hydride, and 28 mg of azobisisobutyronitrile in 40 mL of benzene was heated at reflux for 16 h. CCl_4 (3 mL) was then added, to quench the reaction. The solvent was evaporated, and the mixture was purified by dry-column chromatography using 3% ether/hexanes as the developer. The fraction with R_f 0.7 was excised and extracted with ether and was found, by NMR analysis, to contain starting material and products. No other fraction contained significant amounts of these materials. Column chromatography did not effect separation of these compounds, but it did remove much of the tri-*n*-butyltin chloride produced. Four compounds were present (in addition to the tin chloride): starting material 1, 7-chloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene, 2-H, and 4-H. The absorbances for the protons at C-8 in 2-H and 4-H (δ 4.75 and 4.65, respectively) were well enough separated to make cut-and-weigh integration possible. This showed a 60:40 ratio of 4-H to 2-H.

A solution of 275 mg (1.00 mmol) of 3, 381 mg (1.30 mmol) of tri-*n*-butyltin hydride and 26 mg of azobisisobutyronitrile in 40 mL of benzene was treated as above, except that the reaction time was 7 h. Workup and analysis as was described for 1 gave a ratio of 65:35 for 4-H to 2-H.

Acknowledgment. We are indebted to the National Science Foundation for support of this research.

Remarks on the Chameleon Behavior of an Allyllithium: ^{13}C and ^{6}Li NMR

Gideon Fraenkel,*[1] Adel F. Halasa,[2,3a] Virgil Mochel,[2] Rainer Stumpe,[1,3b] and David Tate[2]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and The Research Laboratories, Firestone Tire and Rubber Company, Akron, Ohio 44317

Received March 8, 1985

Carbon-13 NMR of 5,5-dimethyl-1-lithio-2-hexene (4) in cyclopentane, in the presence of different ligands at different ligand concentrations, and at different temperatures shows the system to contain a mixture of covalent and ionic delocalized forms in fast dynamic equilibrium with the latter prevailing in the presence of vicinal trans diamines, especially at low temperatures. It is concluded that 1,2-addition in RLi-initiated polymerization of dienes results from ionic allylic live ends and not from covalent secondary allyllithium. The latter are energetically unstable compared to the ionic delocalized forms.

Allylic lithium compounds have been studied extensively and variously described (leaving out aggregation and solvation) as ionic (**1**), covalent (**2**), or different species in between (**3**).[4–6]

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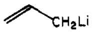

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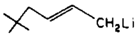
In this article we present new conclusions, based on ^{13}C and ^{6}Li NMR data obtained as a function of temperature and ligand concentration, regarding the structure and dynamic behavior of 1-lithio-5,5-dimethyl-2-hexene (**4**). Compound **4** was chosen because it is quite soluble in a variety of media,[7] including hydrocarbons. Further, in order to investigate possible $^{13}C,^{6}Li$ coupling and increase the signal/noise ratio in ^{13}C NMR, compound **4** has been prepared enriched with both these isotopes, with ^{13}C at C(1) or C(4). Of the two stable isotopes ^{7}Li and ^{6}Li, the latter has the lower quadrupole moment and is less likely to bring about decoupling from ^{13}C due to fast quadrupole relaxation.[8] Hence **4** has been prepared enriched in ^{6}Li.

Results and Discussion

As noted in part elsewhere,[9] the ^{13}C NMR of **4** in a variety of hydrocarbon solvents shows resonances for C(1), C(2), and C(3) around 20, 144 and 100 (vs. Me_4Si) ppm, respectively (see Table I). Two spectra are observed which may be assigned to pseudospecies **4t** (trans) and **4c** (cis), omitting aggregation effects, in agreement with the literature.[7,9] In general carbon shifts in unsolvated organolithium compounds differ little from corresponding hydrocarbon shifts. For instance C(1) of butyllithium at 11 ppm is close to methyl of butane at 13 ppm. Since the shift of C(1) in **4ct** is so similar to C(1) of 5,5-dimethyl-2-hexene, a covalent structure has been assigned.

