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Vinyllithium: Dynamic Behavior in Tetrahydrofuran Solution and Comprehensive Analysis of NMR Spin–Spin Coupling Constants

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Abstract: Vinyllithium (ViLi; isotopically labeled with ^{6}Li) is an 8:1 tetramer/dimer equilibrium in tetrahydrofuran-d_8 (THF-d_8) at −90 °C (1.6 M solution). In the presence of equilmolar amounts of TMEDA (tetramethylethylenediamine), the tetramer:dimer ratio is 1:13 in THF-d_8 at −80 °C (1.9 M solution). Dynamic NMR phenomena are observed in the ViLi tetramer: at −90 °C in THF-d_8, a "static" aggregate is found, whereas at −60 °C rapid *intraaggregate* exchange of the four lithium sites indicates a "fluxional" tetramer. Within a "static" tetramer, rapid tumbling of a monomer unit is deduced from C,Li and H,Li NMR coupling patterns. From tilts within cross peak multiplets in ^{1}H,^{13}C HETCOR spectra of ViLi (due to coupling with the passive ^{6}Li spin), it is concluded that the sign of $^{1}J(^{13}\mathrm{C},^{6}\mathrm{Li})$ is positive. In a fully coupled heteronuclear ^{6}Li,^{1}H shift correlation experiment (FUCOUP), an intense and a weaker cross peak are observed between ^{6}Li,H$^{\mathrm{gem}}$ and ^{6}Li,H$^{\mathrm{trans}}$, respectively, of tetrameric ViLi. This is indicative of scalar ^{6}Li,^{1}H coupling. In a ^{6}Li,^{1}H FUCOUP spectrum with a small (36°) ^{1}H mixing pulse ("β-FUCOUP"), the tilt of the ^{6}Li,H$^{\mathrm{trans}}$ cross peak indicates the sign and magnitude of $^{2}J(^{6}\mathrm{Li},\mathrm{H}^{\mathrm{gem}})$ to be +0.4 Hz. Analogous to the tetramer, ^{6}Li,^{1}H β-FUCOUP of the dimer reveals $^{3}J(^{6}\mathrm{Li},\mathrm{H}^{\mathrm{trans}})$ to be +0.4 Hz. The ^{13}C,^{13}C coupling constant in vinyllithium is extraordinarily small (dimer, 35.0 Hz; tetramer, 36.3 Hz). Likewise, the one-bond ^{13}C,^{1}H coupling constant $^{1}J(\mathrm{C1},\mathrm{H}^{\mathrm{gem}})$ is the lowest reported so far for monosubstituted ethylenes (dimer, 91.7 Hz; tetramer, 93.2 Hz). By combination of ^{13}C gated decoupled and ^{13}C,^{1}H β-FUCOUP data, extreme numbers are also found for geminal $^{2}J(^{13}\mathrm{C},^{1}\mathrm{H})$ coupling constants: dimer, $^{2}J(\mathrm{C1},\mathrm{H}^{\mathrm{cis}}) = +13.5$ Hz; $^{2}J(\mathrm{C1},\mathrm{H}^{\mathrm{trans}}) = -5.9$ Hz; $^{2}J(\mathrm{C2},\mathrm{H}^{\mathrm{gem}}) = -10.5$ Hz; tetramer, $^{2}J(\mathrm{C1},\mathrm{H}^{\mathrm{cis}}) = +13.5$ Hz; $^{2}J(\mathrm{C1},\mathrm{H}^{\mathrm{trans}}) = -6.1$ Hz; $^{2}J(\mathrm{C2},\mathrm{H}^{\mathrm{gem}}) = -12.1$ Hz.

Introduction

NMR spectroscopy of organolithium compounds has revealed a great number of structural details for this amazing and synthetically invaluable class of chemicals.[1] With the advent of two-dimensional (2D) NMR techniques, many of the new NMR methods (e.g., ^{6}Li,^{1}H HOESY) have been applied to organolithium compounds as well.[1a,b,d,2] With respect to the favorable properties of the ^{6}Li isotope (spin $I = 1$; 7.4% natural abundance) over the major abundant ^{7}Li ($I = {}^{3}/_{2}$, 92.6%),[1l] the majority of solution NMR studies of organolithium compounds now employs ^{6}Li-enriched material.[1a–e]

Surprisingly, one of the simplest and most versatile organolithium compounds, vinyllithium (**1**), has not been studied by NMR in much detail. An early paper by Seyferth[3] reported the 60-MHz ^{1}H NMR spectrum of C_2H_3Li in diethyl ether solution at room temperature as well as a simulation of the ABC spin system. Likewise, Fraenkel reported ^{1}H NMR data of **1**.[4] These early data confirmed that configuration inversion at the lithiated carbon atom is very slow on the NMR time scale (ABC instead of A_2B ^{1}H spin system). According to ^{13}C NMR measurements by Fraenkel,[1e] **1** is a dimer/tetramer equilibrium in diethyl ether at 213 K.[5] ^{13}C chemical shifts as well as ^{1}J and ^{2}J(C,H) coupling constants for **1** were reported by van Dongen et al.[6] Recently, we reported ^{6}Li,^{1}H heteronuclear Overhauser effect (HOESY) studies on **1**.[7] By using the ^{6}Li^{1}H HOE buildup rates, quantitative estimates of relative intramolecular Li,H distances were obtained relying on X-ray distances for calibration.

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(2) (a) Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827. (b) Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191. (c) Bauer, W.; Lochmann, L. *J. Am. Chem. Soc.* **1992**, *114*, 7482. (d) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208. (e) Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *Magn. Reson. Chem.* **1992**, *30*, 855. (f) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794. (g) Eppers, O.; Fox, T.; Günther, H. *Helv. Chim. Acta* **1992**, *75*, 883. (h) Balzer, H.; Berger, S. *Chem. Ber.* **1992**, *125*, 733.

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(5) However, we question the existence of the reported dimer in ref 1e. Therein, the chemical shift of the dimer is claimed to be exactly the same as that of the tetramer ($\delta = 183.00$ ppm). Rather, from the material of the present work we believe that vinyllithium is a pure tetramer in diethyl ether. The multiplicity pattern shown in ref 1e for the ^{13}C NMR signal of the lithiated carbon atom might be explained by the existence of different tetrameric ^{6}Li/^{7}Li vinyllithium isotopomers, possibly with a ^{6}Li content larger than natural abundance.

(6) Van Dongen, J. P. C. M.; van Dijkman, H. W. D.; De Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29.

(7) Bauer, W.; Hampel, F. *J. Chem. Soc. D* **1992**, *903*.

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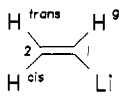


1

$[H_2C{=}CHLi \times THF]_4$

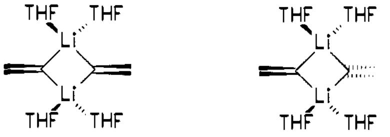
2

On the basis of colligative data, **1** was found to be entirely tetrameric in tetrahydrofuran (THF) solution at +25 °C.[8] In the solid state, vinyllithium (**1**) was reported recently by our group to consist of a tetrameric THF solvate, **2**.[7] The X-ray crystal structure of **2** is shown in Figure 1. An S_4 axis extends vertically through the Li_4C_4 cube with respect to the orientation shown in Figure 1.

In this paper, we report the dynamic behavior of **1** in THF solution, based on ^{13}C NMR chemical shifts and $^{13}C,^{6}Li$ spin–spin coupling constants. Material isotopically enriched (96%) with ^{6}Li was employed throughout. In addition, we describe the determination of all possible internuclear spin–spin coupling constants in both dimeric and tetrameric vinyllithium. Since vinyllithium consists of six atoms (C_2H_3Li), there are $(6 \times 5)/2 = 15$ internuclear spin–spin interactions in a monomeric unit. We report the methods employed to detect the magnitudes and the signs of the coupling constants. Subsequently, the implications for the structure description of **1** from the NMR coupling constants will be discussed. For convenience, we use the nomenclature of formula **1** throughout this paper.

Results

State of Aggregation, Dynamic Behavior, and $^{13}C,^{6}Li$ Coupling Constants. At –90 °C, a 1.6 M solution[9] of **1** in THF-d_8 shows two sets of signals in both the ^1H and the ^{13}C NMR spectrum. Integration of the ^1H signals gives a 16:1 ratio. The ^{13}C NMR signal of C1 of the minor species resonates at $\delta = 190.81$ ppm. Due to resolved $^{13}C,^{6}Li$ coupling, the signal of C1 is split into a 1:2:3:2:1 quintet, $^1J(^{13}C,^{6}Li) = 8.3$ Hz, (Figure 2). Accordingly, the metalated carbon atom must be bound directly to two ^6Li nuclei. This agrees with a dimeric species, **3** (with an assumed number of two THF ligands per lithium in order to achieve the usual tetracoordination[10]).



syn anti

3

From the available data, it is not possible to assign the symmetry of the involved species (C_{2v}, *syn*-**3** or C_{2h}, *anti*-**3**). Likewise, an alternative trimeric species, *syn*-**4**, would reveal similar ^{13}C multiplicities and cannot be ruled out. However, in contrast to dimers, trimers are quite rare in the field of organolithium chemistry, both in the solid state and in solution.[11] Hence, we refer to this species as the "dimer" in the subsequent text. A further alternative, *anti*-**4**, may be ruled out: this isomer should exhibit two ^1H and ^{13}C signal sets in a 1:2 ratio. This is not observed.

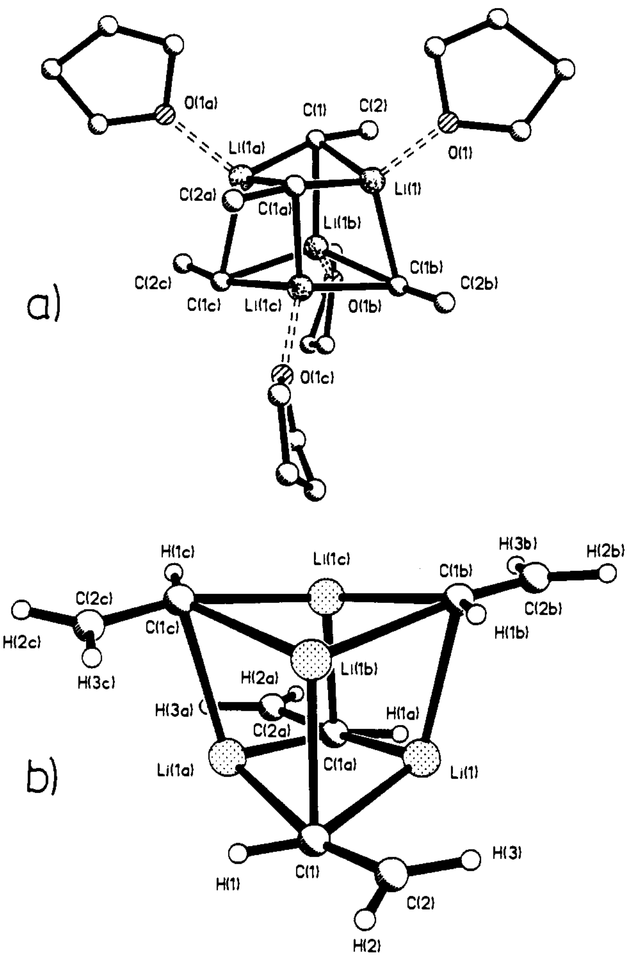


Figure 1. X-ray crystal structure of tetrasolvated (THF) vinyllithium tetramer (**2**) (a) with hydrogen atoms omitted and (b) with THF ligands omitted.

