

Gas Phase and Solution Structures of 1-Methoxyallenyllithium

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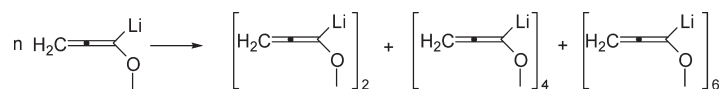
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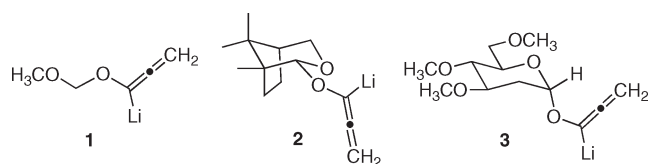


A combined computational and ^{13}C NMR study was used to determine the solution structures of 1-methoxyallenyllithium. The gas phase calculations indicated that this species is aggregated as a hexamer. The NMR spectra in THF solution, together with the calculated aggregation energies and chemical shifts, are consistent with a dimer–tetramer equilibrium.

Introduction

Allenyl ethers can be prepared with ease by isomerizing the corresponding propargyl ethers in the presence of strong base.¹ The chemical reactivity of this class of compounds has been reviewed and is rich and varied.² Our interest has been in the nucleophilic addition reactions of α -lithioallenyl nucleophiles such as **1**,^{3,4} and **3**⁵ to ketones and to morpholino enamides. This is the first step of the allene ether version of the Nazarov reaction.⁶ The α deprotonation of the allenes is easily accomplished by exposure to *n*-butyllithium in ethereal solvent, typically THF, at -78 °C. Deprotonation typically takes place at the α allenic carbon atom. Early in our study of α -lithioallenyl ethers we had observed that the nucleophilicity was attenuated in those compounds that incorporated multiple methoxy groups, e.g., **3**. We had

prepared a series of allenyl ethers from *O*-permethylated pyranoses for use in a chiral auxiliary controlled asymmetric Nazarov cyclization.^{5,7} Good yields for the addition of the derived α -lithio species to morpholino enamides were only observed in the presence of several equivalents of anhydrous LiCl. This is consistent with the LiCl induced disaggregation of the lithioallenes.⁸



The solution state structure of α -lithioallenyl ethers is currently incompletely determined. In an early study, a dimeric structure of 1-methoxyallenyllithium was found in THF of unknown solvation state.⁹ The actual picture is more complex, as described below, with two possible dimeric structures and a tetramer as likely species in THF, and higher aggregates in hydrocarbon solvents. It would potentially be very useful to have an understanding of the factors that influence the solution structure of such species as this would allow predictions to be made concerning their chemical reactivity. In what follows we describe the gas phase and

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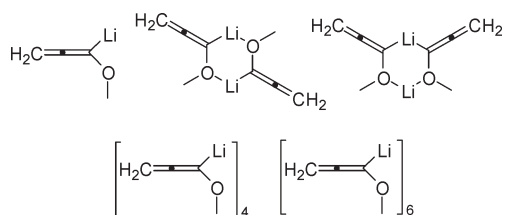
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TABLE 1. Free Energies of 1-Methoxyallenylithium Aggregate Formation in the Gas Phase [with Standard State Correction for 1 M Solution in Hexane] (kcal/mol)

| method/temp (K) | 2 monomer → dimer 1 | dimer 1 → dimer 2 | 2 dimer 1 → tetramer | 3/2 tetramer → hexamer |
|-----------------|---------------------|-------------------|----------------------|------------------------|
| B3LYP 200 | -40.3 [-41.4] | 0.248 | -28.5 [-29.6] | -4.94 [-5.50] |
| B3LYP 298.15 | -36.8 [-38.7] | 0.208 | -24.5 [-26.4] | -2.07 [-3.01] |
| PBE1PBE 200 | -39.0 [-40.1] | 0.220 | -33.9 [-35.1] | -6.65 [-7.20] |
| PBE1PBE 298.15 | -35.6 [-37.5] | 0.179 | -30.0 [-31.9] | -3.78 [-4.72] |
| MP2 200 | -44.7 [-45.8] | 0.428 | -46.2 [-47.3] | -18.5 [-19.1] |
| MP2 298.15 | -41.3 [-43.2] | 0.388 | -42.3 [-44.2] | -15.7 [-16.6] |
| SCS-MP2 200 | -45.4 [-46.5] | 0.477 | -42.0 [-43.1] | -16.5 [-17.0] |
| SCS-MP2 298.15 | -42.0 [-43.8] | 0.437 | -38.1 [-39.9] | -13.6 [-14.5] |