Table I. ^{13}C NMR Shifts (Me_4Si, ppm) of $(CH_3)_3CCH_2CH{=}CHCH_2Li$ in Different Solvents (1 M, 20 °C)

	$C_6D_5{}^{12}CH_3$	C_6D_6	$(CH_2)_5$
C(1)	21.16	19.96	19.6
	21.49	20.82	21.42
C(2)	140.62	144.49	140.13
	144.51		143.94
C(3)	101.88	102.64	101.14
	102.30	102.96	102.0
C(4)	41.87	42.0	41.73
	48.45	48.79	48.05
C(6)	29.65	29.4	32.3
	31.36	31.34	32.56



4t

4c

The cis/trans ratio of compound **4** in cyclohexane varies with temperature, 193–293 K yielding a ΔH of 2.6 ± 0.3 kcal for the conversion cis $\rightleftharpoons$ trans. On cooling these samples of **4** the line widths for C(1) and C(3) increase significantly compared to the other lines in the spectra; thus for **4ct** in toluene-d_8 while at 301 K all lines are ca. 4 Hz wide, by 258 K the widths for C(1) and C(3) are 56 and 132 Hz, respectively, and yet the C(4) width is still 4 Hz. Coupling between ^{13}C and ^{6}Li or ^{7}Li is not observed in the ^{13}C NMR of any of these samples down to 173 K. Strongly irradiating at the ^{6}Li frequency (^{6}Li-enriched

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[1] The Ohio State University.

[2] Firestone Tire and Rubber Co.

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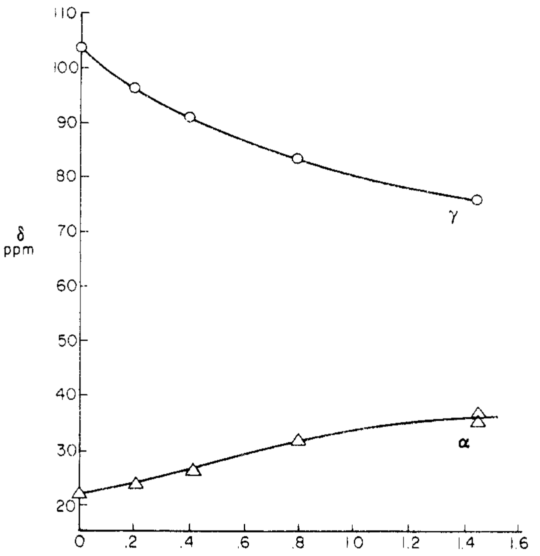


Figure 1. ^{13}C NMR shifts α and γ of 4, 11 M in cyclopentane, 30 °C, in the presence of 1,2-dipiperidylethane (DPE), plotted as M DPE/M 4.

Table II. ^{13}C NMR Limiting Shifts of "(3-Neopentylallyl)lithium" 4 (1 M in Cyclopentane) with Different Ligands

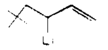
ligand (mol of lig./mol of Li)	T, °C	chem shift, ppm C(1)	C(2)	C(3)
	30	19.6 21.42	140.13 143.94	101.1 102.0
THF (10)	30	30 31	144.0	81
DPE^a (1.4)	30	33 36	146.0	89
DPE (1.45)	−40	39	146	72
BTHF^b (2.8)	30	31 35	144	77 89
THF (pure, Cs salt)	30	51.4	139.5	69

^{a} 1,2-Dipiperidylethane. ^{b} 2,2-Bis(2-tetrahydrofuranyl)propane.

sample) changes the ^{13}C of [1-^{6}Li]**4c,t** hardly at all.