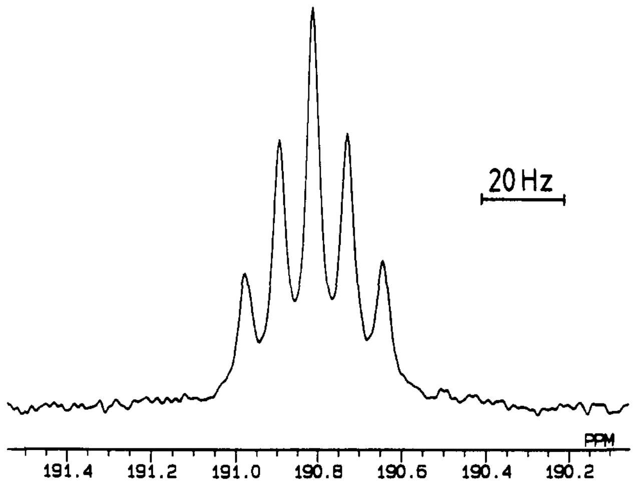


Figure 2. ^{13}C NMR signal of the lithiated carbon atom in the dimeric aggregate of **1** (THF-d_8, 1.6 M, at –100 °C).

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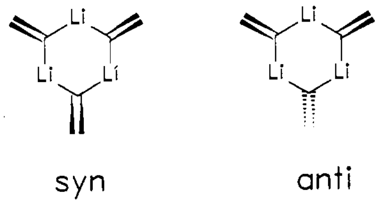
[8] West, P.; Waack, R.; Purmort, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840.

[9] In THF-d_8 solution, **1** partly precipitates at low temperatures after a certain time both in the absence and in the presence of tetramethylethylenediamine (TMEDA). The same holds for solutions of **1** in toluene-d_8 at low temperatures in the presence of TMEDA. Hence, all concentration numbers given in the subsequent text for low-temperature measurements refer to formal concentrations at room temperature. The actual concentrations at low temperatures may be different.

[10] Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

[11] (a) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J.; Bauer, W.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 1696. (b) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; van Lenthe, J. H. *Organometallics* **1991**, *10*, 1623. (c) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. .; Duisenberg, A. J. M.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 2623.



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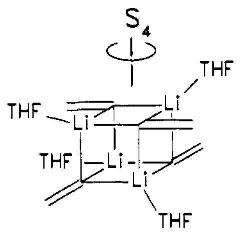
The NMR signal of C1 of the major species (δ = 183.00) resonates by 7.81 ppm upfield from the signal of the dimer. The order of chemical shifts of the lithiated carbon atom of phenyllithium and vinyllithium derivatives is δ (monomer) > δ (dimer) > δ (tetramer) (cf. phenyllithium, δ_{C1} (monomer) = 196.7;[12] δ_{C1} (dimer) = 188.5;[12] δ_{C1} (tetramer) = 176.2[13]). Hence, we conclude that the major species of **1** in THF-d_8 at -90 °C is aggregated to a higher extent than the dimer.

The multiplicity of the C1 NMR signal of the major species is a septet, $^1J(^{13}C,^6Li)$ = 5.9 Hz, at -90 °C in THF-d_8 (Figure 3a). This must result from coupling of ^{13}C with its three directly bound ^6Li coupling partners in a static tetrameric aggregate, **5**. Similar observations have been made in numerous other cases.[1a] Coupling of ^{13}C with the remote diagonal ^6Li nucleus in **5** is not observed in Figure 3a.



5

We assume that the structure of the tetramer in THF-d_8 solution is similar to the solid-state structure shown in Figure 1. Thus, the intensity ratio of 16:1 of the two signal sets for **1** in THF-d_8 (1.6 M) at low temperatures refers to an 8:1 molar ratio of the tetramer and the dimer.

An interesting dynamic phenomenon in **5** is observed in the ^{13}C NMR spectrum when the temperature is raised. At -75 °C, scrambling of the septet is observed (Figure 3b). At still higher temperatures (-60 °C), a well-resolved nine-line multiplet appears (Figure 3c), $^1J(^{13}C,^6Li)$ = 4.4 Hz. This must result from coupling of ^{13}C with *all four* ^6Li nuclei in the tetrameric cluster (**5**). Thus, rapid ***intraaggregate*** exchange of the lithium sites in **5** must take place under these conditions in terms of the NMR time scale. However, ***interaggregate*** exchange processes must still be slow at -60 °C. Rapid intraaggregate dynamic processes of organolithium compounds have been long known, e.g., in propyllithium hexamers, octamers, and nonamers.[14] However, to our knowledge, the observation of a "static" and a "dynamic" aggregate depending on the temperature has been described in only two further cases: tetrameric *tert*-butyllithium (tBuLi) (**6**) converts from a static aggregate at -80 °C to a fluxional aggregate at +26 °C.[15] [^{6}Li][1-*tert*-Butoxy-3-(dimethylamino)-2-phenyl]lithium (**7**) in toluene-d_8 is a static trimer at -5 °C (quintet for C2 in the ^{13}C NMR spectrum), whereas at +25 °C a fluxional trimer is detected (septet for C2).[16] We will discuss the magnitudes and the signs of the observed $^{13}C,^6Li$ coupling constants in subsequent sections.

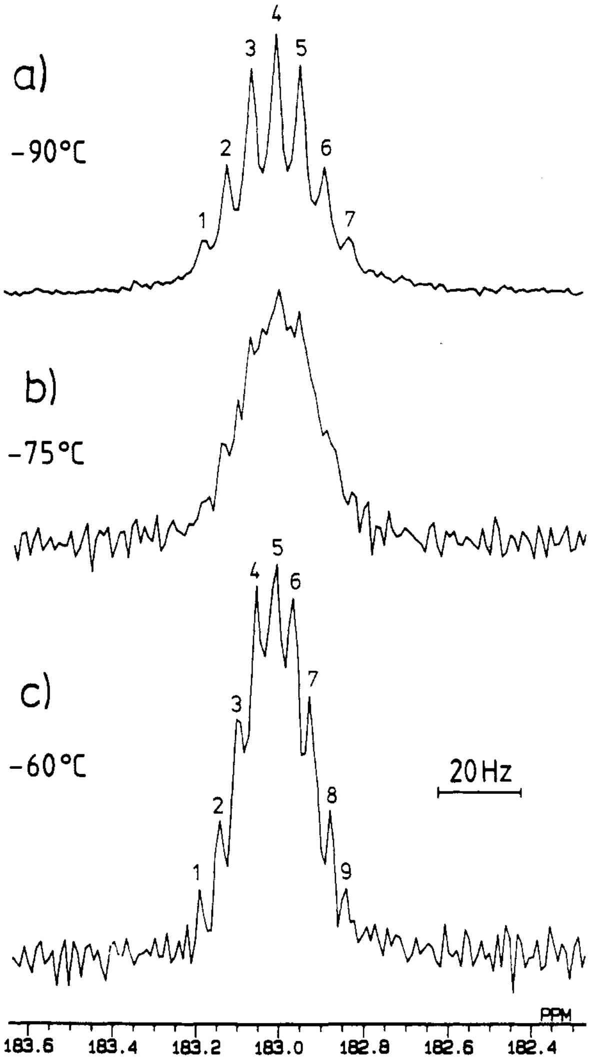
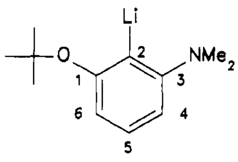


Figure 3. ^{13}C NMR signal of the lithiated carbon atom in the tetrameric aggregate of **1** (THF-d_8, 1.6 M) (a) at -90 °C; (b) at -75 °C; and (c) at -60 °C.

6



7

When the temperature is raised from -90 to -60 °C, the amount of the ViLi dimer decreases (as determined by integration of the appropriate ^{13}C NMR signals in inverse gated decoupled spectra). On going from -60 °C to higher temperatures, the ^1H and ^{13}C NMR signals of the dimer and the tetramer of **1** in THF-d_8 coalesce. At room temperature, a single signal set is observed. Under these conditions, the chemical shifts of **1** are identical to those of the *tetramer* at low temperatures (cf. Table II). Thus, we seemingly observe exclusively the tetramer under these conditions, in agreement with colligative data.[8] This implies that the tetramer/dimer equilibrium of **1** in THF must be *exothermic*. Similar observations (where lower temperatures favor the less aggregated species in THF solution) have been made for other

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(12) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

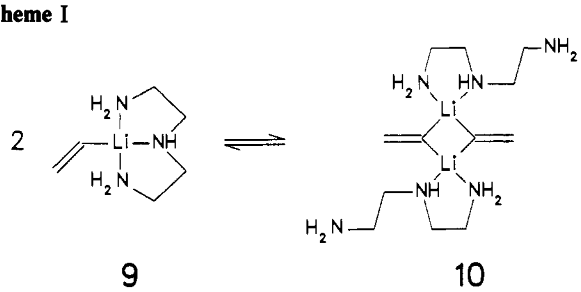
(13) Jackman, L.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627.

(14) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3345.

(15) Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Young, T. C. *Organometallics* **1986**, *5*, 1851.

(16) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 2623.

Scheme I



9 10

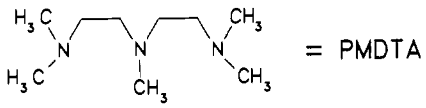
$$2\,\mathbf{9} \rightleftharpoons \mathbf{10} \qquad \Delta H^{0} = -39.7\ \text{kcal/mol} \tag{1}$$

$$2(-18.0) \qquad -73.3$$

systems as well (e.g., nBuLi[1i,17] and 1-lithio-2-(2-lithiophenyl)-1-phenylhex-1-ene;[18] however, opposite cases have been reported as well, i.e., preference of the higher aggregated species at lower temperatures[19-21]). Our chemical shifts obtained for **1** in THF-d_8 at room temperature are similar to those reported by van Dongen et al.[6]

Addition of 1 equiv of the η^2 ligand tetramethylethylenediamine (TMEDA) to a THF-d_8 solution of **1** inverts the molar ratio of the involved aggregates: the tetramer:dimer ratio is 1:13 at −80 °C (1.7 M). However, even in this case the amount of the tetramer increases with higher temperatures. Pure dimeric **1** at temperatures between −90 and −10 °C may be obtained by adding TMEDA (1 equiv) to a toluene-d_8 suspension of **1**, which gives a clear solution at −10 °C; at lower temperatures, crystals of the assumed composition (**1**·TMEDA)$_2$ precipitate. Up to −10 °C, no decomposition of the solvent is observed for this mixture. Likewise, pure dimeric **1** is present at room temperature in a C_6D_6 solution of vinyllithium with an additional 1 equiv of TMEDA.

Attempts to observe *monomeric* **1** solution failed: addition of 1 equiv of the η^3 ligand *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA) (**8**) to a THF-d_8 solution of **1** revealed only *dimeric* **1**. This agrees well with MNDO calculations (Scheme I): conversion of monomeric vinyllithium chelated with diethylenetriamine (**9**) into dimer **10** is a strongly exothermic reaction (eq 1).



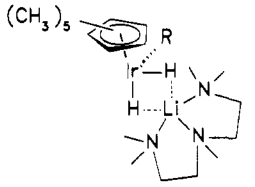
8

Thus, we assume that in the presence of equimolar amounts of **8**, vinyllithium consists of a species analogous to **10** in THF-d_8 solution.

