.22
Br	-25.47	-18.30	8.29
OMe	-46.33	-42.13	2.85
NMe <sub>2</sub>	-31.60	-25.94	2.62

**FIGURE 3.** Optimized geometries of THF-solvated  $\text{H}_2\text{C}=\text{CLiX}$  carbenoid monomers. Solvent hydrogens omitted for clarity.

basis set. With the fluoro-, chloro-, methoxy-, and dimethylaminocarbenoids, the BSSE caused the calculated energy of the dimer to be too stable by about 2–3 kcal/mol, and the BSSE correction brought the B3LYP/6-31+G(d) dimerization energies into good agreement with those calculated with the larger basis set. The BSSE of the bromo carbenoid was much larger than the others, and the BSSE-corrected 6-31+G(d) energy was also in reasonable agreement with that of the larger basis set. These calculations indicate that each of the carbenoids will exist exclusively as a dimer in the gas phase at both 200 and 298 K.

The optimized geometries of THF-disolvated lithiovinylcarbenoids are shown in Figure 3. Two THF ligands per lithium atom were used, in analogy to the structures of halomethyl lithium carbenoids.<sup>12</sup> In each solvated carbenoid except **5c**, the lithium and heteroatoms were coplanar with the vinyl group. Unlike the gas-phase structures, the THF-solvated methoxy- and dimethylaminocarbenoids optimized to structures in which the heteroatom bridged the C–Li bond.

Figure 4 shows the optimized geometries of THF-tetrasolvated lithiovinylcarbenoid dimers. In each case, the geometry optimized to a chairlike conformation similar to those reported for fluoromethyl lithium and chloromethyl lithium.<sup>12</sup> The vinyl C=C bond lengths in structures **1d**–**3d**, shown in Table 5, varied only slightly with the halogen in both the solvated monomer and dimer, with a fluoro substituent having the largest effect. Both the methoxy and amino substituents increased the C=C bond length in the solvated monomers and dimers. This increased bond length cannot be due to purely electronegativity effects, as fluorine is more electronegative than either oxygen or nitrogen. A more plausible explanation is a resonance effect with the lone pair of oxygen or nitrogen, which is consistent with the fact that the amino substituent has the largest effect.

**FIGURE 4.** Optimized geometries of THF-solvated  $\text{H}_2\text{C}=\text{CLiX}$  carbenoid dimers. Solvent hydrogens omitted for clarity.**TABLE 5.** Calculated C=C Bond Lengths in THF-Solvated  $\text{H}_2\text{C}=\text{CLiX}$  Carbenoids

X	C=C monomer (Å)	C=C dimer (Å)
F	1.334	1.341
Cl	1.332	1.338
Br	1.331	1.334
OMe	1.349	1.357
NMe <sub>2</sub>	1.353	1.362

**TABLE 6.** THF-Solvated Dimerization Free Energies and Equilibrium Constants of  $\text{H}_2\text{C}=\text{CLiX}$  Carbenoids at 200 K

X	B3LYP/6-31+G(d)	B3LYP/6-311+G(2df,2pd)	BSSE	$K_{\text{eq}}$
F	-10.39	-11.17	2.33	$1.62 \times 10^{12}$
Cl	0.545	0.404	2.16	0.362
Br	-13.40	-0.054	19.85	1.15
OMe	-10.13	-9.93	3.17	$7.11 \times 10^{10}$
NMe <sub>2</sub>	-12.78	-7.10	3.25	$5.80 \times 10^7$

**TABLE 7.** THF-Solvated Dimerization Free Energies and Equilibrium Constants of  $\text{H}_2\text{C}=\text{CLiX}$  Carbenoids at 298 K

X	B3LYP/6-31+G(d)	B3LYP/6-311+G(2df,2pd)	BSSE	$K_{\text{eq}}$
F	-6.33	-7.11	2.33	$1.65 \times 10^5$
Cl	5.21	5.07	2.16	$1.92 \times 10^{-4}$
Br	-9.75	3.59	19.85	$2.32 \times 10^{-3}$
OMe	-5.88	-5.68	3.17	$1.47 \times 10^4$
NMe <sub>2</sub>	-7.49	-1.81	3.25	21.4

The dimerization free energies of the THF solvated carbenoids were calculated at 200 and 298 K, and the results are listed in Tables 6 and 7, respectively. As with the unsolvated carbenoids, the basis set superposition errors accounted for some of the difference in the calculated dimerization energies using the two different basis sets, except in the case of the chlorocarbenoid, in which the two basis sets generated nearly identical results. The calculated BSSE for the solvated bromocarbenoid was even larger than the unsolvated case, a fact that is also reflected in the dimerization energy with the larger basis set.

The dimerization equilibrium constants were derived from the free energy of dimerization at the B3LYP/6-

311+G(2df,2pd)//B3LYP/6-31+G(d) level. At 200 K, the fluoro-, methoxy-, and dimethylaminocarbenoids are predicted to exist exclusively as dimers in solution, while the chloro- and bromocarbenoids will have both monomer and dimer present at equilibrium. At 298 K, the fluoro- and methoxycarbenoids will still be primarily dimeric in solution, the dimethylaminocarbenoid will be largely dimeric with some monomer present, and the chloro- and bromocarbenoids will be primarily monomeric.

### Conclusions

Lithium vinylcarbenoids can adopt several geometries depending on their substituents and solvent effects. In the gas phase, monomeric lithiovinyl halides adopt geometries similar to those of halomethylolithiums, and the methoxy- and dimethylaminocarbenoids adopt a geometry in which the lithium atom coordinates to a

vinyl hydrogen. The gas-phase dimers form planar rings, except for the dimethylaminocarbenoid, which forms a chairlike structure. Each of the carbenoids forms a chairlike dimer in solution. Gas-phase dimerization energies predict that dimers will be formed exclusively with each of the carbenoids studied, but the dimerization energies in THF solution are structure-dependent, with the chloro- and bromocarbenoids forming significant amounts of monomer at 200 K and existing primarily as monomers at 298 K.

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**Supporting Information Available:** Tables of optimized geometries and energies of compounds **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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