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Structural Distortions and Dynamic Behavior of the Elusive "L"-Shaped *cis*-Bicyclo[3.3.0]octenyllithium: X-ray Crystallographic and NMR Studies

Gideon Fraenkel,* Xiao Chen, Judith Gallucci, and Yan Lu

Department of Chemistry, Ohio State University, Columbus, Ohio 43210

fraenkel@mps.ohio-state.edu

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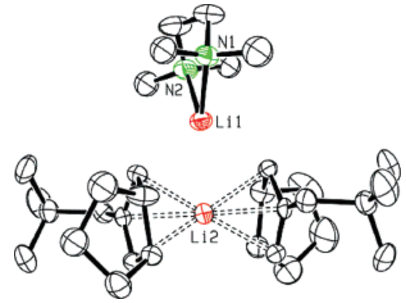
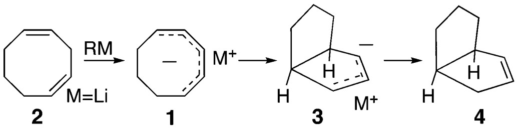


Substituted *cis*-bicyclo[3.3.0]octenyllithium prepared by addition of *t*-BuLi to 3-methylene-1,4-cyclooctadiene in the presence of TMEDA crystallizes as a dimer with one unsolvated Li^+ sandwiched between the external faces of two allyl anions in a triple ion, and external to it the second Li^+ is bidentately complexed to TMEDA, **8**. Within each allyl unit, the allyl bonds have different lengths, and all four rings deviate from coplanarity which relieves strain in the rings despite introducing partial localization of the allyl anions. A similar structure prevails in solution as shown by ^{7}Li NMR and the results of ^{7}Li{^{1}H} HOESY and ^{1}H, ^{1}H NOESY experiments. Carbon-13 NMR line shape changes indicate that the system undergoes a fast allyl bond shift concerted with conformation shifts of the out of plane carbons, ca. $\Delta G^\ddagger = 9$ kcal·mol^{-1}. Cyclopentyllithium prepared by CH_3Li cleavage of the trimethylstannyl derivative slowly undergoes an allowed ring opening to pentadienyllithium as well as deprotonating the solvent. The different behavior of dienylic lithium species is attributed to the relative separation of their termini.

Introduction

The allowed disrotatory cyclization of cyclooctadienyl metal compounds **1** from metalation of 1,4-cyclooctadiene, **2**, is a well-known route to *cis*-bicyclo[3.3.0]-2-octenyl metal compounds, **3**.[1a−d,2a−d] In principle, species **3** provides an unprecedented opportunity to investigate the structure and dynamics of a little known "L"-shaped allylic lithium compound with nonequivalent allyl faces. Issues of interest include the distribution of coordinated Li^+ between the two faces and the diastereoselectivity of reactions of **3** with electrophiles. Unfortunately, only bicyclooctene **4** has been recovered from most of these experiments most likely due to deprotonation of solvent by **3**[2]. However, Williams and Reeves have reported how a similar set of reactions ensues following addition of RLi reagents to triene **5** and leading via cyclization of **6** to a variety of electrophile capture products **7** from interception of the proposed bicyclo intermediate **8**.[3]



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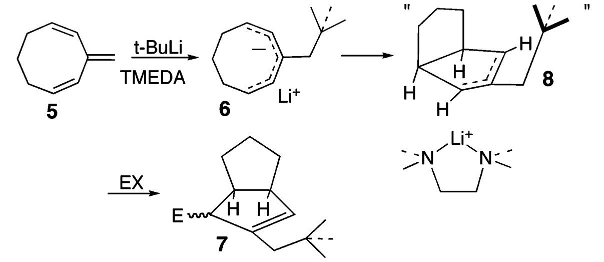

Results and Discussion

Herein we report that solution NMR and X-ray crystallography of the product of t-butyllithium with triene **5** confirm the bicyclic framework of **8** and reveal some interesting unexpected structural details and dynamic effects.