Geminal and Vicinal ^{1}H,^{1}H Coupling Constants. At a magnetic field strength of 9.4 T (^{1}H = 400 MHz), the ^{1}H NMR spectrum of the dimer/tetramer mixture of **1** in THF-d_8 at −90 °C may be analyzed according to first-order rules (cf Figure 4). The coupling constants, obtained are as follows. Dimer: $^{3}J(H^{gem},H^{trans}) = 18.6$ Hz; $^{3}J(H^{gem},H^{cis}) = 23.9$ Hz; $^{2}J(H^{trans},H^{cis}) = 8.8$ Hz. Tetramer: $^{3}J(H^{gem},H^{trans}) = 19.0$ Hz; $^{3}J(H^{gem},H^{cis}) = 23.9$ Hz; $^{2}J(H^{trans},H^{cis}) = 7.4$ Hz.

A drawback of the employed high magnetic field strength is loss of information: the signs of the coupling constants may not be extracted from the weakly coupled spin system of **1** under these conditions. Whereas vicinal (^{3}J) ^{1}H,^{1}H coupling constants are positive throughout, geminal (^{2}J) coupling constants in vinyl derivatives have been found to change their sign depending on the electronegativity of the substituent.[22] Simulated ^{1}H NMR spectra of **1** for a field strength of 9.4 T are completely insensitive to the input sign of $^{2}J(H^{trans},H^{cis})$. By contrast, the sign of coupling constants may be extracted from strongly coupled spin systems.[23] In an early NMR study on **1**,[3] the experimental 60-MHz ^{1}H NMR spectrum fitted with a simulated spectrum, obviously by using a positive geminal H^{trans},H^{cis} coupling constant. However, it was not reported whether a simulation using $^{2}J(H^{trans},H^{cis}) < 0$ led to strongly different results. We have repeated the measurements at 1.4 T along with a simulation with both positive and negative geminal coupling constants. The calculated spectra differ largely. Clearly, from simple visual inspection, only the simulated spectrum with *positive* $^{2}J(H^{trans},H^{cis})$ fits with the experimental spectrum.

Two- and Three-Bond ^{6}Li,^{1}H Coupling Constants. Whereas scalar coupling between ^{13}C and ^{6}Li may be often observed under conditions of slow chemical metal exchange, resolved coupling between two chemically nonequivalent ^{6}Li nuclei in a molecule has been observed only recently by Günther et al. in a one-dimensional ^{6}Li spectrum.[24] Likewise, resolved scalar coupling between protons and lithium has been described only in a few cases. Bergman[25] reported $^{1}J(^{1}H,^{7}Li) = 8.4$ Hz, as detected in the ^{1}H NMR spectrum of the transition metal hydride **11** in toluene-d_8 between +20 and −40 °C. By analogy, **12** reveals a 1:1:1:1 quartet in the ^{1}H NMR spectrum, $^{1}J(^{1}H,^{7}Li) = 6.4$ Hz, in toluene-d_8 at −20 °C.



11 R = SiMe$_3$
12 R = H

Scalar coupling between lithium and hydrogen ($^{1}J(^{1}H,^{7}Li) = 10.5$ Hz) was reported recently by Heine and Stalke[26] for the alumino complex **13** in toluene-d_8 between −30 and −70 °C.

$$[(SiMe_3)_2N]AlH_2Li \times 2\ Et_2O \quad \mathbf{13}$$

Resolved scalar coupling across more than one bond between hydrogen and lithium has been reported recently by Field et al. for a dilithiated compound.[27] From temperature dependent line broadening in the ^{1}H NMR spectrum of ethyllithium, Brown and Ladd[28] concluded the existence of scalar $^{2}J(^{1}H,^{6,7}Li)$ coupling. Recently, Eppers and Günther[29] determined $^{2}J(^{1}H,^{6}Li) = 0.34 \pm 0.07$ Hz for the methyllithium tetramer from line shape analysis of ^{1}H-coupled and ^{1}H-decoupled ^{6}Li NMR spectra. We have recorded ^{7}Li NMR spectra (natural abundance lithium) of the vinyllithium tetramer with and without proton decoupling. At −90 °C in THF-d_8, the line width of the ^{7}Li signal increases from

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(17) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848.

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3.2 to 4.0 Hz when the ^1H decoupler is turned off, indicating nonresolved scalar Li,H coupling.

We report here an alternative method for the detection of $^{2,3}J(^1H,^6Li)$ scalar couplings in vinyllithium (**1**) which is based on polarization transfer. The basic pulse sequence for heteronuclear shift correlation is given in eq 2. For $\phi = 90°$, this sequence

$$90°(I)\text{–}t_1\text{–}\phi(I),\ 90°(S)\text{–acquisition} \qquad (2)$$

is referred to as fully coupled (FUCOUP) spectroscopy.[30] As opposed to the customary heteronuclear shift correlation experiment by Freeman and Morris,[31] no fixed delays are built into this sequence. Thus, no initial guesses about the magnitude of the involved coupling constants must be made. FUCOUP has been applied for long-range heteronuclear carbon–proton shift correlations.[32] A drawback of the FUCOUP experiment is a loss of intensity due to signal splitting from non-refocused heteronuclear scalar coupling in ω_1 and ω_2, as well as the lack of spectral simplification.

A modification of sequence 2, first described by Bax and Freeman,[33] additionally allows the determination of the relative signs of coupling constants in cases where more than two nonisochronous spins are involved. When the ^1H mixing pulse in sequence 2 is considerably smaller than 90°, the magnetization transfer is restricted mainly to directly connected transitions in the energy level diagram of the spin system.[34] Coherences between parallel transitions are effectively suppressed by using this method. Thus, in an AMX spin system, only those AX cross peaks are observed which do not originate from a flip of the "passive" spin M induced by the mixing pulse. This considerably simplifies the cross peak multiplet structure. Moreover, a tilt is introduced into the cross peak multiplet. If the slope of the tilt in the AX cross peak of an AMX spin system is positive (with respect to increasing frequency in both dimensions), then J_{AM} and J_{MX} have like signs.[35] For the same reason, tilted cross peak multiplets are found in homonuclear E.COSY spectra[36] and in so-called "β-COSY" or "COSY-45" spectra.[34] In the following, we refer to the FUCOUP experiment (eq 2) with $\phi < 90°$ as "β-FUCOUP".

We have applied $^6Li,^1H$ FUCOUP to vinyllithium. Provided that there is nonzero coupling between lithium and hydrogen, appropriate cross peaks should be observed in a $^6Li,^1H$ FUCOUP spectrum of **1**. This is shown for tetrameric **1** in Figure 4. Under conditions of slow lithium exchange (i.e., in THF-d_8 at −90 °C), an intense cross peak multiplet is detected for ^6Li and H^{gem}, and a less intense cross peak for ^6Li and H^{trans}, indicating scalar coupling between the involved nuclei. The cross peak intensities reflect the magnitude of the involved coupling constants. Hence, under the conditions of Figure 4 the relative magnitudes of Li,H coupling constants are $J(Li,H^{gem}) > J(Li,H^{trans}) > J(Li,H^{cis})$.

When the pulse width of the mixing pulse in the $^6Li,^1H$ FUCOUP experiment on **1** is set to 36°, the cross peak multiplet between Li and H^{trans} shows a detectable tilt (Figure 4f). The involved ^1H resonance lines are, expectedly, those which correspond to the passive coupling between H^{trans} and H^{gem}. The magnitude of the tilt (as deduced from ω_2 cross sections (Figure 4g)) is identical to a coupling constant of $^2J(^6Li,H^{gem}) = +0.4$ Hz.[37] This is similar to the number detected by Günther for $^2J(^6Li,^1H)$ in tetrameric methyllithium (0.34 Hz).[29] Due to the digital resolution in the ω_2 domain of Figure 4, we estimate the accuracy of our reported numbers to be ±0.2 Hz.

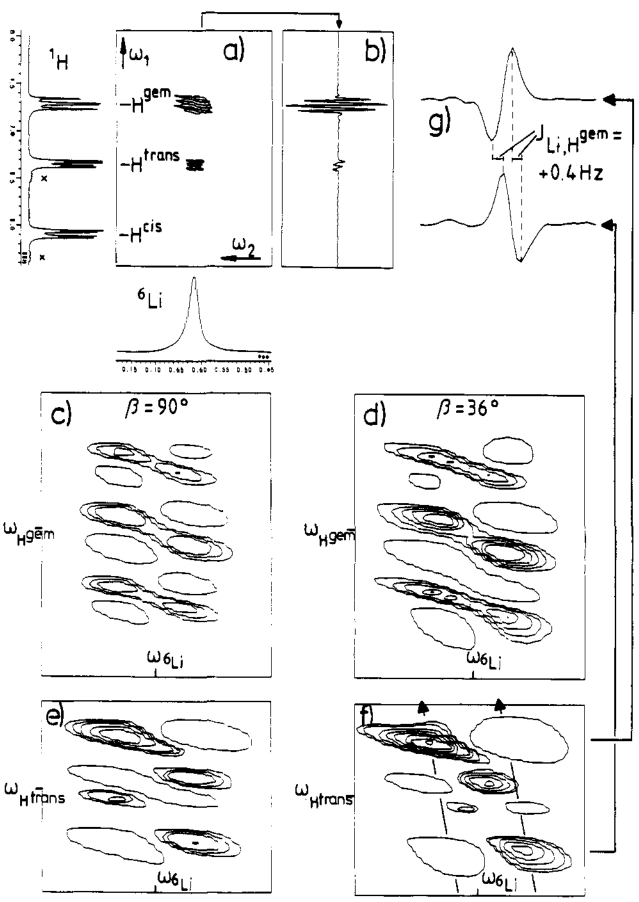

Figure 4. $^6Li,^1H$ FUCOUP spectra of the vinyllithium tetramer, 1.8 M, −90 °C, THF-d_8: (a) contour plot; the ω_2 domain (^6Li) is zoomed by a factor of 12.5 with respect to the spectral width; x = signals of the dimer; (b) ω_1 cross section cut at the position indicated in a; (c–f) zoomed cross peaks of H^{gem} and H^{trans}, respectively, with a mixing pulse flip angle of 90° (c, e) and 36° (d, f); positive cross peaks are drawn with more than one contour, whereas negative cross peaks are drawn with only one contour; (g) ω_2 cross sections of f cut at the indicated positions.

The sign of the coupling constant $^2J(^6Li,H^{gem})$ is deduced from the positive slope of the tilt in the cross peak multiplet of Figure 4f, which indicates *like* signs for $^3J(H^{gem},H^{trans})$ and $^2J(^6Li,H^{gem})$. Since H,H coupling constants of vicinal olefinic protons are positive throughout,[22] $^2J(^6Li,H^{gem})$ must likewise by *positive*.

An analogous tilt for the cross peak multiplet of H^{gem} (Figure 4d) due to coupling $^3J(^6Li,H^{trans})$ is not clearly resolvable. Thus, we estimate the involved coupling constant $^3J(^6Li,H^{trans})$ to be less than ca. 0.2 Hz.

An inherent problem of $^6Li,^1H$ β-FUCOUP is concerned with the obtainable line width of the ^6Li signal: since the cross peaks appear antiphase in ω_2, line widths larger than $J(^6Li,^1H)$ lead to partial cancellation and thus reduced sensitivity of the experiment.