solution structures of the simplest member of this compound class, 1-methoxyallenylithium. By analogy to structurally related lithium vinylidene carbenoids, we examined the monomer, two isomeric dimers, tetramer, and hexamer of 1-methoxyallenylithium.

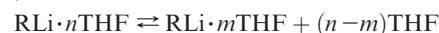


Computational Methods

All geometry optimizations, frequency calculations, and NMR chemical shift calculations were performed with the Gaussian 03 program.¹⁰ Geometry optimizations were performed with the B3LYP and PBE1PBE functional, using the 6-31+G(d) basis set. Frequencies were calculated at the B3LYP/6-31+G(d) level at the B3LYP geometries. The geometries were then reoptimized at the MP2/6-31+G(d) level. Scaling of the same and opposite spin components of the MP2 energy has reportedly resulted in improved correlation energies.¹¹ These spin-component scaled MP2 (SCS-MP2) energies were calculated from the $\alpha\alpha$, $\alpha\beta$, and $\beta\beta$ components of the MP2 energy: $\text{SCS-MP2} = E_{\text{HF}} + \frac{6}{5}(\alpha\beta) + \frac{1}{3}(\alpha\alpha + \beta\beta)$. B3LYP free energy corrections were calculated at 200 and 298.15 K from the frequency calculations and added to the electronic energies at each level of theory, in order to obtain approximate free energies of each species.

Solvent effects were modeled by placing explicit THF ligands on the lithium atoms. Two ligands were used for each monomer, and either two or four ligands for the dimers. Special care is

taken to ensure consistent handling of standard states.^{12,13} Specifically, a correction term $RT \ln(c^\circ RT/P^\circ)$ must be added per mole of each species in the reaction under consideration, which represents the change in free energy involved in compressing the system from standard pressure P° (or a concentration of P°/RT) used in gas phase calculations to the standard concentration of $c^\circ = 1 \text{ mol/L}$ commonly used for solutions. This term is numerically equal to +1.1119 kcal/mol at 200 K and +1.8900 kcal/mol at 298.15 K. While it cancels from both sides when the net change in the number of moles due to reaction $\Delta n = 0$, it is a non-negligible correction in cases where $\Delta n \neq 0$. Yet another correction is required for cases where a THF ligand dissociates, as in



for which

$$\Delta G^\circ = -RT \ln \frac{[\text{RLi} \cdot m\text{THF}]}{[\text{RLi} \cdot n\text{THF}]} - (n-m)RT \ln \frac{[\text{THF}]}{c^\circ} \quad (1)$$

Since the concentration of pure THF is different from the standard concentration c° , it was evaluated from its molar volume at 1 atm and 200 or 273.15 K, using the empirical expression provided by Govender et al.,¹⁴ and incorporated into the second term of eq 1. Numerically, this correction to ΔG° amounts to -1.0273 and -1.4883 kcal/mol per THF at 200 and 298.15 K, respectively. This approach to modeling solvation effects on organolithium compounds has been used in other studies,¹⁵⁻²⁰ and has been found to give results in agreement with available experimental results.

Isotropic ¹³C NMR chemical shifts were calculated at the B3LYP/6-31+G(d) and, where possible, at the MP2/6-31+G(d) levels of theory. It was found that the B3LYP chemical shifts were consistent with the experimental chemical shifts, as described below. Chemical shift calculations were performed on the MP2 optimized geometry for each species, and for tetramethylsilane (TMS), and the chemical shifts of each carbon atom relative to TMS were obtained by subtraction.

