5828 *J. Am. Chem. Soc.* **1996,** *118,* 5828−5829

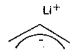
Observation of a Partially Delocalized Allylic Lithium and the Dynamics of Its 1,3 Lithium Sigmatropic Shift

Gideon Fraenkel* and Fayang Qiu

Department of Chemistry, Ohio State University
Columbus, Ohio 43210

Received February 12, 1996

Allyllithiums have been variously described, omitting solvation and aggregation, as contact ion-pairs, **1**, including delocalized anions, a localized species, **2**, or something in between **3**.



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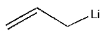

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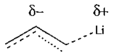
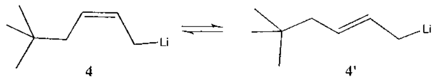


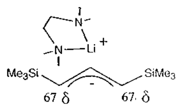
3

Most spectroscopic,[2,3] X-ray crystallographic,[4] and calculational[5] investigations support the delocalized structures, though there are a few cases reported to be localized, for example, unsolvated 3-neopentylallyllithium[6],**4,4′**.



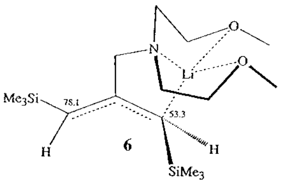
4 4'

Although theory does not rule out the possible existence of a continuum of intermediate states, **3**, such species have not been reported to date. Herein we describe the first example of such a structure.



5

A deuterium perturbation of equilibrium NMR experiment carried out with compound **5** established it to be delocalized.[4e,7,9] Low-temperature, 150 K, ^{13}C NMR data revealed the coordinated ligand TMEDA to be unsymmetrically sited with respect to the allyl loop. Line shape analysis of signal-averaging effects uncovered the dynamics of reorientation of the ions with respect to each other within the ion-pair, with a $\Delta H^{\ddagger}$ of 7 kcal/mol.[8] In contrast, an internally solvated version of **5**, **6**, shown with two



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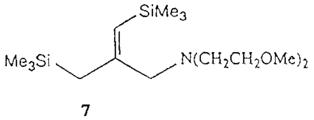
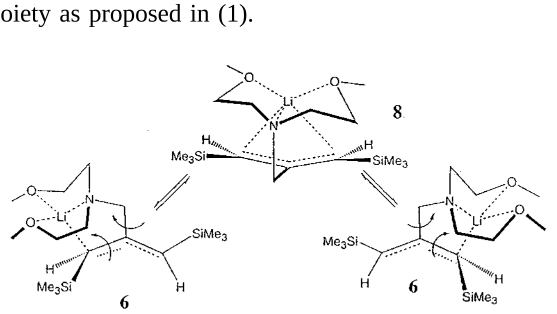


7

^{13}C shifts, obtained by metalating **7**, using CH$_3$^{6}Li in THF, behaved quite differently from **5**. At 240 K in THF-d_8 solution **6** displayed nonequivalent terminal allyl ^{13}C's as well as two different NMR shifts for the methylsilyls, both proton and ^{13}C. The allyl ^{13}C peak at 51.3 δ (C$_1$) is significantly broader (3.7 Hz) than that at 78.1 δ, (C$_3$) (2.3 Hz), implying a weak partially averaged one-bond coupling between the 51.3 δ ^{13}C and ^{6}Li and establishing the site of lithium. The terminal C$_1$, C$_3$ ^{13}C shifts of **6** lie between those of delocalized **5**, 67 δ, and the values reported for unsolvated **4,4′** 19.1 and 21.4, C$_1$, 101.1 and 102, C$_3$, δ units. The assignment to cis and trans are uncertain. Hence **6** is one of the hitherto missing species with intermediate C, Li ionicity and correspondingly different allyl π bond orders. That **6** should behave so differently from the established delocalized **5** must be due to internal coordination of Li in **6**. Construction of models shows that tridentate coordination of Li, to nitrogen and two oxygens, requires that lithium and nitrogen lie within the allyl carbon plane with the two oxygens on opposite sides, as drawn in **6**. Note also that the X-ray crystallographic structure of **5**·TMEDA places lithium normal to the center of the allyl plane, an arrangement not possible in internally solvated **6**. This is one of few cases in which solvation of Li renders a C, Li bond more covalent, rather than the inverse which usually obtains. The energetically favorable arrangement to coordinate Li places Li close to C$_1$.

With increasing temperature above 240 K the methylsilyl ^{13}C and proton resonances each broaden and average due to what is most likely a 1,3-sigmatropic shift of lithium. Similar effects are seen in the C$_1$, C$_3$ ^{13}C resonances which broaden and disappear into the base line, with increasing temperature. The large C$_1$, C$_3$ shift difference of 24.8 δ precludes observations of an averaged C$_1$, C$_3$ resonance by room temperature. Above room temperature the sample decomposes slowly. Line shape analysis of both the proton and ^{13}C methylsilyl doublets gives for this proposed lithium shift $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of, respectively, 18 kcal/mol and 7.5 eu. The process is first order. Its large $\Delta H^{\ddagger}$ value bespeaks of a significant change in bonding proceeding from ground to transition state, **8**. This would be consistent with an increase in conjugation within the allylic moiety as proposed in (1).