When applied to *dimeric* vinyllithium, the $^6Li,^1H$ β-FUCOUP experiment reveals the spectra shown in Figure 5. Contrary to the observations made for the tetramer, the cross peak multiplet between ^6Li and H^{trans} is now more intense than between ^6Li and H^{gem}. Thus, the trans-vicinal coupling constant $^3J(^6Li,H^{trans})$

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(37) For a one-dimensional ^6Li NMR experiment with resolved $^6Li,^1H$ scalar coupling, it might correctly be anticipated that for tetrameric **1** the ^6Li signal splits into a *quartet* due to coupling with the three nearest H^{gem} nuclei. However, the observed tilt in Figure 4f is caused in a 2D experiment by the passive spin H^{trans} which "sees" only one coupling partner H^{gem}. Thus, the observed tilt is due to a doublet caused by coupling between lithium and a single H^{gem}.

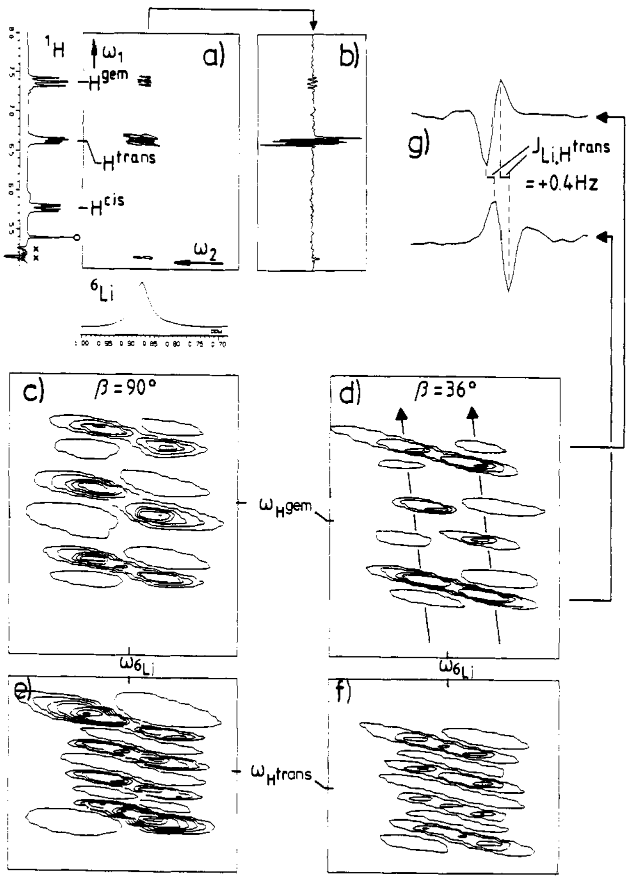

Figure 5. ^{6}Li,^{1}H FUCOUP spectra of the vinyllithium dimer, 1.9 M, −90 °C, THF-d_8, in the presence of 1 equiv of TMEDA. The ^{1}H signals of TMEDA are deliberately folded in and appear as downward signals in the one-dimensional ^{1}H spectrum at the low-frequency end: (a) contour plot; the ω_2 domain (^{6}Li) is zoomed by a factor of 12.5 with respect to the spectral width; o = ethylene; x = TMEDA signal; (b) ω_1 cross section cut at the position indicated in a; (c–f) zoomed cross peaks of H$^{\rm gem}$ and H$^{\rm trans}$, respectively, with a mixing pulse flip angle of 90° (c, e) and 36° (d, f); positive cross peaks are drawn with more than one contour, whereas negative cross peaks are drawn with only one contour; (g) ω_2 cross sections of d cut at the indicated positions.

must be larger than the geminal coupling constant, $^2J(^6{\rm Li},{\rm H^{gem}})$ under these conditions. As was the case for the tetramer, the cis-vicinal coupling constant, $^3J(^6{\rm Li},{\rm H^{cis}})$, must be vanishingly small in the dimer, indicated by the lack of an appropriate cross peak.

Small cross peaks are found between Li and the deliberately folded-in proton CH$_3$ signals of the chelate ligand, TMEDA. At present, it is not clear whether this is indicative of scalar $^3J(^6{\rm Li},{\rm NC}H_3)$ coupling or if this cross peak is an artifact. The applied phase cycle of the FUCOUP pulse sequence suppresses unwanted cross peaks due to heteronuclear Overhauser effects (HOESY).[1a,7,38,39] However, in a ^{6}Li,^{1}H FUCOUP experiment there is inherently no filter function in the ω_1 (^{1}H) evolution period which would reject the ^{1}H TMEDA signals that lie outside the measured ^{1}H spectral width. Since the ^{1}H TMEDA CH$_3$ signal is very intense, the cross peak between Li and NCH$_3$ might as well be a nonsufficiently suppressed HOESY artifact.

When the length of the FUCOUP mixing pulse is set to 36°, the spectra of Figure 5d,f are obtained for the vinyllithium dimer. As was the case for the tetramer under comparable conditions (Figure 4), tilted cross peaks are observed. However, since for the dimer $^3J(^6{\rm Li},{\rm H^{trans}})$ is larger than $^2J(^6{\rm Li},{\rm H^{gem}})$, a significant tilt is found in the ^{6}Li,H$^{\rm gem}$ cross peak multiplet (Figure 5d). As expected, the tilt involves the coupling H$^{\rm gem}$,H$^{\rm trans}$ of the ^{1}H resonance lines, whereas the lines of the coupling H$^{\rm gem}$,H$^{\rm cis}$ appear untilted. From the observed magnitude of the tilt, it is concluded that $^3J(^6{\rm Li},{\rm H^{trans}}) = 0.4 \pm 0.2$ Hz. As was the case for the tetramer, the slope of the observed tilt indicates that the signs of $^3J({\rm H^{gem}},{\rm H^{trans}})$ and $^3J(^6{\rm Li},{\rm H^{trans}})$ are alike. Since the homonuclear vicinal coupling constant is positive, $^3J(^6{\rm Li},{\rm H^{trans}})$ must be positive as well.

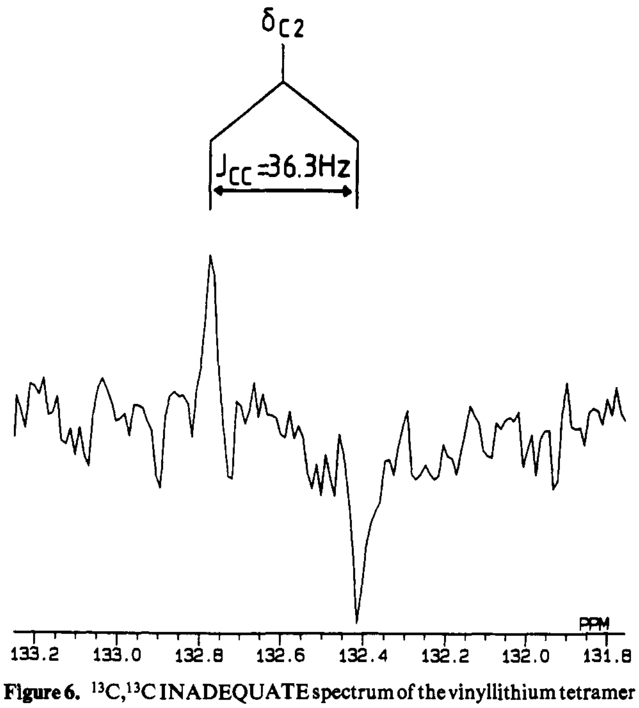

Figure 6. ^{13}C,^{13}C INADEQUATE spectrum of the vinyllithium tetramer in THF-d_8, 2.6 M, +30 °C. The zoomed signal of C2 is depicted.

^{13}C,^{13}C Coupling Constants. Carbon–carbon connectivities may be conveniently exploited by using the ^{13}C,^{13}C INADEQUATE technique in weakly coupled spin systems.[40–42] Applied to tetrameric vinyllithium in THF-d_8 at +30 °C, the INADEQUATE spectrum shown in Figure 6 is obtained for the ^{13}C signal of C2 in **1**. The antiphase doublet reveals $^1J({\rm C1},{\rm C2}) = 36.3$ Hz, which is extraordinarily small as compared to "normal" olefinic systems. This will be discussed below.

Under the conditions of Figure 6, the signal-to-noise ratio of the complementary carbon atom C1 is too low for proper analysis of $^1J({\rm C1},{\rm C2})$. Attempts to elucidate $^1J({\rm C1},{\rm C2})$ of the tetramer at low temperatures (<0 °C) within reasonable measuring times failed. This is due to signal intensity losses from increasing line broadening and splitting into the separate tetramer and dimer signals of **1** at low temperatures. In addition, **1** partly precipitates under these conditions.

The carbon–carbon coupling constant in the vinyllithium dimer was obtained for a 0.8 M solution of **1** at +37 °C in C$_6$D$_6$ in the presence of 1 equiv of TMEDA. From the ^{13}C chemical shifts (δ (C1) = 192.74; δ (C2) = 130.85), it may be concluded that **1** is a pure dimer under these conditions (cf. Table I). The magnitude of $^1J({\rm C1},{\rm C2})$ of dimeric **1** was derived from the separation of the ^{13}C satellites of the main signal of C2 in an ordinary ^{13}C{^{1}H} spectrum: $^1J({\rm C1},{\rm C2}) = 35.0$ Hz, i.e., slightly less (by 1.3 Hz) than the number found for the tetramer.

Sign Determination of $^1J(^{13}{\rm C1},^6{\rm Li})$ and Alternative Determination of $J(^6{\rm Li},^1{\rm H})$. Carbon-lithium coupling constants have been observed now in numerous cases, preferably at low temperatures.[1] They have been used to characterize the aggregate state of

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[42] Buddrus, J.; Bauer, H. *Angew. Chem.* **1987**, *99*, 642; *Angew. Chem., Int. Ed. Engl.* **1897**, *26*, 625.

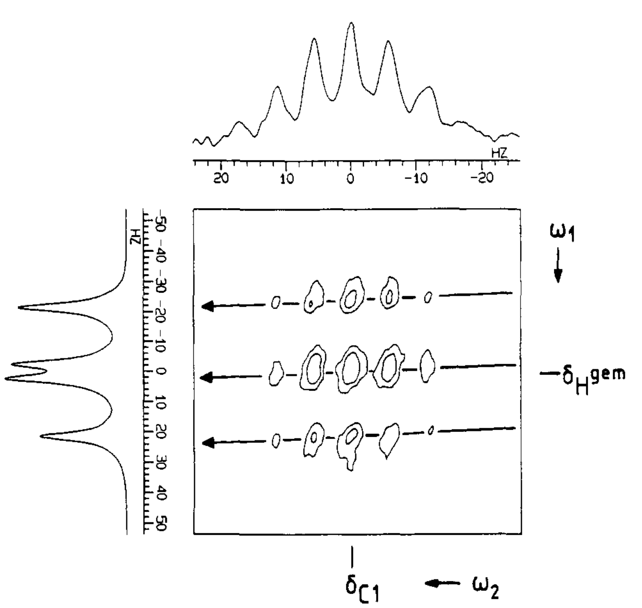

Figure 7. ^{13}C,^{1}H HETCOR spectrum between H^{gem} and C1 of tetrameric vinyllithium (**1**) 1.3 M in THF-d_8, at −100 °C.

organolithium compounds. Their usage for the identification of dimeric and tetrameric vinyllithium has been described above. However, to our knowledge, there is no unambiguous determintion of the *sign* of the carbon–lithium coupling constants described in the literature.

A skillful means for obtaining the sign of $^{1}J(^{13}C,^{6}Li)$ is provided by polarization transfer methods. Consider the spin system H^{gem}–C1–Li in vinyllithium (**1**). As is known from the results described above, there is mutual coupling of all three nuclei (albeit the magnitude of $^{2}J(^{6}Li,H^{gem})$ in tetrameric vinyllithium is quite small (0.4 Hz)). This may be exploited in a heteronuclear 2D NMR experiment to extract the sign of $^{1}J(^{13}C,^{6}Li)$. A prerequisite to this approach is a sufficiently long spin lattice relaxation time of ^{6}Li as well as slow chemical lithium exchange.