Results and Discussion

The calculated free energies of dimer, tetramer, and hexamer formation in the gas phase are shown in Table 1. Approximate free energies in a 1 M hexane solution were obtained by adding the standard state corrections to the gas phase free energy of each species. The dimerization energies

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calculated by all four methods are within about 4 kcal/mol of each other. The differences between the 2 DFT methods, and between the unscaled MP2 and SCS-MP2, are less than 1.5 kcal/mol. The free energies of the tetramer formation from the dimer, and hexamer formation from the tetramer, are calculated to be more exergonic by the MP2 method than by the two DFT methods. The PBE1PBE calculations are in slightly better agreement with the MP2 calculations, compared to B3LYP, and the SCS-corrected MP2 calculations predict slightly less exergonic energies of tetramer and hexamer formation than the uncorrected MP2 calculations. All four computational methods predict the hexamer to be favored in the gas phase. Two different structures for the dimer were found, analogous to those reported for halovinylolithium carbenoids.²¹ The optimized gas phase geometries are shown in Figure 1.

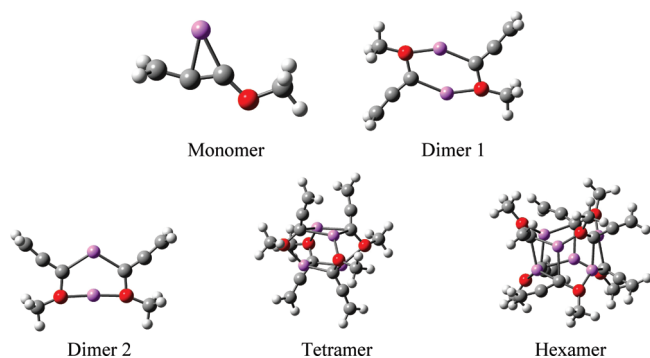


FIGURE 1. Optimized geometries of gas phase 1-methoxyallenyl-lithium aggregates.

The ^{13}C NMR chemical shifts were calculated for the gas phase 1-methoxyallenylithium aggregates at the B3LYP/6-31+G(d) and MP2/6-31+G(d) levels of theory, with the carbon atoms numbered as shown below. Since the gas phase structures are not expected to be greatly different from those in nonpolar solvents, the NMR spectra were acquired in d_{14} -hexane at 243 K ($-30\text{ }^\circ\text{C}$), the minimum temperature for which the compound is sufficiently soluble in hexane. The spectra were also acquired at 253 and 263 K, and the residual 1-methoxyallene disappeared at the higher temperatures. The spectra are shown in Figure 2, and the calculated and observed chemical shifts are listed in Table 2. For all species other than the monomer, the B3LYP and MP2 chemical shift calculations were almost an exact match to the experimental chemical shifts for C-3 and the methoxy carbon. The chemical shifts of these two carbons would be expected to differ only slightly with different aggregation states, as they are farthest removed from the lithium-carbon core. The B3LYP calculations

TABLE 2. Calculated ^{13}C Chemical Shifts for Gas Phase 1-Methoxyallenylithium Aggregates (ppm from TMS)

| method | aggregate | C1 | C2 | C3 | methoxy C |
|--------|-------------------------|-------|-------|------|-----------|
| B3LYP | monomer | 127.0 | 169.0 | 63.1 | 53.4 |
| B3LYP | dimer 1 | 142.9 | 194.5 | 74.2 | 58.1 |
| B3LYP | dimer 2 | 144.3 | 193.6 | 74.4 | 58.0 |
| B3LYP | tetramer | 143.0 | 187.5 | 72.9 | 59.2 |
| B3LYP | hexamer | 138.7 | 184.1 | 75.4 | 59.7 |
| MP2 | monomer | 120.6 | 158.3 | 66.0 | 51.9 |
| MP2 | dimer 1 | 136.5 | 186.0 | 72.8 | 59.7 |
| MP2 | dimer 2 | 137.8 | 185.2 | 73.0 | 59.9 |
| expt | tetramer and/or hexamer | 148 | 198 | 75 | 58 |