X-ray crystallography shows **8**[4] to be a dimer, Figure 1a, which is partially disordered. One Li^+, unsolvated, is sandwiched between the external faces of two allyl planes in a triple ion.

One of the bicyclic ligands contains two disordered carbon atoms located in the saturated ring: C(7A) and C(7AA) are two sites for one disordered carbon atom, while C(6A) and C(6AA) are two sites for a second disordered carbon atom. The other Li^+ is bidentately coordinated to TMEDA and lies just 2.495(8) Å from the sandwiched Li^+. The TMEDA ligand also is disordered with each carbon atom disordered over two sites, but with the nitrogen atoms ordered. Dimeric ion pairs which incorporate triple ions for other systems were originally proposed from kinetic data[5] and established from NMR studies.[6,7] This paper is the first to report a triple ion which is part of an allylic lithium compound.

Within each allylic unit the carbon carbon bonds are of significantly different lengths the distances being 1.366(5) Å and 1.459(5) Å in one, **a**, and 1.364(5) Å and 1.428(5) Å in the other, **b**, allyl unit, see Figure 1b. These results establish the partially localized characters of the allyl parts. This is also reflected in the nonequivalence of all the other bond lengths in **8**. In addition, both the saturated and cycloallylic rings in **8** show significant deviations from coplanarity. Thus, in the ordered unit labeled as **b**, see Figure 1a, C7b is 0.445(5) Å from the mean plane defined by atoms C8b, C4b, C5b, and C6b. For the cyclopentenyl part of **b**, C3b and C4b lie on opposite sides of the plane defined by C2b, C1b, and C8b at distances of 0.171(3) Å and −0.178(3) Å, respectively. Within the ordered part of partially disordered **a** we note that C8a is 0.335(4) Å normal to the mean plane defined by C1a, C2a, C3a, and C4a. Considering the nonplanarity of the individual rings and the nonequivalence of the allyl bonds, it is interesting that the distances between the sandwiched Li^+ and the six allyl carbons all lie within the range 2.15−2.30 Å. It thus would appear that compared to a potential symmetrical (mirror plane) structure the actual structure of **8** owes its stability to relief of strain within the rings despite loss of conjugation within the allylic anions.

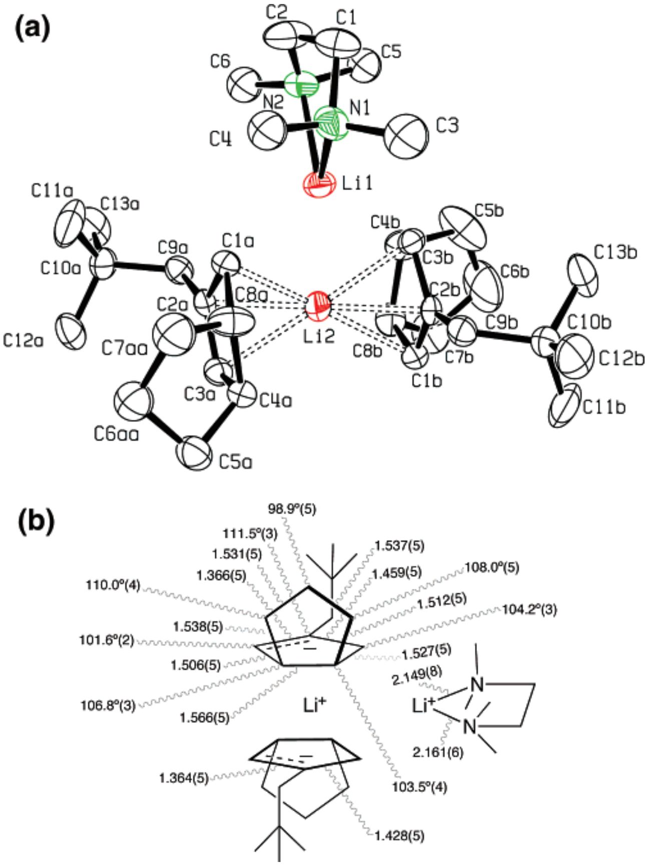

FIGURE 1. (a) ORTEP drawing of compound **8** showing 50% ellipsoids. Hydrogen atoms have been omitted for clarity. Only one set of atoms in each of the disordered regions is shown for clarity. Atoms C6a and C7a of one of the bicyclooctenyl ligands and atoms C1D, C2D, C3D, C4D, and C6D of the TMEDA ligand are omitted. (b) Compound **8**, selected structural parameters. For simplicity, rings have been drawn coplanar.