In a conventional ^{13}C, ^{1}H shift correlation experiment on the claimed three-spin system, the ^{6}Li nucleus is the passive spin, which does not change its spin state during the course of the pulse sequence. Thus, cross peaks in a ^{13}C,^{1}H shift correlation experiment are observed only between directly connected transitions, and a tilt is introduced in the cross peak multiplet. The angle of the tilt is indicative of the relative signs of the coupling constants between the active and the passive spins. This is similar to the β-FUCOUP experiment described above for the determination of $^{2,3}J(^{6}Li,^{1}H)$ in **1**. Much use of this technique has been made by Wrackmeyer et al. for the extraction of the relative signs of coupling constants in systems containing three different isotopes.[43]

Figure 7 shows a proton–carbon shift correlation spectrum between H^{gem} and C1 of tetrameric **1** under the conditions of slow lithium exchange. The spectrum was recorded with ^{13}C decoupling during ω_1 and ^{1}H decoupling during ω_2. The splitting observed in ω_1 (^{1}H) is due to the coupling constants $^{3}J(H^{gem},H^{trans})$ and $^{3}J(H^{gem},H^{cis})$. The splitting observed in ω_2 (^{13}C) is due to the coupling constant $^{1}J(^{13}C1,^{6}Li)$. The coupling constant $^{2}J(^{6}Li,H^{gem})$ is not resolved in the one-dimensional ^{1}H spectrum in Figure 7. However, a slight, albeit detectable, tilt of the cross peak multiplet contours as indicated is observed in Figure 7. From the slope of the tilt, it may be extrapolated that the "passive" coupling constants, $^{2}J(^{6}Li,H^{gem})$ and $^{1}J(C1,^{6}Li)$, have *like* signs. As was concluded above, the sign of $^{2}J(^{6}Li,H^{gem})$ in tetrameric **1** is *positive*. Hence, $^{1}J(C1,^{6}Li)$ must be *positive* as well. Though not measured explicitly, it is reasonable to assume that the same holds for $^{1}J(C1,^{6}Li)$ in the vinyllithium dimer.

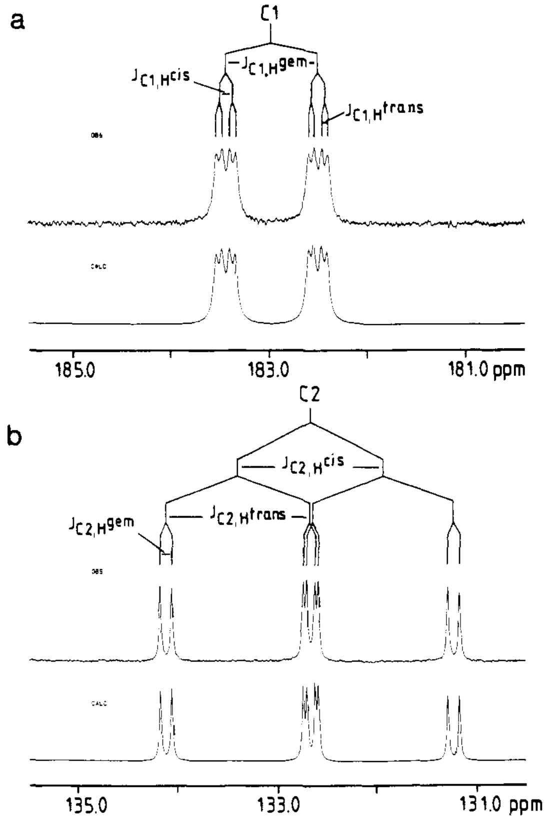

Figure 8. Gated decoupled ^{13}C NMR spectrum of the vinyllithium tetramer, 2.6 M, in THF-d_8 at +30 °C (top) and simulated spectrum by using the coupling constants obtained from first-order analysis (bottom): (a) signal of C1, Lorentzian line width of simulation = 6.0 Hz; (b) signal of C2, Lorentzian line width of simulation = 2.3 Hz.

In Figure 7, the cross peaks relevant to the outermost signals of the ^{13}C septet are not visible due to their low intensity. However, their position on the indicated tilt axis may be easily reconstructed. The displacement in ω_1 of these outermost cross signals is 3.8 Hz. This corresponds to the *sum* of the coupling constants of H^{gem} with all ^{6}Li coupling partners. Provided that there is equal coupling between a given H^{gem} and its three ^{6}Li neighbors, this corresponds (due to spin $I(^{6}Li) = 1$) to $^{2}J(^{6}Li,H^{gem}) = 3.8/6 = 0.6$ Hz. This number is different from the number found by ^{6}Li,^{1}H β-FUCOUP (0.4 Hz, see above). The discrepancy might be attributed to limited digital resolution in the spectra of Figures 4 and 7. In addition, the recording temperatures are slightly different (Figure 4, −90 °C; Figure 7, −100 °C).

Sign and Magnitude of One- and Two-Bond ^{13}C, ^{1}H Coupling Constants in Vinyllithium. The determination of the magnitude of ^{13}C,^{1}H coupling constants may be easily achieved by recording ^{1}H-coupled ^{13}C NMR spectra ("gated decoupling" technique). This is shown in Figure 8 for tetrameric vinyllithium (**1**) in THF-d_8 at +30 °C, i.e., under conditions of rapid metal exchange. In addition, Figure 8 shows simulated spectra of the ^{1}H-coupled ^{13}C NMR signals of vinyllithium.

The input parameters employed for the simulated spectra in Figure 8 were obtained from first-order analysis of the ^{13}C spectrum. As is obvious, despite neglect of the principally indicated higher order analysis, matching of the experimental and the calculated spectra is excellent. This is due to the reasonably large chemical shift differences of the ^{13}C satellites in the ^{1}H NMR spectrum of **1** at the employed field strength.[44]

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[43] (a) Wrackmeyer, B.; Horchler, K. *Magn. Reson. Chem.* **1990**, *28*, 56. (b) Wrackmeyer, B.; Zhou, H. *Magn. Reson. Chem.* **1990**, *28*, 1066. (c) Kupče, Ē.; Wrackmeyer, B. *Magn. Reson. Chem.* **1991**, *29*, 351. (d) Kupče, Ē.; Wrackmeyer, B. *J. Magn. Reson.* **1992**, *91*, 343. (e) Kupče, Ē.; Wrackmeyer, B. *J. Magn. Reson.* **1992**, *97*, 568. (f) Wrackmeyer, B.; Schiller, J. *Z. Naturforsch.* **1992**, *47b*, 662.

The signal of C1 is split into a doublet of a doublet of doublets, $|J|$ = 93.2, 13.5, and 6.1 Hz, due to coupling with H^{gem}, H^{cis}, and H^{trans}, respectively. Our number found for $^{1}J(C1,H^{gem})$ differs slightly from the data reported by van Dongen et al.[6] (J = 88 Hz). The nontrivial assignment of the two coupling constants, $^{2}J(C1,H^{cis})$ and $^{2}J(C1,H^{trans})$, was achieved by a ^{13}C,^{1}H FUCOUP experiment (^{13}C,^{1}H shift correlation without decoupling during ω_1 and ω_2; see previous sections and Figure 9). The signal of C2 in Figure 8 is split into a doublet of a doublet of doublets with $|J|$ = 146.8, 143.5, and 12.1 Hz, respectively. Whereas it is evident that the 12.1-Hz splitting results from C2,H^{gem} coupling in **1**, the 146.8- and 143.5-Hz couplings were assigned by ^{13}C,^{1}H FUCOUP to be due to $^{1}J(C2,H^{cis})$ and $^{1}J(C2,H^{trans})$, respectively (cf Figure 9). Van Dongen et al.[6] report 149 and 145 Hz for the same data, however, without assignment to H^{cis} and H^{trans}.

Principally, the relative signs of the determined ^{13}C,^{1}H coupling constants may be extracted from higher order spectra.[45] By neglecting the metal nucleus in **1**, a ^{13}C vinyllithium isotopomer consists of an ABCX spin system. However, at the field strength employed for our measurement (9.4 T), first-order spectra are observed. These are insensitive to the sign of the carbon–proton coupling constants. This has been verified in the present case: simulation of the spectrum shown in Figure 8 with positive and negative $^{2}J(C2,H^{gem})$ coupling constants leads to completely identical results.

An alternative approach to the determination of the sign of ^{13}C,^{1}H coupling constants is provided by 2D NMR. ^{13}C,^{1}H shift correlation without decoupling in ω_1 and ω_2 and with a small ^{1}H mixing pulse flip angle (β-FUCOUP) may be employed for this purpose. By using the same fundamentals as employed for the determination of the sign of $J(^{1}H,^{6}Li)$ in **1** (see above), the sign of the direct (^{1}J) and of the geminal (^{2}J)^{1}H,^{13}C coupling constants may be derived. Whereas direct ^{13}C,^{1}H coupling constants have been found to be generally positive,[45] both positive and negative numbers are found for geminal (^{2}J)^{13}C,^{1}H coupling constants, depending on the type of molecule involved.[45]

Figure 9 shows a ^{13}C,^{1}H β-FUCOUP spectrum of the vinyllithium dimer in the presence of TMEDA and in toluene-d_8 solution at +27 °C. Pulse sequence 2 with $I = {}^{1}H$ and $S = {}^{13}C$ was employed, with a mixing pulse flip angle of $\phi = 45°$. The skewed arrows in Figure 9 indicate the tilts within the cross peak multiplets. These are due to coherence transfer only between directly connected transitions where the spin states of the passive nuclei remain unchanged.

In Figure 9a, the cross peak multiplet between C1 and H^{gem} reveals two passive couplings with opposite tilts. From the cross peaks C1,H^{trans} and C1,H^{cis}, it becomes clear that the smaller geminal C,H coupling constant is associated with H^{trans} and the larger one with H^{cis}. The tilt in the C1,H^{gem} cross peak due to passive C1,H^{trans} coupling is negative. This indicates that the coupling constants involved, $^{2}J(C1,H^{trans})$ and $^{3}J(H^{gem},H^{trans})$, have ***unlike*** signs. Since the vicinal "key" coupling constant, $^{3}J(H^{gem},H^{trans})$, is positive throughout,[46] $^{2}J(C1,H)^{trans})$ must be ***negative***. By analogy, the positive tilt in the C1,H^{gem} cross peak multiplet due to passive C1,H^{cis} coupling indicates ***like*** signs of $^{2}J(C1,H^{cis})$ and $^{3}J(H^{gem},H^{cis})$. Consequently, since $^{3}J(H^{gem},H^{cis})$ is positive, $^{2}J(C1,H^{cis})$ must be ***positive*** as well.

Similar conclusions, i.e., negative $^{2}J(C1,H^{trans})$ and positive $^{2}J(C1,H^{cis})$, may be drawn from inspection of the C1,H^{trans} and C1,H^{cis} cross peak multiplets: the indicated positive tilt in the C1,H^{trans} cross peak multiplet indicates ***like*** signs of $^{2}J(C1,H^{cis})$ and $^{2}J(H^{trans},H^{cis})$. As was deduced above, $^{2}J(H^{trans},H^{cis})$ is positive. Consequently, $^{2}J(C1,H^{cis})$ must be ***positive*** as well.