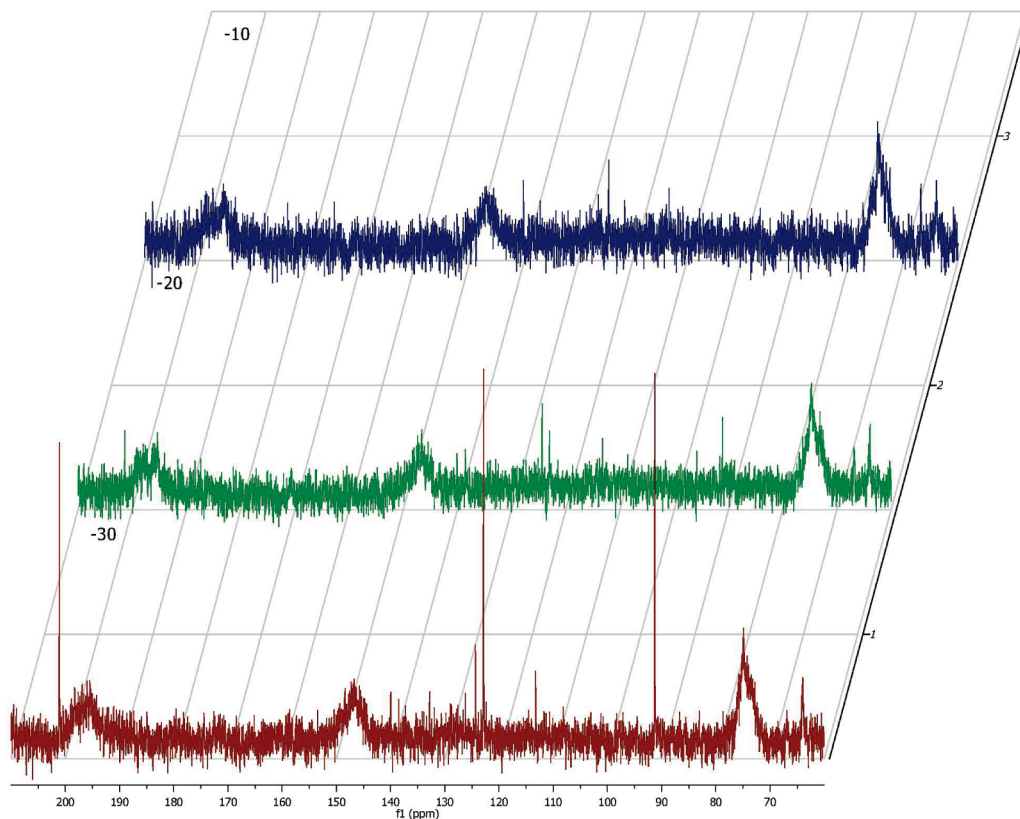
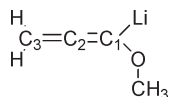


FIGURE 2. ^{13}C NMR spectra of 1-methoxyallenylithium in d_{14} -hexane at 243, 253, and 263 K.

indicated a chemical shift range of about 6 ppm for C-1 in the different aggregates. The B3LYP chemical shift calculations were rerun with the PCM continuum solvent model with heptane as the solvent (hexane is not available for PCM), but the chemical shifts changed by less than 1 ppm. Although a scaling factor may be required to obtain highly accurate chemical shift data for C-1 and C-2, it appears that the B3LYP method is at least as reliable as the more expensive MP2 method for this system. This is fortunate because the gas phase tetramer, hexamer, and most of the THF solvated systems are too large for MP2 chemical shift calculations. Therefore, the B3LYP chemical shifts were used for the solvated systems.



On the basis of the DFT and MP2 calculated aggregation energies, we would expect a 1 M solution of the 1-methoxyallyllithium to exist primarily as the hexamer. However, comparison of the calculated and experimental chemical shifts suggests a lower aggregate in hexane. Solubility in hexane is low at temperatures where the 1-methoxyallyllithium is stable, and the dissolved compound is much more dilute than 1 M. As dilution often favors lower aggregates, some tetramer and possibly even some dimer may be present. At 243 K and above, interaggregate exchange is expected to be rapid on the NMR time scale, preventing the observation of the different aggregates if more than one species is present. Although there is some uncertainty in the aggregation state in hexane, it appears likely that the hexamer and/or tetramer are the major species.