Lithium-6 NMR of [1-^{6}Li]**4c,t**, 0.3 M in cyclopentane, consists of a sharp line with a width of 1.7 Hz at 273 K, which broadens to 3.5 Hz at 258 K and 16.9 Hz at 243 K. Failure to observe ^{13}C,^{6}Li coupling if it exists in **4**, ca. 6–8 Hz, could be due to fast lithium quadrupole induced relaxation,[8,9] as well as fast (relative to the NMR time scale) C,Li bond exchange among covalent aggregates. Recall that several alkyllithium compounds in hydrocarbon media, e.g., *n*-propyl[10] and 2-butyl,[11] exist as equilibrium mixtures of different aggregates whose distributions vary with temperature.

Finally the possible 3-lithio isomer of **4**, **5**, is not detected by NMR; if present in low concentrations it does not convert to the **4ct** components at rates fast relative to the NMR time scale, since the ^{13}C shifts of **4c** and **4t** are not averaged under our conditions.



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In summary, unsolvated **4** appears to consist of covalent species where cis ⇌ trans isomerization is slow relative to the NMR time scale, but shifts among aggregates, (if there are two or more) often visible in other systems, are averaged by C,Li bond exchange processes, fast even at 200 K.

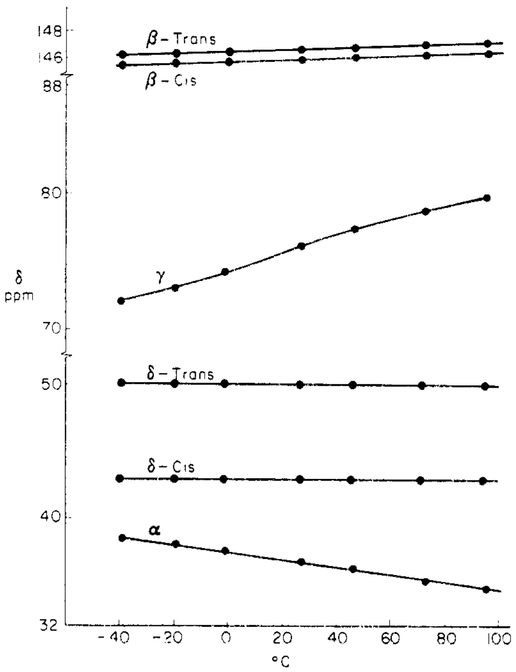
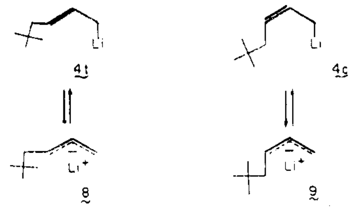
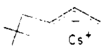


Figure 2. ^{13}C NMR shifts of **4**, 1.1 M in the presence of 1.4 M DPE, as a function of temperature.

Scheme I



The addition to **4ct** in cyclopentane of a wide variety of ethers and trans amines in increasing concentration causes the shifts of C(3) to move upfield and ^{13}C(1) to move downfield, while that of ^{13}C(2) remains largely unchanged. These shifts reach limiting values which depend on the nature of the ligand and the temperature (see Table II and Figure 1).[12] The decrease of the shift between C(1) and C(3) is also seen on cooling samples of **4ct** complexed to different ligands (Figure 2) as well as on changing to more electropositive metals.[12,13] The smallest C(1)–C(3) ^{13}C shift difference has been reported for (3-neopentylallyl)cesium with C(1), C(2), and C(3) at 51.4, 139.5, and 69 ppm, respectively.[12,13] These latter values accord theoretically with delocalized anions, cis and trans in ion pairs, **6** and **7**, where aggregation and ion solvation has been omitted. It is clear that interconversion of the cis,trans isomers is slow relative to the NMR time scale.