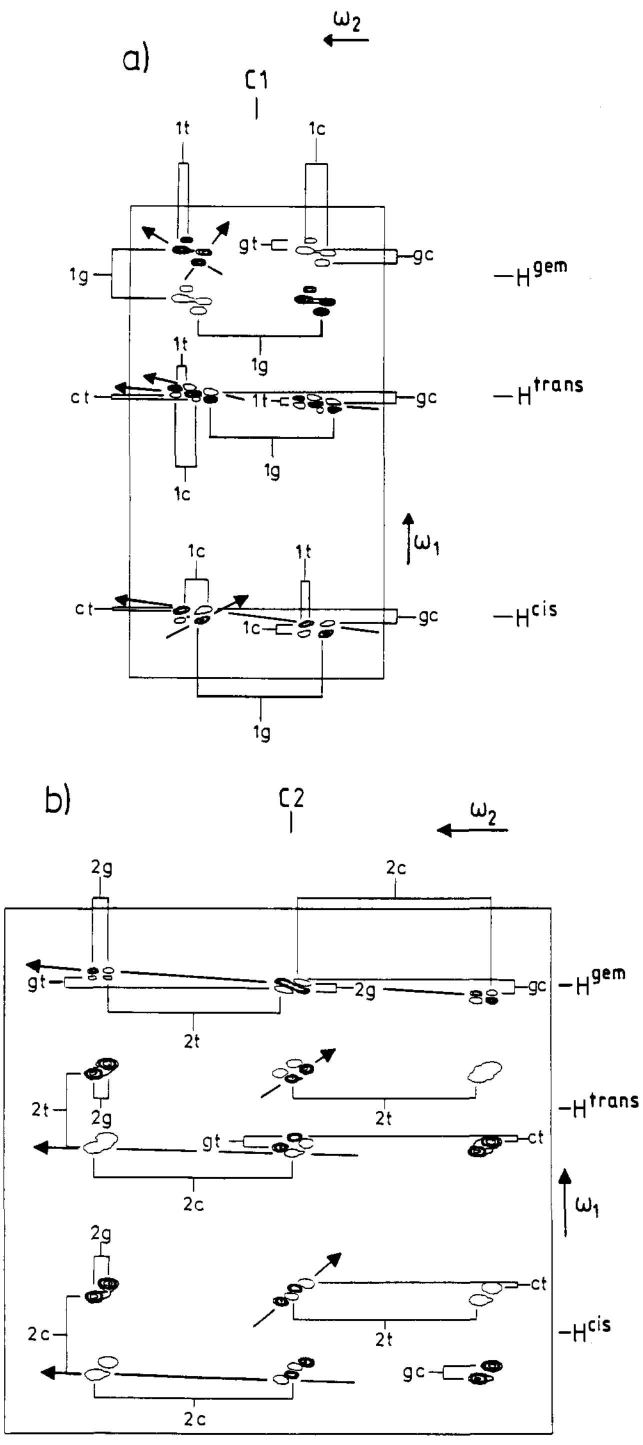

Figure 9. ^{13}C,^{1}H β-FUCOUP spectrum of the vinyllithium dimer, 1.4 M in toluene-d_8, +27 °C, in the presence of 1.9 equiv of TMEDA, ^{1}H mixing pulse angle Φ = 45°. Positive peaks are drawn with more than one contour, whereas negative peaks are drawn with only one contour. Numbers 1 and 2 denote carbon atoms C1 and C2, and letters c, g, and t denote hydrogen atoms H^{cis}, H^{gem}, and H^{trans}, respectively. Combinations of these numbers and/or letters indicate the appropriate scalar couplings: (a) cross peak pattern of C1; the contours of the weak signals which involve H^{trans} are cut at a 5-fold-lower level than the contours which involve H^{gem} and H^{cis}; (b) cross peak pattern of C2, drawn at the same horizontal and vertical scale as in a; the contour levels are cut at a level lower by a factor of 1.7 as compared to a.

Likewise, the observed tilt in the C1,H^{cis} cross peak multiplet is negative (unlike signs of $^{2}J(C1,H^{trans})$ and $^{2}J(H^{trans},H^{cis})$), indicating a ***negative*** coupling constant, $^{2}J(C1,H^{trans})$.

Figure 9b shows the cross peak multiplet which involves C2. The C2,H^{gem} cross peak shows a positive tilt, which indicates that

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(44) See, however, the general discussion on the analysis of the higher order ^{1}H-coupled ^{13}C NMR spectra in ref 45.

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Table I. Summary of Chemical Shifts (Diagonal, δ, ppm) and Coupling Constants (Off-Diagonal, Hz) in Dimeric Vinyllithium

	Li	C1	C2	H^{gem}	H^{trans}	H^{cis}
Li	$0.86^{b,c}$	$+8.3^{a}$ $+8.3^{b}$	$<\|0.5\|^{b}$	$<\|0.2\|^{b}$	$+0.4^{b}$	$<\|0.1\|^{b}$
C1		190.81^{a} $192.64^{b,c}$	$+35.0^{d}$	$+93.0^{a}$ $+92.0^{b}$ $+91.7^{d}$	-5.9^{a}	$+13.5^{d}$
C2			128.86^{a} $130.88^{b,c}$	-10.7^{a} -10.7^{b} -10.5^{d}	$+138.0^{b}$ $+140.0^{d}$	$+148.0^{b}$ $+146.3^{d}$
H^{gem}				7.29^{a} $7.38^{b,c}$	$+18.6^{a}$ $+18.3^{b}$	$+23.9^{a}$ $+23.2^{b}$
H^{trans}					6.50^{a} $6.63^{b,c}$	$+8.8^{a}$ $+8.5^{b}$
H^{cis}						5.66^{a} $5.74^{b,c}$

[a] In THF–d_8 at –90 °C, concentration = 2.0 M. [b] In THF-d_8 with an additional 1 equiv of TMEDA at –80 °C. [c] Concentration = 2.0 M. [d] In C_6D_6 with 1.5 equiv of TMEDA at +37 °C, concentration = 3.4 M.

Table II. Summary of Chemical Shifts (Diagonal, δ, ppm) and Coupling Constants (Off-Diagonal, Hz) in Tetrameric Vinyllithium

	Li	C1	C2	H^{gem}	H^{trans}	H^{cis}
Li	$0.62^{b,e}$	$+5.9^{a}$ $+4.4^{b}$	$<\|0.5\|^{a}$	$+0.4^{a}$	$<\|0.1\|^{a}$	$<\|0.1\|^{a}$
C1		$183.00^{a,d}$ 183.78^{c}	$+36.3^{c}$	$+94.6^{a}$ $+93.2^{c}$	-6.1^{c}	$+13.5^{c}$
C2			$132.69^{a,d}$ 132.58^{c}	-10.7^{a} -12.1^{c}	$+145.2^{a}$ $+143.5^{c}$	$+145.2^{a}$ $+146.8^{c}$
H^{gem}				$7.29^{a,d}$	$+19.0^{a}$	$+23.8^{a}$
H^{trans}					$6.65^{a,d}$	$+7.4^{a}$
H^{cis}						$5.91^{a,d}$

[a] Static aggregate at –90 °C in THF-d_8. [b] Fluxional aggregate at –60 °C in THF-d_8. [c] At +30 °C in THF-d_8, concentration = 2.3 M. [d] Concentration = 2.0 M. [d] Concentration = 1.6 M.

the signs of $^{1}J(\mathrm{C2,H^{trans}})$ and $^{3}J(\mathrm{H^{gem},H^{trans}})$ are alike. Since the vicinal $^{3}J(\mathrm{H^{gem},H^{trans}})$ coupling constant is positive, $^{1}J(\mathrm{C2,H^{trans}})$ must have the expected positive sign. Similar conclusions may be drawn for the positive coupling constant $^{1}J(\mathrm{C2,H^{cis}})$.

In the C2,H^{trans} cross peak multiplet of Figure 9b, a negative tilt it observed between the passive couplings $^{2}J(\mathrm{C2,H^{gem}})$ and $^{3}J(\mathrm{H^{gem},H^{trans}})$ (unlike signs). With the given positive vicinal coupling constant $^{3}J(\mathrm{H^{gem},H^{trans}})$, this indicates a *negative* geminal coupling constant $^{2}J(\mathrm{C2,H^{gem}})$. Identical conclusions may be drawn from the C2,H^{cis} cross peak multiplet, where the negative tilt indicates unlike signs of $^{2}J(\mathrm{C2,H^{gem}})$ and $^{3}J(\mathrm{H^{gem},H^{cis}})$, with consequently *negative* $^{2}J(\mathrm{C2,H^{gem}})$.

Summary of Chemical Shifts and Spin-Spin Coupling Constants. Tables I and II give an overview of the chemical shifts and coupling constants in dimeric and tetrameric vinyllithium, as derived in the previous sections. Diagonal numbers indicate chemical shifts, whereas off-diagonal elements represent coupling constants.

In some cases, different numbers are given in Tables I and II for a distinct chemical shift or coupling constant. These have been obtained under different conditions (temperature, solvent, ligand), as is indicated by appropriate footnotes.

Discussion

^{13}C Chemical Shifts. The chemical shift of C1 in tetrameric vinyllithium (δ = 183.00 ppm) is larger by 59.5 ppm than the number found for ethylene (δ = 123.5 ppm[45]). Such drastic downfield shifts are generally observed for lithiated sp^2 carbon atoms[1i] and may be attributed to the paramagnetic term, σ_{para}, in the ^{13}C shielding constant.[47] The term σ_{para} is inversely proportional to the mean excitation energy, ΔE, for magnetic mixing of electronic ground states and $n \rightarrow \pi^*$ excited states.[48] A detailed study of this phenomenon on phenyllithium was provided by Jones et al.[49] The more ionic the bond, the smaller ΔE and the larger the contribution of σ_{para} to the ^{13}C chemical shift. Obviously, ΔE must be smaller in vinyllithium as compared to ethylene. This correlates with a bathochromic shift in the UV spectrum of vinyllithium (λ_{max} = 280 nm in THF[50]) as compared to ethylene (λ_{max} = 198 nm, gaseous[51]).

Table III. Ab Initio Calculated Numbers (6-31++G** Basis Set) of s-Character and of Covalent Bond Order in Aliphatic, Olefinic, and Acetylenic Organolithium Compounds, as Well as Their Products[55]

species	C–Li covalent bond order	% s-character of carbon	product (covalent bond order × % s)
CH_3Li	0.144	19	2.7
$CH_2{=}CHLi$	0.099	28	2.8
$HC{\equiv}CLi$	0.046	52	2.4

The lithiated carbon atom of dimeric **1** with TMEDA as a ligand resonates at even lower field (δ = 192.64 ppm). This nearly 10 ppm downfield shift as compared to the tetramer is similar to the situation found in phenyllithium (see Results section above). For phenyllithium, the downfield shift of C1 with decreasing aggregate size correlates with a decrease of the C1, Li bond distance (tetramer, r(C1,Li) = 2.33 Å;[52] dimer, r(C1,Li) = 2.24 Å;[53] monomer, r(C1,Li) = 2.14 Å[54]). We assume that the same holds for vinyllithium, i.e., a shorter C1, Li bond distance is expected for the dimer as compared to the tetramer. In the latter aggregate, r(C1,Li) is 2.26 Å.[7] The chemical shift of C1 in dimeric **1** is additionally dependent on the ligand: with THF instead of TMEDA, a slightly different number is found (δ = 190.81 ppm).