Calculations were performed on THF solvated 1-methoxyallyllithium aggregates by placing one or more THF ligands on each lithium atom, and optimizing the molecule with its inner solvation sphere. Appropriate corrections for standard states were made as described in the Computational Methods section. The THF solvated dimers could potentially exist as either the disolvates or tetrasolvates. The free energies of tetrasolvate formation were calculated according to eq 2, and the results are given in Table 3. There is a considerable difference between the calculated solvation energies using the DFT and MP2 methods. The unscaled MP2 and SCS-MP2 calculations predicted quantitative formation of the tetrasolvated dimers, although the SCS-MP2 calculations found the free energy to be less exergonic relative to the unscaled MP2 calculations. The B3LYP calculations favored the disolvated dimers in comparison with the MP2 calculations. The PBE1PBE results were similar to B3LYP, but they predicted the formation of the tetrasolvated dimers to be somewhat more exergonic. We have previously investigated the effects of the computational method on other organolithium systems,^{22,23} and concluded that the B3LYP method underestimates the free energy of solvation of lithium by THF. We therefore

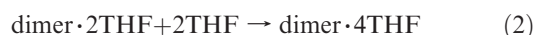
TABLE 3. Free Energies of Tetrasolvated 1-Methoxyallyllithium Dimer Formation from the Disolvated Dimers (kcal/mol)

| method | temp (K) | dimer 1 | Dimer 2 |
|---------|----------|---------|---------|
| B3LYP | 200 | -1.34 | 2.96 |
| B3LYP | 298.15 | 3.73 | 8.17 |
| PBE1PBE | 200 | -5.73 | -1.20 |
| PBE1PBE | 298.15 | -0.667 | 4.01 |
| MP2 | 200 | -30.5 | -22.2 |
| MP2 | 298.15 | -25.3 | -17.0 |
| SCS-MP2 | 200 | -24.7 | -17.8 |
| SCS-MP2 | 298.15 | -19.6 | -12.5 |

TABLE 4. Free Energies of 1-Methoxyallyllithium Aggregate Formation in THF Solution (kcal/mol)

| method/ temp (K) | 2 monomer · | dimer 1 · 4THF | 2 dimer 1 · 4THF → |
|---------------------|--------------|----------------|--------------------|
| | 2THF → dimer | → dimer | tetramer · 4THF + |
| | 1 · 4THF | 2 · 4THF | 4THF |
| B3LYP 200 | -12.8 | 2.62 | -4.40 |
| B3LYP 298.15 | -8.23 | 2.62 | -9.04 |
| PBE1PBE 200 | -15.0 | 2.51 | -3.48 |
| PBE1PBE 298.15 | -10.4 | 2.50 | -8.12 |
| MP2 200 | -36.8 | 4.65 | 6.87 |
| MP2 298.15 | -32.2 | 4.64 | 2.24 |
| SCS-MP2 200 | -33.1 | 4.22 | 5.43 |
| SCS-MP2 298.15 | -28.5 | 4.22 | 0.790 |

conclude that the THF tetrasolvate is the predominant form of the 1-methoxyallyllithium dimers. This problem did not arise with the tetramers because due to steric constraints, only one THF ligand could be placed on each lithium atom.



The free energies of THF solvated aggregates of 1-methoxyallyllithium were calculated according to eqs 3 and 4, and the results are summarized in Table 4. The optimized geometries are shown in Figure 3. The DFT and MP2 methods all predict the monomer to completely dimerize in THF, but the unscaled MP2 and SCS-MP2 calculations predicted the reaction to be much more exergonic. The relative energies of the two dimers are nearly independent of temperature, and dimer 1 is favored by 2.6 and 2.5 kcal/mol at the B3LYP and PBE1PBE levels, respectively, and by 4.6 kcal/mol at the unscaled MP2 level. Thus, dimer 2 is expected to be a minor species in solution. It may not be observable due to low concentration and/or rapid intramolecular exchange, which typically occurs at lower temperatures than intermolecular exchange. It may nevertheless be a significant reactive intermediate.