Then NMR data for **8** in solution are consistent with the crystallographic structure, see Figure 2, which includes the ^1H and ^{13}C shifts. Shift assignments were established by HETCOR (^1H, ^{13}C), proton−proton NOESY, and $^7Li\{^1H\}$ HOESY experiments, respectively. In particular, the HOESY experiment reveals the proximity of Li^+ to the bridge and terminal allyl protons, respectively, while the NOESY procedure shows *tert*-butyl protons are close to the methylene protons α to the bridge at 1.765 δ. Thus, we conclude that Li^+ and the *tert*-butyl group lie on opposite sides of the cyclopentenyl planes with Li^+ external to these two planes.

Lithium-7 NMR of **8** consists of a sharp line at 290 K. With decreasing temperature this resonance broadens and resolves into a doublet by 160 K with separation 1.21 ppm indicating two nonequivalent lithiums as in the crystallographic structure. From the ^7Li line width at 240 K k_1 for mutual exchange of $^7Li^+$'s is 1.57×10^3 s^{-1}.

Although the crystallographic structure of **8** implies that all carbons in the bicyclooctenyl anion are in nonequivalent sites the NMR spectra show mirror plane symmetry. That this is most likely the result of a fast overall inversion process is evidenced by the behavior of the terminal allyl ^{13}C resonance. At 290 K, it consists of a sharp line with shift 77 δ. With decreasing

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[4] Crystallographic data for **8**: $C_{32}H_{58}Li_2N_2$, $M = 484.68$, monoclinic, Cc, $a = 11.372(1)$ Å, $b = 17.364(2)$ Å, $c = 16.532(3)$ Å, $\beta = 99.110(5)°$, $V = 3223.4(7)$ Å^3, $T = 150$ (2) K, $Z = 4$, μ (Mo Kα) = 0.056 mm^{-1}, 23008 reflections measured, 2856 unique [R(int) = 0.030]. The final R1 is 0.054 with $I > 2\sigma(I)$, and ωR2 is 0.147 on all the data.

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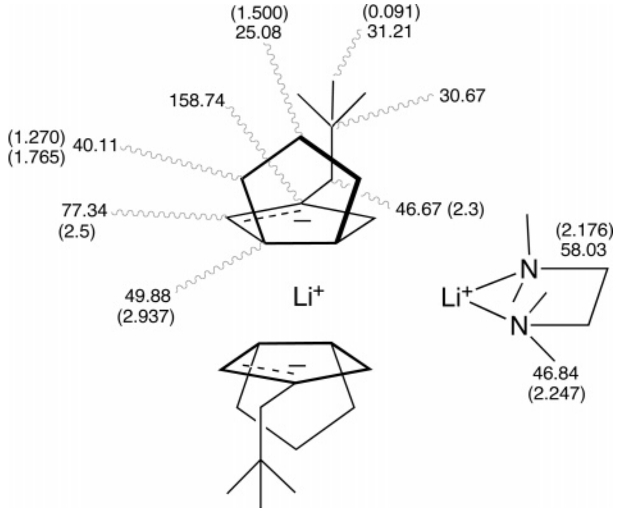


FIGURE 2. Compound **8** in diethyl-ether-d_{10}, 280 K, selected ^{13}C and (^{1}H) NMR chemical shifts, both δ units.

