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NMR Spectroscopy of Organolithium Compounds, Part XIX[1]

Reaction of (*Z*)-1,2-Bis(trimethylsilyl)-1-phenylethene with Lithium: Dianion Formation, Schlenk Dimerization, and ^{13}C,^{6}Li Coupling in a Benzyllithium System

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Abstract: Lithium reduction of (*Z*)-1,2-bis(trimethylsilyl)-1-phenylethene (**1**) yields the dianion of the (*E*)-isomer (**3**) and via Schlenk dimerization dilithium 1,4-diyl-1,4-diphenyl-1,2,3,4-tetrakis(trimethylsilyl)butane (**4**). The NMR parameters for both systems are reported and their solution structures are discussed. The formation of **4** is reversible and a unique feature of **4** is the scalar $^{1}J(^{13}C,^{6}Li)$ spin-spin coupling constant of 2.7 Hz for the C-Li bond, which is resolved even at room temperature.
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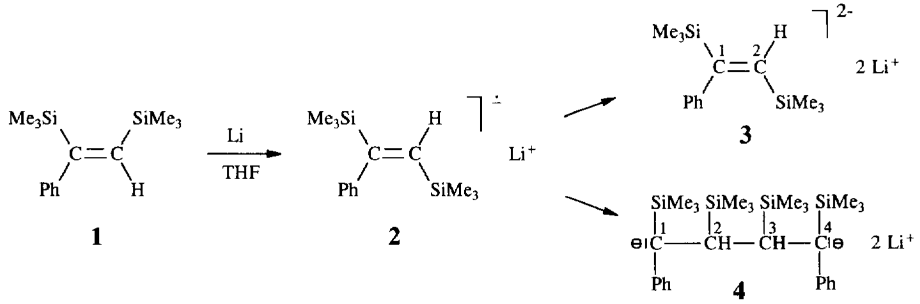
In connection with NMR studies on the structure of dilithiostyrene derivatives[1] and of dianions derived by lithium reduction of cyclic π-systems,[2] we became interested in the reaction of (*Z*)-1,2-bis(trimethylsilyl)-1-phenylethene (**1**) with lithium metal. Results of this investigation are reported in the present communication.

If **1** is treated with [^{6}Li]lithium chunks in [D_8]THF for two hours, the ^{1}H NMR spectrum reveals, apart from four $SiMe_3$ resonances around 0 ppm, ten multiplets between δ 5.0 and 6.5 and two singlets at δ 2.51 and -0.13 (Fig. 1). From a 2D-COSY experiment it follows that these signals belong to two distinct, internally coupled spin systems, which, in turn, suggests the formation of two reaction products. According to findings reported for vinylsilanes and for alkylsubstituted styrenes,[3-6] we expect initial formation of the radical anion, which should, following observations made for (*Z*)-propenyltrimethylsilane,[7] exist in the isomeric (*E*)-configuration (**2**). Further reduction of **2** would lead to the dianion **3**, while Schlenk-type dimerization[8] on the other hand is expected to yield dilithium 1,4-diyl-1,4-diphenyl-1,2,3,4-tetrakis(trimethylsilyl)butane (**4**):



Since the ratio of the two overlapping ^{1}H spectra varies strongly with the reaction conditions, two products are indeed formed and ^{1}H and ^{13}C NMR spectral analysis, based on several 1D and 2D techniques,[9] established their structure as **3** and **4**. The resulting NMR assignments, which we discuss in the following, are collected in Table 1 together with the data for the (*E*)-isomer of **1** (**5**) and α-trimethylsilylbenzyllithium (**6**).[10]

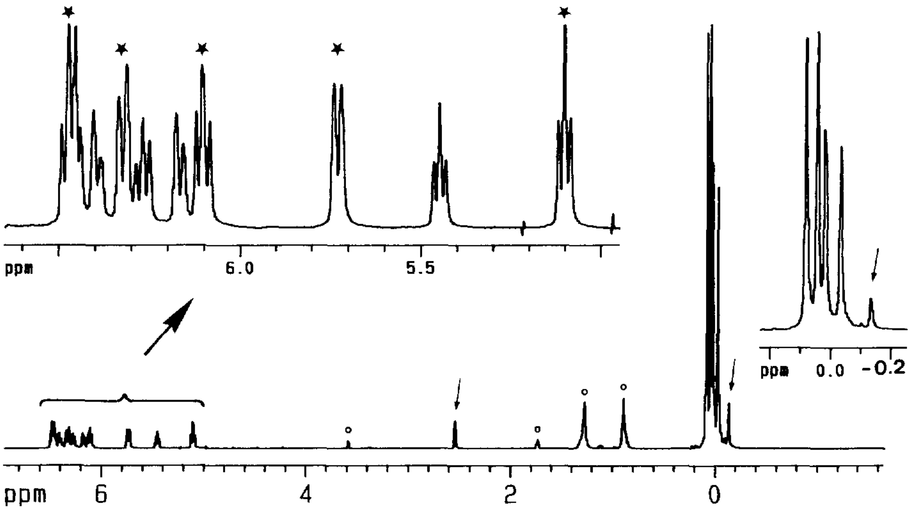
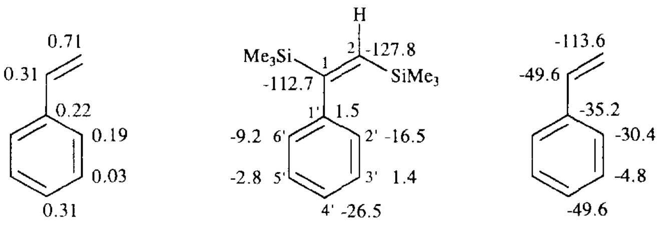