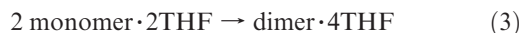
The DFT and MP2 calculations disagree about whether 1-methoxyallyllithium is a dimer or tetramer in solution. The calculations refer to a 1 M solution, and more dilute solutions are often less aggregated. The B3LYP and PBE1PBE calculated energies are within 1 kcal/mol of each other, and predict the tetramer to be the major species in solution, with higher temperatures favoring the tetramer and lower temperatures favoring the dimer. The unscaled MP2 and SCS-MP2 calculations generated similar energies of tetramer formation, and predict the dimer to be the major species at 200 and 298.15 K, with the tetramer favored

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by higher temperatures. A similar disagreement between B3LYP and MP2 calculations arose in a study of lithium enolate aggregates, with the MP2 calculations underestimating the stability of the THF solvated tetramer.²³



Comparison of the calculated and observed chemical shifts indicates that C1 of the tetramer resonates upfield of

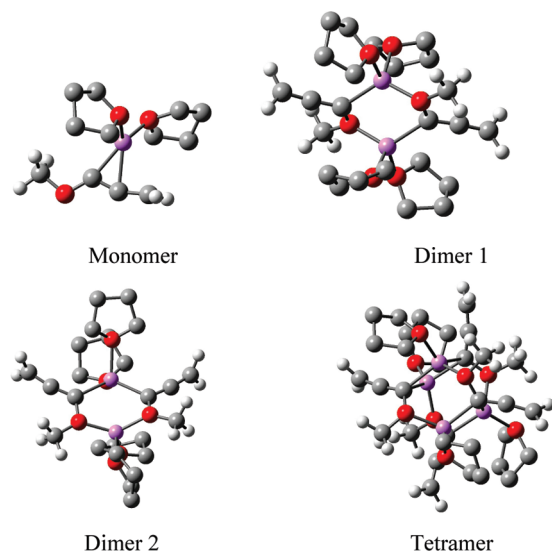


FIGURE 3. Optimized geometries of THF solvated 1-methoxyallenylithium aggregates.

the dimer by about 3–6 ppm, and C2 of the tetramer resonates downfield of the dimer by about 1–2 ppm (Table 5, Figures 4 and 5). At 173 K, the dimer is the major species in equilibrium with a small amount of tetramer. The amount of tetramer increases at 193 and 223 K. Upon further warming to 243 K, only one peak is visible, apparently from rapid interaggregate exchange. This is consistent with both the B3LYP and MP2 calculations, which indicate that the tetramer is favored by higher temperatures. Since the experimental concentration of the 1-methoxyallenyl-lithium was close to the standard state concentration of 1 M, we conclude that the B3LYP calculations overestimate the stability of the tetramer, and the MP2 calculations overestimate the stability of the dimer. Averaging the B3LYP and MP2 free energies of tetramer formation generates values that are in better agreement with the experimental data, compared to either the MP2 or B3LYP energy alone. It should also be noted that the calculated chemical shifts of the monomer are quite different from those of the dimer or tetramer, and no peaks close to those values were observed. Thus, if the 1-methoxyallenyl-lithium monomer exists in THF solution, it is at concentrations too low to be observed by ¹³C NMR.

TABLE 5. Calculated ¹³C Chemical Shifts for Gas 1-Methoxyallenyl-lithium Aggregates in THF (ppm from TMS)

| method | aggregate | C1 | C2 | C3 | methoxy C |
|--------|-----------|-------|-------|------|-----------|
| B3LYP | monomer | 136.2 | 164.1 | 55.4 | 63.8 |
| B3LYP | dimer 1 | 153.7 | 193.5 | 67.4 | 57.3 |
| B3LYP | dimer 2 | 152.0 | 190.9 | 67.2 | 58.3 |
| B3LYP | tetramer | 147.9 | 194.7 | 72.1 | 59.1 |
| Expt. | major | 154 | 195 | 70 | 57 |
| Expt. | minor | 151 | 197 | 70 | 57 |