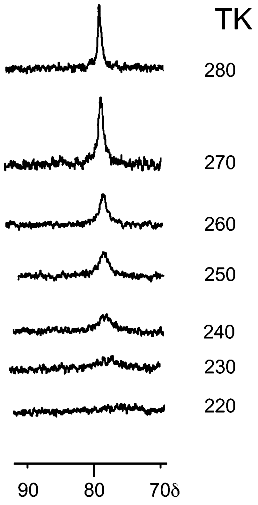


FIGURE 3. Terminal allyl ^{13}C NMR, 75−47 MHz, of **8** at different temperatures.

temperature, this resonance progressively broadens and it disappears into the baseline by 190 K, Figure 3. No resonances attributable to the terminal allyl carbons of **8** appear down to 160 K. The latter broadening is most likely the result of a fast bond shift, as proposed in Figure 4, too fast to resolve the individual terminal carbon resonances at 160 K. This allyl bond shift would necessarily be accompanied by fast conformational shifts within the rings which would average the ^{13}C chemical shifts of C5a with C7a, C4a with C8a, C8b with C4b, and C5b with C7b, as is observed; see Figure 4. These latter shifts would be too small to decoalesce by 160 K.

The results described above present strong support that **8** assumes the same structure in the solid state as in solution.

While the terminal allyl ^{13}C shift of **8** could not be resolved by 160 K it is estimated to be ca. 40 ppm by comparison with NMR data for other partially localized allylic lithium compounds.[8] Using this value together with the line width of the terminal ^{13}C resonance of **8** at 250 K gives a k_1 of 7.5 × 10^{4} s^{-1} or $\Delta G^{\ddagger} = 9$ kcal·mol^{-1}. It is likely that the process is entropy neutral.

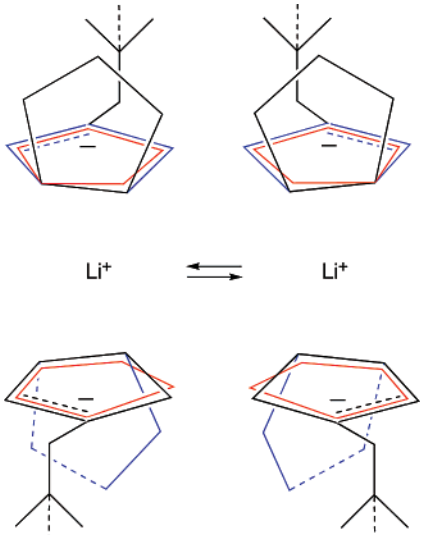
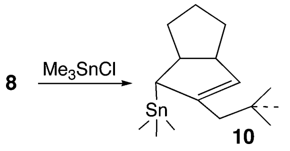


FIGURE 4. Proposed overall allyl bond shift in **8**; TMEDA complexed Li^{+} has been omitted. Pentagon indicates reference plane.

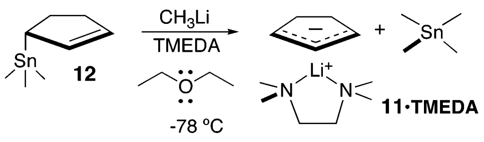
It is attractive to speculate that the transition structure for the above bond shift passes through a symmetrical mirror plane state which, compared to the ground state incorporates increased conjugation within the allylic anions together with increased strain within the five members rings due to planarization; see Figure 4.

Compound **8** was reacted with trimethylchlorostannane to give, to the limit of NMR detection only the anti product **10**, as determined from a combination of HETCOR and NOESY experiments. As recently reported diastereomeric selectivity varies in the reactions of different electrophiles with substituted *cis*-bicyclo[3.3.0]octenyllithium.[3]



Main group cycloalkenyl metal compounds are not well known, although several cyclopentenyl-[9] and cyclohexenyl-[10] metal compounds, respectively, have been used as intermediates in different reactions.