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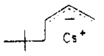

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All samples of **4** in the presence of different ligands, reported in this article as well as previously, show two sets of "3-neopentylallyl" ^{13}C resonances.[13-15] The shifts all

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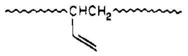
lie between those for **4** in hydrocarbon and the values for (3-neopentylallyl)cesium in THF. The simplest explanation that accounts for the wide variations which these data exhibit under different conditions is that *all the solutions* (including **4** in hydrocarbon alone) *contain a mixture of cis and trans covalent species in fast dynamic equilibrium with ion pairs containing delocalized cis and trans allylic anions* (Scheme I).[7] Interconversion of ionic and covalent forms as well as exchange of allylic moieties among different aggregates is fast relative to the NMR time scale down to 190 K, while rotation about the C(2),C(3) bond is slow. Lower temperatures, better ligands, and more electropositive metals favor the ionic more solvated forms. This also accords with the well-known observation that low temperature favors separated ion pairs over tight ion pairs, since the former are more strongly solvated.[20]

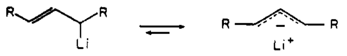
Anionic polymerization of 1,3-butadiene, using alkyllithium as initiator, leads to different patterns of polymer microstructure, depending on the conditions of the reaction. Thus the mechanism of the polymerization must depend critically on the structure of the allylic lithium "live end".[17] It is well-known that while polymerization of butadiene with butyllithium in hydrocarbon solvents gives at most 9% of 1,2 microstructure **10**, in the presence of ethers or trans amines there is much more 1,2 microstructure;[18] the polymer obtained from *n*-butyllithium and butadiene in the presence of 1,2-dipiperidylethane, 273 K, is >99% 1,2.[19] Since **4** with 1,2-dipiperidylethane consists mainly of ion pairs containing delocalized allylic anions, one must conclude that 1,2 propagation takes place at delocalized live ends and not from localized 3-lithio allylic live end. It is then the inescapable conclusion that *a 3-substituted allyl anion will react with 1,3-diene at the substituted carbon.*



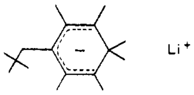
$\sim\sim\sim\underset{\diagdown\!\!\diagdown}{C}HCH_2\sim\sim\sim$

10

Further, these results collectively imply that a covalent secondary allylic lithium compound, **11**, will always be unstable relative to its delocalized form, **12**. Covalent RLi compounds almost always exist as bridged aggregates. In the case of **11**, steric interactions may render the covalent allyllithium aggregates energetically unstable relative to the ionic forms. This effect was advanced to explain why the substituted lithium cyclohexadienide **13** was observed to exist in the delocalized form in all media including hydrocarbon solvents and never as a covalent species.[20]



11 **12**



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Experimental Section

Carbon-13 NMR was carried out by using JEOL PS-100 and Bruker WM-300 equipment. Lithium-6 NMR was obtained with the Bruker spectrometer, at a frequency of 44.7 MHz, 22-μs pulse (30°), with an acquisition time of 8.19 s and simultaneous proton decoupling.

(Neopentylallyl)lithium **4** was prepared by stoichiometric reaction under argon of [^{6}Li]*tert*-butyllithium and 1,3-butadiene, ca. 0.3 M in cyclopentane, at °C, in 85–90% conversion. The [^{6}Li]*tert*-butyllithium was obtained from the reaction of di-*tert*-butylmercury with lithium-6 dispersion-alloyed with sodium (2%). The lithium sodium alloy must be prepared in a steel vessel. In separate runs **4** was prepared from [1-^{13}C]1,3-butadiene and [2-^{13}C]1,3-butadiene. Compound **4** was also made by cleaving the corresponding mercury compound with lithium-6 dispersion in cyclopentane. Both preparations of **4** gave the same NMR spectroscopic results.

Acknowledgment. This research was supported by the National Science Foundation Grant CHE-8304636 which also helped finance the high-field NMR equipment at Ohio State University, the Firestone Tire and Rubber Co., and the NATO Office of Scientific Affairs. R.W.S. thanks the Deutsche Forschungsgemeinschaft for partial support. We are grateful to Dr. Charles Cottrell of the Central Campus Instrumentation Center, Ohio State University, for assistance with NMR technology.

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