Fig. 1. 400 MHz ^{1}H NMR spectrum of **3**/**4** in [D$_8$]THF at 240 K; δ values (ppm) rel. to TMS; o solvent signals and residual signals of *n*-hexane (see exp. part)

Table 1. ^{1}H, ^{6}Li, ^{13}C, and ^{29}Si Chemical Shifts (δ, ppm rel. to TMS [^{1}H, ^{13}C, ^{29}Si] and 0.1M LiBr [^{6}Li]) for **3** (=dianion), **4** (=dianionic Schlenk dimer), **5** (=(*E*)-isomerized educt **1**), and **6**[10] and Δδ values for **3-5** and **4-6**

	2'-H	**3'-H**	**4'-H**	**5'-H**	**6'-H**	**2-H**	**1-Si(C<u>H</u>$_3$)$_3$**	**2-Si(C<u>H</u>$_3$)$_3$**	**^{6}Li**	**1-, 2-<u>Si</u>(CH$_3$)$_3$**
3	5.73	6.48	5.11	6.12	6.34	-0.13	0.04	0.08	-1.76	-14.7, -30.4
5	6.94	7.23	7.14	7.23	6.94	6.39	0.05	-0.19		-5.3, -10.3
Δδ	-1.21	-0.75	-2.03	-1.11	-0.60	-6.52	-0.01	0.27		**-9.4, -20.1**
	C-1'	**C-2'**	**C-3'**	**C-4'**	**C-5'**	**C-6'**	**C-1**	**C-2**	**1-Si(<u>C</u>H$_3$)$_3$**	**2-Si(<u>C</u>H$_3$)$_3$**
3	147.56	111.49	129.80	100.05	125.67	118.81	54.91	16.60	1.87	11.21
5	146.06	127.98	128.43	126.54	128.43	127.98	167.62	144.38	-1.46	0.35
Δδ	**1.50**	**-16.49**	**1.37**	**-26.49**	**-2.76**	**-9.17**	**-112.71**	**-127.78**	3.33	10.86
	2'-H	**3'-H**	**4'-H**	**5'-H**	**6'-H**	**2-H**	**1,4-Si(C<u>H</u>$_3$)$_3$**	**2,3-Si(C<u>H</u>$_3$)$_3$**	**^{6}Li**	**1,4-,2,3-<u>Si</u>(CH$_3$)$_3$**
4	6.37	6.46	5.45	6.28	6.15	2.51	-0.04	0.02	0.37, -1.20	-11.3, 6.0
	C-1'	**C-2'**	**C-3'**	**C-4'**	**C-5'**	**C-6'**	**C-1**	**C-2**	**1,4-Si(<u>C</u>H$_3$)$_3$**	**2,3-Si(<u>C</u>H$_3$)$_3$**
4	154.96	117.33	128.74	104.04	126.87	117.09	57.65	32.89	2.23	4.33
6	159.7	120.4	128.2	107.8	128.2	120.4	40.9	---	2.9	---
Δδ	-4.7	-3.1	0.5	-3.8	-1.3	-3.3	16.8	---	-0.7	---

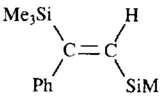
The low-field signals marked * in Fig. 1 and the high-field singlet at δ -0.13 as well as the highly shielded ^{13}C resonances of C-1 and C-2 (Table 1) are compatible with **3** where the negative charge is partly distributed over the phenyl ring. 1D NOE effects between the *ortho*-protons (2',6'-H) and the protons of *both* SiMe$_3$ groups establish the (*E*)-configuration.[11] The differential ^{13}C chemical shifts observed for **3** with respect to **5** reflect the charge densities predicted for styrene dianion within the simple HMO model[12] (Fig. 2), but indicate considerable charge localization at C-1 and C-2. In line with these findings are the high-field shifts for the ^{29}Si resonances (Δδ = -9.4 and -20.1 ppm for 1-Si and 2-Si, respectively, with respect to **5**). At the same time, the benzene ring apparently carries less charge than predicted. All Δδ(^{13}C) and the Δδ values of the two ^{29}Si resonances add up to 322 ppm which is the value expected for a total charge excess of two electrons.[13]