Some insights into the behavior of cyclopentenyl anions have been obtained from a study of cyclopentenyllithium **11**, now isolated for the first time. This compound was prepared by CH$_3$-Li cleavage of the trimethylstannyl derivative **12**,[11] in the presence of TMEDA and separately with PMDTA. NMR data for these samples are summarized in Figure 5. The cyclopentenyl resonances remain unchanged between 290 and 180 K. In



particular, both allyl termini have the same shift in ^{13}C and proton NMR. By contrast, on cooling **11•TMEDA** there is

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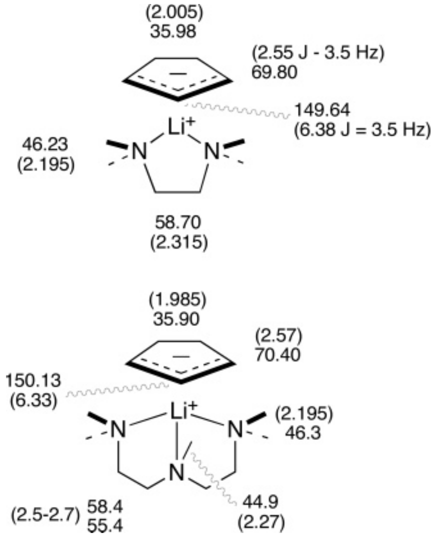
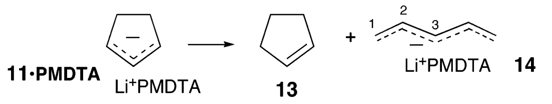


FIGURE 5. ^{13}C and (^{1}H) NMR shifts, δ scale, of cyclopentenyllithium in diethyl ether-d_{10}, 280 K. Top: TMEDA complex. Bottom: PMDTA complex.

broadening of the CH$_2$N ^{13}C resonance of complexed TMEDA. At 180 K ^{13}C NMR of **11** prepared in the presence of PMDTA shows separate resonances for free and complexed ligand. These two average by 250 K due to fast exchange of PMDTA between the latter free and complexed states.

On standing, the solution of **11** with PMDTA develops new ^{13}C resonances at 130.9, 33.71, and 23.61, all δ units close to those reported for cyclopentene[12] at 130.8, 32.8, and 23.3 δ units, respectively. In addition, the latter solution of **11** develops weak ^{13}C resonances at 66 δ, 143.7 δ, and 78.7 δ which are similar to those reported for C$_1$, C$_2$, and C$_3$ of pentadienyllithium **14**, by Ford[13] at, respectively, 66 δ, 143.9 δ, and 86.9 δ and by Bates[2c] at, respectively, 71.1 δ, 142.2 δ, and 142.2 δ.



Thus, in summary, the fate of cyclopentadienyllithium is to deprotonate the solvent and to undergo an allowed ring opening.

In summary, we have shown that the bicyclic allylic anion in **8** is a highly unsymmetric species with both rings being nonplanar and the allylic bond lengths being different, which indicates a partially localized allylic anion. The compound undergoes a rapid inversion which involves allyl bond shifts as well as transfer of the out of plane sites on the two rings.

While the thermodynamic fate of **8** is to remain closed that of cyclopentyl anion as in **11•PMDTA** is to deprotonate the solvent and to open to pentadienyllithium.

Experimental Section

2-Neopentyl-*cis*-bicyclo[3.3.0]octenyllithium, TMEDA 8. A solution of 3-methylene-1,4-cyclooctadiene (232 mg, 1.93 mmol) and TMEDA (237 mg, 2.04 mmol) in 4 mL of pentane was treated dropwise at −90 °C with *tert*-butyllithium (1.13 mL, 1.7 M, 1.92 mmol). After being stirred for 2 h with warming to room temperature, the reaction mixture was concentrated in vacuo and washed with dry pentane, 3 × 4 mL, and then dried again in vacuo. A 0.35 M solution was prepared of the title product in diethyl ether-d_{10} for NMR studies. NMR data are summarized in Figure 2.