^{13}C,^{6}Li Coupling Constants and Residual Dynamics in a "Static" Tetramer. It has been found empirically[1a] that $^{1}J(^{13}\mathrm{C},^{6}\mathrm{Li})$ coupling constants obey the rule expressed in eq 3,

$$^{1}J(^{13}\mathrm{C},^{6}\mathrm{Li}) = 17/n \text{ Hz} \tag{3}$$

where n is the number of lithium atoms bound directly to a carbon atom in terms of the NMR time scale. Thus, for dimers, static tetramers, and fluxional tetramers, the numbers 8.5, 5.7, and 4.3 Hz are expected, respectively. The experimentally found relevant numbers for **1** agree (J = 8.3, 5.9, and 4.4 Hz, respectively; see Tables I and II).

Curiously, in all cases known so far, $^{1}J(^{13}\mathrm{C},^{6}\mathrm{Li})$ is virtually independent of the hybridization of the lithiated carbon atom, i.e., aliphatic, olefinic, and acetylenic species give identical ^{13}C,^{6}Li coupling constants, provided that the aggregate sizes are identical. This enigma seems to have been solved recently by high-level ab initio calculations:[55] on going from aliphatic to acetylenic organolithium compounds, the s-character of the C, Li bond *increases* in the same way as is found for C, H bonds. However, whereas the covalency of a C, H bond is virtually independent of the C-hybridization, the covalent character of the C, Li bond *decreases* on going from aliphatic to acetylenic species. The product (s-character × covalent bond order; Table III) is approximately constant for C, Li bonds, which explains the observed insensitivity of $^{1}J(^{13}\mathrm{C},^{6}\mathrm{Li})$ on carbon hybridization.

The coupling constant between C2 and the metal in vinyllithium must be below ca. 0.5 Hz (no splitting is observed for the ^{13}C NMR signal of C2 under slow metal exchange conditions). To our knowledge, no ^{13}C,^{6}Li coupling constants across more than one bond have been reported as yet. This agrees with the general

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observation that ${}^2J({}^{13}C,{}^1H)$ and ${}^3J({}^{13}C,{}^1H)$ coupling constants are smaller by a factor of 10–20 as compared to ${}^1J({}^{13}C,{}^1H)$.[45]

For the first time, the sign of ${}^1J({}^{13}C,{}^6Li)$ has been determined in this work to be *positive*. Since the magnetogyric ratios of both ${}^{13}C$ and ${}^6Li$ are positive, the reduced coupling constant,[45] ${}^1K({}^{13}C, {}^6Li)$, must be positive as well. This agrees with reduced coupling constants between ${}^{13}C$ and other main group metal isotopes, which are reported to be predominately positive.[45]

The ${}^{13}C,{}^6Li$ coupling pattern of the "static" tetramer in Figure 3a suggests that there is *identical* coupling between C1 and its nearest Li coupling partners. However, this is incompatible with an entirely static tetramer as indicated by the X-ray structure (Figure 1), which correctly predicts only identical chemical shifts for the monomeric ViLi units due to the S_4 symmetry of the molecule. With respect to Figure 1, different coupling constants may be expected between C(1) and Li(1), Li(1a), and Li(1b). Thus, either the differences in the coupling constants involved are too small to be resolved in Figure 3a or a still rapid dynamic process averages the nearest lithium positions. This process might be a "tumbling" of a monomer ViLi unit around an axis which extends diagonally through a vinyllithium tetramer cube (i.e., rotation of C(1)–C(2) around axis C(1)–Li(1c) in Figure 1). In addition, this process might proceed symmetry correlated between all monomer units. In that case, the involved exchange rates might as well be slow ($\tau_c \approx 1/J$). At present, we believe that the latter dynamic process is responsible for the observed equivalence of all C,Li coupling constants in the "static" ViLi tetramer.

${}^{13}C,{}^{13}C$ Coupling Constants. The ${}^{13}C,{}^{13}C$ coupling constants in dimeric ($J = 35.0$ Hz) and tetrameric ($J = 36.3$ Hz) vinyllithium are the smallest ones reported so far for monosubstituted olefins. Actually, these numbers are similar to numbers generally found for C, C *single* bonds.[45] A comparably low coupling constant, ${}^1J(C1,C2) = 27.8$ Hz, has been observed recently for phenyllithium.[16] Some further characteristic data for ${}^1J(C,C)$ in olefins are ethylene, 67.6 Hz;[57] methacrylic acid, 70.5 Hz;[58] and 2-chloropropene, 80.8 Hz.[58]

For hydrocarbons, the magnitude of ${}^1J(C_A,C_B)$ is correlated with the fractional s-character of C_A and C_B according to eq 4.[59]

$$ {}^1J(C_A,C_B) = ks_As_B + c \tag{4} $$

Whereas for C,H coupling constants the Fermi contact mechanism (J^{FC}) is considered to be effective exclusively,[45] the orbital–dipole (J^{OD}) and spin–dipole (J^{SD}) mechanisms may be effective for C,C coupling constants as well.[60] This may lead to deviations from the simple relationship of eq 4. Likewise, inductive effects must be considered in substituted systems as well.[61]

It is known that ${}^1J({}^{13}C,{}^{13}C)$ in olefinic and aromatic systems decreases with increasing electropositive character of the substituent.[45] A linear correlation between ${}^1J({}^{13}C,{}^{13}C)$ and the π bond order in substituted benzenoid hydrocarbons has been reported.[62,63] According to these data, the π bond order in vinyllithium should be extraordinarily small. This correlates with the C, C bond length found by X-ray analysis for tetrameric **1** (r(C,C) = 1.41 Å[7]), which is considerably longer than in ethylene (r(C,C) = 1.33 Å[64]). The slightly smaller ${}^{13}C,{}^{13}C$ coupling constant in dimeric (35.0 Hz) as compared to tetrameric (36.3 Hz) vinyllithium might be indicative of a somewhat longer C, C bond to the former aggregate. This has yet to be justified by X-ray analysis.

${}^6Li,{}^1H$ Coupling Constants. For tetrameric vinyllithium, the geminal ${}^2J({}^6Li,{}^1H^{gem})$ coupling constant was determined in this work by ${}^6Li,{}^1H$ β-FUCOUP to be very small (+0.4 Hz). An even smaller vicinal coupling constant, ${}^3J({}^6Li,{}^1H^{trans})$, was indicated by the appearance of appropriate weaker cross peaks (Figure 4). The lack of a cross peak in Figure 4 which involves H^{cis} showed that ${}^3J({}^6Li,H^{cis})$ must be vanishingly small.

The determined coupling constant ${}^2J({}^6Li, H^{gem})$ may be compared to the geminal ${}^1H,{}^1H$ coupling constant in ethylene ($J = +2.3$ Hz[65]). After correction by a factor of $\gamma({}^6Li)/\gamma({}^1H) = 0.147$, a "reduced" ${}^1H,{}^1H$ coupling constant of 0.4 Hz would result for ethylene. This is identical to the number found for ${}^2J({}^6Li,H^{gem})$ in the vinyllithium tetramer. However, the similarity should not be taken as indicative of a high degree of covalent lithium–carbon bond order in vinyllithium. This becomes obvious from the observations made for dimeric vinyllithium: here, the largest ${}^6Li,{}^1H$ coupling constant involves H^{trans} rather than H^{gem}. By using ${}^6Li,{}^1H$ β-FUCOUP, the sign and magnitude of ${}^3J({}^6Li,H^{trans})$ were found to be +0.4 Hz. In ethylene, the trans-vicinal ${}^1H,{}^1H$ coupling constant is 19.1 Hz,[65] equivalent to a "reduced" coupling constant of 2.8 Hz (via multiplication by 0.147; see above). This number is considerably larger than ${}^3J({}^6Li,H^{trans})$ observed in dimeric vinyllithium.

The results obtained by ${}^6Li,{}^1H$ β-FUCOUP (Figure 4) support the earlier assumption that in a "static" tetramer a still rapid dynamic process (which might as well be slow in the case of symmetry-correlated motion of the monomeric units) must average the nearest three lithium coupling partners of a given H^{gem}. In Figure 4g, the ω_2 cross section shows only one antiphase signal. In the case of a completely static tetramer (as in the X-ray structure, Figure 1), splitting due to three different Li,H^{gem} couplings should be observed.

It is not clear why in the case of the dimer the trans-vicinal Li,H coupling constant is larger than ${}^2J(Li,H^{gem})$ whereas the opposite situation is found in tetrameric **1**. Apparently, this is due to the different geometrical arrangements of the lithium atoms around C1 in dimeric and tetrameric vinyllithium. Attempts to rationalize the determined Li,H coupling constants by INDO[66] calculations failed. MNDO-optimized geometries of the tetramer and the dimer as well as the usual lithium parametrization[67] were employed for these calculations.

We speculate that the mechanism of the ${}^6Li,{}^1H$ coupling is not much different from that of ${}^1H,{}^1H$ and ${}^{13}C,{}^1H$ coupling in ethylene, i.e., the Fermi contact term (J^{FC}) should be dominant over the orbital (J^{OD}) and the dipolar (J^{SD}) terms.[68] An alternative "through space" mechanism[69] may be ruled out: whereas the remote hydrogen H^{trans} reveals Li,H coupling in the tetramer and the dimer, no such coupling is observed for the spatially close hydrogen atom, H^{cis}, in both aggregates.

${}^1H,{}^1H$ Coupling Constants. Generally, in monosubstituted vinyl compounds, the geminal coupling constant, ${}^2J(H^{trans},H^{cis})$, increases with lower electronegativity of the substituent (vinyl chloride, −1.4 Hz;[46] ethylene, +2.3 Hz[65]). For vinyllithium, the reported number of ${}^2J(H^{trans},H^{cis}) = +7.1$ Hz[3] obviously refers to the *tetrameric* aggregate since it coincides with our number found for the tetramer (+7.4 Hz). By contrast, our analogous number found for the dimer is even higher (+8.8 Hz).

A decrease in the number of cis- and trans-vicinal H,H coupling constants has been generally found with increasing electronegativity of the substituent in monosubstituted vinyl compounds.[46] Thus, the vicinal cis/trans coupling constants are 4.7/12.8 Hz in vinyl fluoride,[70] 11.6/19.1 Hz in ethylene,[65] and 14.7/20.4 Hz

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in vinyltrimethylsilane.[71] As expected, this trend continues for vinyllithium (dimer, 18.6/23.9 Hz; tetramer, 19.0/23.8 Hz). By using Pauling's electronegativity scale, these data fit reasonably well into the empirical correlations[22] given for monosubstituted ethylenes in eqs 5 and 6.

Therein, E is the electronegativity number, and $\Delta E = E(\mathrm{X}) - E(\mathrm{H})$.

$$^{3}J_{\mathrm{cis}} = 11.7 - 4.7\Delta E \qquad (5)$$

$$^{3}J_{\mathrm{trans}} = 19.0 - 3.3\Delta E \qquad (6)$$

^{13}C,^{1}H Coupling Constants. a. Direct (^{1}J) Coupling Constants. For vinyllithium (**1**), the magnitude of $^{1}J(\mathrm{C1,H^{gem}})$ is extremely low (dimer, 91.7 Hz; tetramer, 93.2 Hz). To our knowledge, these numbers are the smallest ones reported so far for monosubstituted olefins. They are even smaller than the numbers found for sp^3 carbon atoms (ethane, $^{1}J_{\mathrm{C,H}} = 124.9$ Hz[45]). As was found for $^{1}J(\mathrm{C,C})$ in monosubstituted benzenes,[57,58,72] $^{1}J(\mathrm{C1,H^{gem}})$ decreases in monosubstituted ethylenes with decreasing electronegativity of the substituent at the carbon atom under consideration. Some typical numbers[73] of $^{1}J(\mathrm{C1,H^{gem}})$ in monosubstituted ethylenes are 200.2 (vinyl fluoride), 190.9 (vinyl iodide), 176.7 (acrylonitrile), 162.3 (acrolein), and 140.3 Hz (tetravinylsilane).