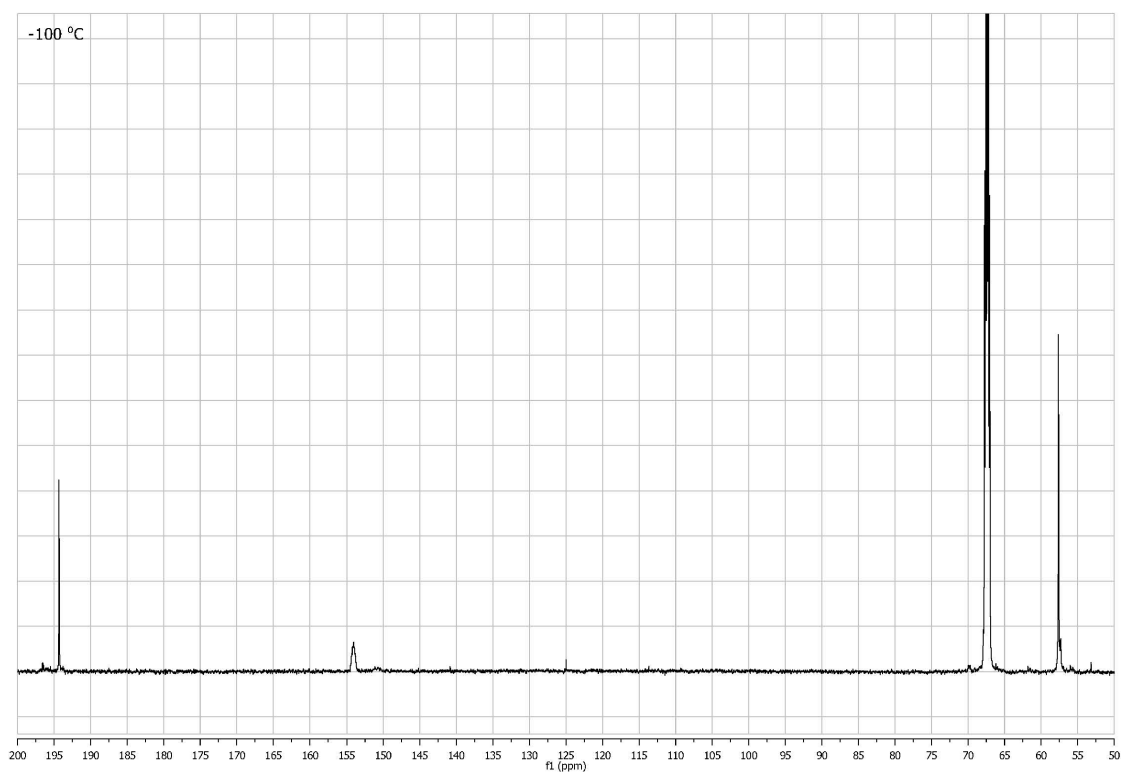


FIGURE 4. ¹³C NMR spectrum of 1-methoxyallenylithium in *d*₈-THF at 173 K.