2-Neopentyl-*cis*-bicyclo[3.3.0]-1-octene, 7 E = H. A solution of 3-methylene-1,4-cyclooctadiene **5** (0.2 g, 5.8 mmol) in diethyl ether, 3 mL, was treated dropwise at −78 °C with *tert*-butyllithium (3.44 mL, 1.7 M, 5.85 mmol). The mixture was stirred for 3 h at −78 °C and then for 1 h at room temperature. The reaction mixture was quenched with water and extracted into diethyl ether. The combined ether extracts were dried with MgSO$_4$ and concentrated to give the title compounds as a colorless liquid.

Racemic *trans*-2-Neopentyl-3-trimethylstannyl-4,5-trimethylenecyclopentene, 10. A solution of triene **5** (0.7 g, 5.8 mmol) in diethyl ether was treated dropwise at −78 °C with t-butyllithium (3.44 mL, 5.85 mmol) in pentane. The mixture was stirred for 3 h at −78 °C, then at room temperature for 1 h. The reaction mixture was cooled again to −78 °C and reacted with a solution oftrimethylstannyl chloride (1.04 g, 5.22 mmol) in 3 mL diethyl ether. After warming to room temperature for over 1 h the reaction mixture was quenched with aqueous NH$_4$Cl−H$_2$O and extracted into diethyl ether and then concentrated. Distillation of the residue, bp 77−78 °C/0.1 Torr, gave 1 g of the title compound in 56.2% yield. ^{13}C NMR (CDCl$_3$): −0.091 (SnCH$_3$), 25.61 (CH$_2$(CH$_2$)$_2$), 32.71, 37.14 (CH$_2$(CH$_2$)$_2$), 44.85 (CH$_2$C(CH$_3$)$_3$), 46.27 (H-CSn), 46.27 (CHCH-Sn), 50.41 ((CH−CH=C−CH$_2$), 126.72 (CH=C−CH$_2$), 144.4 (CH$_2$$C$=CH).

Cyclopentenyllithium•TMEDA, 11·TMEDA. A 25 mL Schlenk tube was charged with 6 mL of dry diethyl ether, TMEDA (348.6 mg, 3 mmol), and 3-trimethylstannyl-1-cyclopentene[11] (692.7 mg, 3 mmol) under an argon flow. Methyllithium (2.0 mL, 1.5 M, 3.0 mmol) in diethyl ether was added by syringe at −78 °C. A white solid soon formed. The mixture was stirred at room temperature for 2 h, 1 mL of THF was added at −50 °C, and stirring was continued for 1 h at room temperature. Solvent was removed in vacuum, and the residue was washed with pentane three times (3 × 6 mL). An NMR tube was flame dried under vacuum and charged with product (35 mg) under argon before it was transferred to a high vacuum line (10^{-6} Torr) trapped with liquid nitrogen. Volatile impurities were pumped out into a liquid nitrogen trap. After 3 h, THF-d_8 (0.5 mL) was vacuum transferred to the NMR tube cooled by a liquid nitrogen bath. Under high vacuum, the NMR tube was sealed with a small hot flame.

Cyclopentenyllithium·PMDTA, 11·PMDTA. A 25 mL Schlenk tube was charged with 6 mL of dry diethyl ether, PMDTA (519.9 mg, 3 mmol), and 3-trimethylstannyl-1-cyclopentene (692.7 mg, 3 mmol) under an argon flow. Methyllithium (2.0 mL, 1.5 M, 3.0 mmol) in diethyl ether was added by a syringe at −78 °C. The mixture was stirred at room temperature for 2 h, and then 1 mL of THF was added at −50 °C and stirring continued 1 h at −50 °C. Solvent was removed in vacuum, and the residue was washed with 5 mL pentane one time at −78 °C. An NMR tube was flame dried under vacuum and charged with title product (49 mg) under argon before it was transferred to a high vacuum line (10^{-6} Torr) trapped with liquid nitrogen. Volatile impurities were pumped out in to a liquid nitrogen trap. After 3 h, diethyl ether-d_{10} (0.5 mL) was vacuum transferred to the NMR tube cooled by a liquid nitrogen bath. Under high vacuum, the NMR tube was sealed with a small hot flame.

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Supporting Information Available: Synthetic procedures, NMR spectra, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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