(1)

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(1) (a) Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. H., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol 7, p 97. (b) Seyferth, D.; Jula, T. F. *J. Organomet. Chem.* **1967**, *8*, C13. (c) Schlosser, M.; Stahle, N. *Angew. Chem.* **1980**, *92*, 477. (d) Stähle, M.; Schlosser, M. *J. Organomet. Chem.* **1981**, *220*, 277. (e) Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *198*, C1. (f) Brownstein, S.; Bywater, S.; Warsfold, D. J. *J. Organomet. Chem.* **1980**, *199*, 1.

(2) (a) West, P.; Purmort, J. I.; McKinley, S. V. *J. Am. Chem. Soc.* **1968**, *90*, 797. (b) O'Brian, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (c) Benn, R.; Rufinska, A. *J. Organomet. Chem.* **1982**, *239*, C19.

(3) (a) Bates, R. B.; Beavers, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 5001. (b) Dolinskaya, E. R.; Poddabnyi, I. Ya.; Tseretech, I. Yu. *Dokl. Akad. Nauk. SSSR* **1970**, *191*, 802. (c) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459.

(4) (a) Koster, H.; Weiss, E. *Chem. Ber.* **1982**, *115*, 3422. (b) Schumann, U.; Weiss, E.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1987**, *322*, 299. (c) Sebastian, J. F.; Grunwell, J. R.; Hsu, B. *J. Organomet. Chem.* **1974**, *78*, C1. (d) Boche, G.; Etzrodt, H.; Marsh, M.; Massa, H.; Baum, G.; Dietrich, H.; Mahdi, W. *Angew. Chem.* **1986**, *98*, 84. (e) Boche, G.; Fraenkel, G.; Cabral, J.; Harms, K.; van Eikema-Hommes, N. J. P.; Lorenz, J.; Marsch, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 4307−4314.

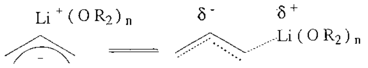
(5) (a) Erusalimski, C. B.; Kormer, V. H. *Zh. Org. Khim.* **1984**, *20*, 2028. (b) Tidwell, E. R.; Russell, B. R. *J. Organomet. Chem.* **1974**, *80*, 175. (c) Boche, G.; Decher, G. *J. Organomet. Chem.* **1983**, *259*, 31. (d) Clarke, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Organomet. Chem.* **1978**, *150*, 1. (e) Clarke, T.; Rhode, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (f) Bushby, R. J.; Tytho, M. P. *J. Organomet. Chem.* **1984**, *270*, 265.

(6) (a) Fraenkel, G.; Halasa, H. F.; Mochel, V.; Stumpe, R.; Tate, P. *J. Org. Chem.* **1985**, *50*, 4563−4565. (b) Glaze, W. H.; Jones, P. C. *J. Chem. Soc. D* **1969**, 1434. (c) Glaze, W. H.; Hanicac, J. E.; Moore, M. L.; Chandpuri, J. *J. Organomet. Chem.* **1972**, *44*, 39. (d) Glaze, W. H.; Hanicac, J. E.; Chandpuri, J.; Moore, M. L.; Duncan, D. P. *J. Organomet. Chem.* **1973**, *51*, 13. (e) Bywater, S.; Lachance, P.; Worsfold, D. J. *J. Phys. Chem.* **1975**, *79*, 2142.

(7) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Faller, J. W.; Murray, H. H.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 2306.

S0002-7863(96)00440-4 CCC: $12.00

Such a process is the inverse of that proposed to account for the influence of lithium ligand on the barriers to internal rotation in conjugated allylic lithiums—that there is an increase in C, Li covalency in the transition state compared to the ground state,[3a,12] (2). The results presented herein do not provide an understanding as to the role changes in lithium ligand coordination might play in the lithium shift process. Such considerations are omitted from this discussion.



(2)

This study shows that delocalization within the allyl moieties of allylic lithium compounds is variable both in their ground states and in the transition states for rearrangement reactions and is largely determined by the nature of lithium ligand coordination, especially its stereochemistry. It is not a foregone conclusion that lithium ligand coordination favors a decrease of carbon lithium covalence; it may be the other way around.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation Grant No. CHE 9317218 and in part by the Office of Research, Ohio State University. NMR equipment used in this research was also financed, in part, by the National Science Foundation. Dr. Charles Cottrell, Central Campus Instrumentation Center, helped us with excellent technical advice.

JA960440J

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(8) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382−1386.

(9) The corresponding experiment with allyllithium in THF gave a similar result: Winchester, W. R.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 177.

(10) (a) Gutowsky, H. S.; Saika, H. *J. Chem. Phys.* **1953**, *21*, 1688. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1957**, *25*, 1288. (c) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980; Chapter 6.

(11) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459.

(12) Fraenkel, G.; Chow, H.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 2585.