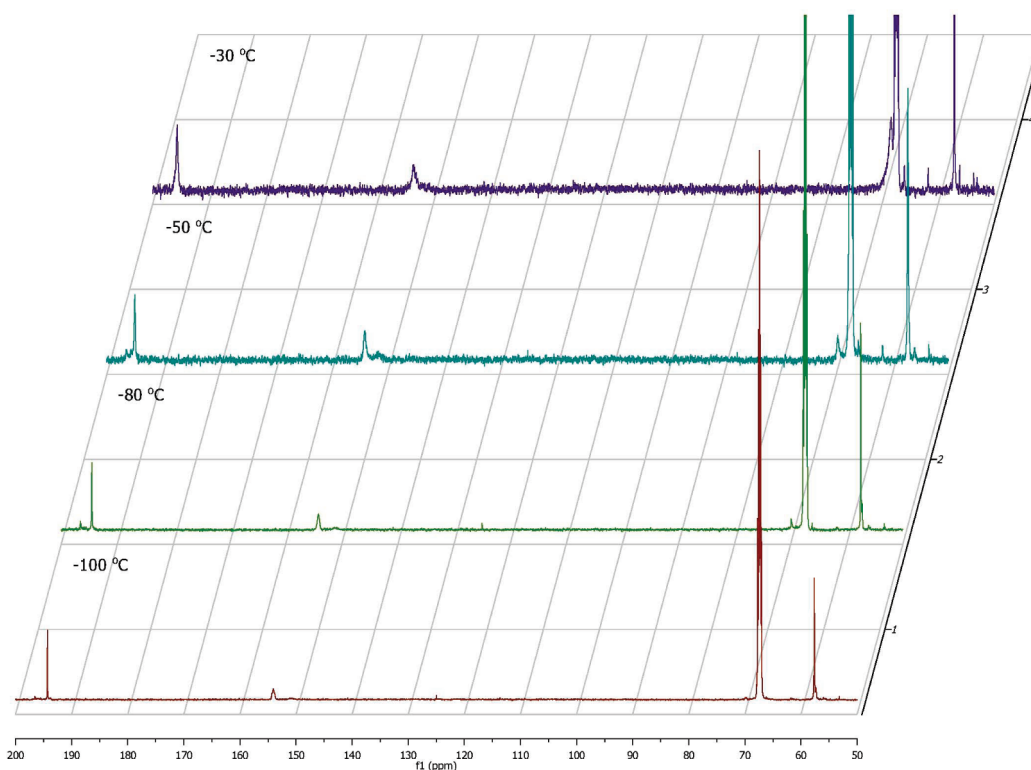


FIGURE 5. Stacked plot of ^{13}C NMR spectra of 1-methoxyallenyllithium in d_8 -THF at 173 (bottom), 193, 223, and 243 K (top).

Conclusions

According to our investigation, in the gas phase 1-methoxyallenyllithium exists as a hexamer. Because of limited solubility, hexane solutions of 1-methoxyallenyllithium are quite dilute, and there is some uncertainty about the aggregation state. It appears that the tetramer and/or hexamer are the major species. Most synthetic work is done in THF solution, and the calculated and observed chemical shifts are consistent with a dimer–tetramer equilibrium. The dimer is favored by lower temperatures and the tetramer is favored by higher temperatures. Compared to the experimental data, the two sets of DFT calculations overestimate the tetramer stability, while the stability of the dimer is overestimated at the MP2 level. B3LYP calculated ^{13}C chemical shifts were in reasonable agreement with experiment, and aided assignment of the dimer and tetramer structures. MP2 chemical shift calculations were computationally massive and could be performed only on the smaller systems. While the absolute values of the chemical shifts differed between the MP2 and B3LYP methods, they were in agreement with the trends of chemical shifts and aggregate structure.

Experimental Methods

Preparation of 1-Methoxyallenyllithium in d_{14} -Hexane. An oven-dried NMR tube was charged with methoxyallene (40 mg, 0.57 mmol) under nitrogen. The solvent, d_{14} -hexane (750 μL), was added by syringe through a septum, and the solution was cooled to -78°C . A 2.78 M solution of *n*-butyllithium in hexanes (0.25 mL, 1.2 equiv) was added and the solution was

aged for 15 min. The total concentration of 1-methoxyallenyllithium was 0.57 M. The solution was then frozen in liquid nitrogen and the NMR tube flame-sealed. The ^{13}C NMR spectra in hexane were recorded at 243, 253, and 263 K at 125.75 MHz with a 3 s delay between pulses. All spectra were broadband decoupled.

Preparation of 1-Methoxyallenyllithium in d_8 -THF. An oven-dried NMR tube was charged with methoxyallene (50 mg, 0.71 mmol) under nitrogen. The solvent, d_8 -THF (750 μL), was added by syringe through a septum, and the solution was cooled to -78°C . A 2.46 M solution of *n*-butyllithium in hexanes (0.35 mL, 1.2 equiv) was added and the solution was aged for 15 min. The total concentration of 1-methoxyallenyllithium was 0.65 M. The solution was then frozen in liquid nitrogen and the NMR tube flame-sealed. The ^{13}C NMR spectra in THF were recorded at 173, 193, 223, and 243 K (Figure 5) at 125.75 MHz with a 3 s delay between pulses. All spectra were broadband decoupled.

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Supporting Information Available: Tables of MP2 optimized geometries and energies of all methoxyallenyllithium structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.