It is well-known that in hydrocarbons the magnitude of $^{1}J(\mathrm{C,H})$ depends on the s-character of the C, H bond (% s = 0.2(^{1}J(C,H))[45]). However, the extension of this simple rule to *substituted* systems has been criticized. The decrease in $^{1}J(\mathrm{C1,H^{gem}})$ of monosubstituted olefins with dereasing electronegativity of the substituent was claimed to be ascribable to inductive effects.[61] Recent high-level ab initio calculations[74] show that the former simple "% s" approach may be valid for substituted olefins, provided that the C, H bond order is taken into account as well.

Albeit much weaker, an analogous substituent effect is found for the magnitude of the $^{1}J(\mathrm{C2,H^{trans}})$ and $^{1}J(\mathrm{C2,H^{cis}})$ coupling constants in monosubstituted ethylenes. Thus, $^{1}J(\mathrm{C2,H^{trans}})$/$^{1}J(\mathrm{C2,H^{cis}})$ are 162.2/159.2 Hz (vinyl fluoride) and 156.1/156.5 Hz (tetravinylsilane).[45] Again, our observed numbers for dimeric **1** ($^{1}J(\mathrm{C2,H^{trans}}) = 138.0$ Hz; $^{1}J(\mathrm{C2,H^{cis}}) = 148.0$ Hz) are the lowest numbers reported so far for monosubstituted ethylenes.

It has been claimed (from the analysis of vicinal ^{1}H,^{1}H coupling constants[22]) that in monosubstituted ethylenes, the substituent exerts a larger influence on H$^{\mathrm{trans}}$ than on H$^{\mathrm{cis}}$. This is reflected in the C,H coupling constants observed for vinyllithium: $^{1}J(\mathrm{C2,H^{trans}})$ is considerably *smaller* (up to 10 Hz, depending on conditions; see Tables I and II) than $^{1}J(\mathrm{C2,H^{cis}})$. By contrast, in vinyl fluoride $^{1}J(\mathrm{C2,H^{trans}})$ is *larger* than $^{1}J(\mathrm{C2,H^{cis}})$; see numbers given above.

b. Geminal (^{2}J) Coupling Constants. The magnitude of geminal (^{2}J) C,H coupling constants in monosubstituted ethylenes exhibits a strong dependence on the substituent. This is exemplified in Table IV. All our numbers determined for $^{2}J(\mathrm{C,H})$ in vinyllithium are at the extreme ends in Table IV. The geminal coupling constant between C1 and H$^{\mathrm{trans}}$ becomes more negative with decreasing electonegativity of the substituent.[75] The opposite tendency is found for $^{2}J(\mathrm{C,H})$ between C1 and H$^{\mathrm{cis}}$. The difference between the electropositive silicon substituent ($^{2}J(\mathrm{C1,H^{cis}}) = -0.8$ Hz, X = SiCl$_3$) and lithium ($^{2}J(\mathrm{C1,H^{cis}}) = +13.5$ Hz, X = Li) is extraordinarily large. The trend of $^{2}J(\mathrm{C1,H^{cis}})$ in Table IV goes parallel with the geminal $^{2}J(\mathrm{H^{trans},H^{cis}})$ coupling constants in monosubstituted ethylenes (see above).

Table IV. Geminal ^{2}J(C,H) Coupling Constants (Hz) in Monosubstituted Ethylenes, after Ref[75] except for X = Li (this work)

substituent X	$^{2}J(\mathrm{C1,H^{trans}})$	$^{2}J(\mathrm{C1,H^{cis}})$	$^{2}J(\mathrm{C2,H^{gem}})$
Li (dimer)	−5.9	+13.5	−10.7
SiCl$_3$	−2.5	−0.8	−6.9
H	−2.4	−2.4	−2.4
CH$_3$	−1.1	−2.6	+0.4
I	+4.2	−7.8	+4.0
Cl	+7.1	−8.3	+6.8

The tendency toward more negative $^{2}J(\mathrm{C2,H^{gem}})$ coupling constants with decreasing electronegativity of the substituent is well continued in vinyllithium ($^{2}J(\mathrm{C2,H^{gem}}) = -10.7$ Hz).

Conclusions

Vinyllithium is a dimer/tetramer equilibrium in THF-d_8 at low temperatures. The identification was achieved by analysis of ^{13}C,^{6}Li coupling constants and multiplicities. For the tetramer, an interesting dynamic phenomenon is observed: whereas at −90 °C the aggregate is "static", an *intraaggregate* carbon–lithium bond exchange process is fast relative to the NMR time scale at −60 °C. Interchange of the four lithium positions is observed under these conditions.

Furthermore, we conclude that within a "static" vinyllithium tetramer there is "tumbling" of a monomer unit around an axis which extends through C1 and the diagonal lithium atom of the tetramer cube. This process averages the three lithium atoms bound directly to C1 of a vinyl monomer unit.

We have determined in this work all possible H,H, H,C, C,C, Li,H, and Li,C coupling constants in both dimeric and tetrameric vinyllithium. The measurement of the very small Li,H coupling constants ($^{2}J(\mathrm{^{6}Li,H^{gem}}) = +0.4 \pm 0.2$ Hz, tetramer; $^{3}J(\mathrm{^{6}Li,H^{trans}}) = +0.4 \pm 0.2$ Hz, dimer) was achieved by ^{6}Li,^{1}H β-FUCOUP. By using this technique, the sign and magnitude of lithium–hydrogen coupling constants may be derived from tilts in cross peak multiplets, similar to homonuclear β-COSY and E.COSY experiments.

The magnitudes of the C,C coupling constants (35.0 Hz in the dimer, 36.3 Hz in the tetramer) are, to our knowledge, the smallest numbers reported so far for monosubstituted olefins). Likewise, $^{1}J(\mathrm{C1,H^{gem}})$ is extremely small (91.7 Hz in the dimer, 93.2 Hz in the tetramer). Actually, $^{1}J(\mathrm{C1,H^{gem}})$ amounts to only ca. 60% of the number found for ethylene (156.4 Hz).

By using ^{1}H,^{13}C HETCOR we were able to demonstrate that the sign of $^{1}J(\mathrm{C1,^{6}Li})$ is *positive*. This conclusion was achieved by analysis of the tilt introduced from coupling with the "passive" spin, ^{6}Li, in the C1,H$^{\mathrm{gem}}$ cross peak multiplet of the tetramer.

The signs of geminal (^{2}J) carbon–hydrogen coupling constants were derived from tilts within cross peak multiplets in ^{1}H,^{13}C β-FUCOUP spectra. Whereas $^{2}J(\mathrm{C1,H^{cis}})$ is the uppermost positive number reported so far for monosubstituted ethylenes (+13.5 Hz in the dimer and the tetramer), the remaining constants are the uppermost negative numbers described to date ($^{2}J(\mathrm{C1,H^{trans}}) = -5.9$ Hz (dimer) and −6.1 Hz (tetramer); $^{2}J(\mathrm{C2,H^{gem}}) = -12.1$ Hz (dimer) and −10.7 Hz (tetramer)). The general trends for the observed H,H, H,C, and C,C coupling constants in monosubstituted ethylenes are well continued in vinyllithium. However, a large gap in these numbers is observed between the data for lithium and the data for the more electronegative element, silicon. We suspect that the numbers for X = Na...Cs are still more extreme.

We have exemplified that the β-FUCOUP technique may serve as a versatile tool in the determination of the magnitude of ^{6}Li,^{1}H coupling constants which are smaller than the line widths of the

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involved resonance signals. Likewise, similar to the well-known homonuclear E.COSY and β-COSY experiments, the sign of heteronuclear coupling constants may be easily derived by using β-FUCOUP. This has been examplified in the present work for ^{6}Li,^{1}H and ^{13}C,^{1}H pairs of nuclei.

Experimental Section

Vinyllithium-^{6}Li (96% ^{6}Li isotope enrichment) was prepared under dry argon from tetravinyltin and nBu^{6}Li[1i] in hexane according to the method described by Seyferth.[3] **CAUTION**: Amorphous vinyllithium is highly pyrophoric when exposed to air!

NMR samples of vinyllithium (**1**) in THF-d_8 were prepared by careful dissolution of **1** in the NMR tube at low temperatures. Due to formation of THF solvates, this process is exothermic. Without external cooling, partial decomposition of THF occurs (formation of ethylene and lithium acetaldehyde enolate[76]). Solutions of vinyllithium in THF-d_8 are stable at room temperature over many days. Solutions of vinyllithium in C_6D_6 or toluene-d_8 were prepared by dispersing the solid material in the solvent and subsequent slow addition of 1 equiv of TMEDA to give a clear solution.

NMR spectra were recorded on a JEOL GX400 spectrometer (9.4 T, ^{1}H = 400 MHz) under conditions previously described.[21,77] ^{1}H and ^{13}C spectra were recorded on a 5-mm dual probehead. Spectra which involve measurement of the ^{6}Li isotope were recorded on a 10-mm multinuclear probehead by using 5-mm sample tubes. Measurements at temperatures <0 °C were carried out on nonspinning samples. Pure absorption phase quadrature detection in ω_1 of 2D spectra was achieved by the States method.[78]

The spin simulation (Figure 8) was carried out by using the JEOL program COMIC. The spectrum was treated as a homonuclear ^{13}C spectrum, with the chemical shift of the ^{1}H resonance lines set ca. 60 ppm off the ^{13}C chemical shift. This explains the very slight intensity distortions ("roof effect") of the simulated ^{13}C spectra in Figure 8.

Selected instrumental parameters of the individual spectra shown in this paper were as follows.

Figure 5 (^{6}Li,^{1}H β-FUCOUP spectrum of the vinyllithium dimer): 1.9 M solution in THF-d_8 with an additional 1 equiv of TMEDA, −90 °C; pulse sequence 2; spectral widths, 1200 Hz (f_1 = ^{1}H) and 250 Hz (f_2 = ^{6}Li), 512 complex data points in t_2, zero filled to 1024; 256 increments in t_1, zero filled to 512 complex data points in t_1, 16 scans per t_1 increment; interpulse delay 2.0 s; Gaussian apodization in both dimensions.

Figure 7 (^{1}H,^{13}C shift correlated spectrum between H^{gem} and C1 in the vinyllithium tetramer): 1.3 M solution in THF-d_8, −100 °C; spectral widths 220 Hz (f_1 = ^{1}H) and 150 Hz (f_2 = ^{13}C), 512 complex data points in t_2, 64 increments in t_1, zero filled to 256 complex data points in t_1, 16 scans per t_1 increment, interpulse delay 3.5 s; Gaussian apodization in both dimensions.

Figure 9 (^{1}H,^{13}C β-FUCOUP spectrum of the vinyllithium dimer): 1.4 M solution in toluene-d_8 in the presence of 1 equiv of TMEDA, +27 °C; spectral widths, 1265 Hz (f_1 = ^{1}H) and 9009 Hz (f_2 = ^{13}C); 1024 complex data points in t_2, zero filled to 2048; 128 increments in t_1, zero filled to 256 complex data points in t_1; 128 scans per t_1 increment; interpulse delay 2.3 s; Gaussian apodization in both dimensions.

MNDO calculations were carried out on a Silicon Graphics IRIS INDIGO workstation by using the vectorized AMPAC (VAMP 4.4) program. Lithium parameters were those supplied by Clark and Thiel.[67]

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