A **B** **C**

Fig. 2. HMO charge densities for styrene dianion (**A**), $\Delta\delta(^{13}C)$ values **3-5** (**B**), and $\Delta\delta(^{13}C)$ values calculated from **A** using the equation $\Delta\delta(^{13}C)_i = 160\ \Delta\rho_i$[13]

The NMR parameters for **3** resemble those reported for the dianion of 1-phenyl-1,2,2-tris(trimethylsilyl)ethene (**7**), where the X-ray analysis established an orthogonal arrangement for the phenyl ring and the formal double bond with two non-eqivalent lithium positions.[14] However, since only one ^{6}Li NMR signal is observed for **3** even at 200 K, where **7** shows two distinct ^{6}Li resonances,[14] we must assume a fast equilibrium with lithium exchange (**D** $\rightleftarrows$ **E**) as found for **7** at elevated temperatures as well as for 1,1-diphenyl-2,2-bis(trimethylsilyl)ethene dianion (**8**) even at 200 K.[14] On the other hand, the ^{1}H,^{6}Li HOESY spectrum shows cross peaks between ^{6}Li and 2'-H, 2-H, 1-SiMe$_3$ and/or 2-SiMe$_3$.[15] This is compatible with a double lithium bridged structure **9**, as observed for systems like the THF complex of dilithio-tetrakis(trimethylsilyl)ethene[16] or the TMEDA complex of dilithio-1,2-diphenylethene.[17] Further experimental work is thus needed to decide between the two alternatives **D** $\rightleftarrows$ **E** and **9**.



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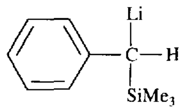

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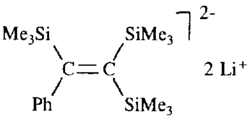

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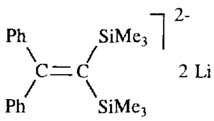

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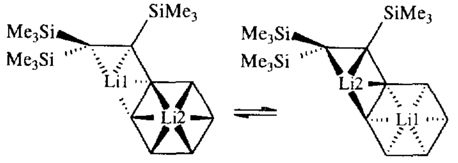
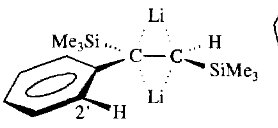


D **E**



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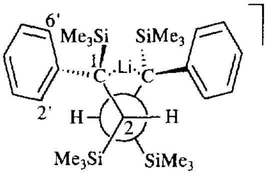

10

The NMR data of **4** are in line with a structure where the phenyl ring shows hindered rotation due to partial charge delocalization and a high double bond character of the C-1-C-1' bond. Since the spectrum does not change in the temperature range between 200-294 K, a fairly high rotational barrier is indicated. The dimerization of **2** to form **4**, on the other hand, is nicely proven by the detection of the H^{13}C(2)-^{12}C(3)-H' fragment in the HMBC experiment.[18] The NMR data of the benzyllithium partial structure are close to those found for **6**,[10] except that C-1,4 are less shielded due to the substituent effects of C-2 and C-3 (α-effect $\approx$ β-effect $\approx$ +9 ppm).[19] A unique feature of **4** is, however, the 1:1:1 triplet observed for C-1,4, which shows a ^{13}C,^{6}Li spin-spin coupling of 2.7 Hz even at RT. This agrees with findings made just recently for benzyllithium systems where the cation is held in close contact to the benzylic carbon by intramolecular complexation.[20,21] For the parent system itself, a coupling of 3.4 Hz was measured only under special conditions (^{13}C labelling, low temperature [180 K], low concentration [0.005 M], TMEDA complexation).[21]

For a more detailed picture of the solution structure of **4** the finding of *two* ^{6}Li signals (Table 1) is important.[22] Only the low-field signal shows ^{13}C,^{6}Li coupling and thus belongs to a Li cation in a contact ion pair. We thus assume structure **10** for **4**, where the second Li cation exists solvens separated; **10** resembles the structure proposed for dimers found in the reduction of alkyl substituted styrenes.[5] It is further supported by the ^{1}H,^{6}Li HOESY spectrum, which shows cross peaks between the ^{6}Li resonance at 0.37 ppm and the signals of 2'-H, 6'-H, and 2,3-H as well as the protons of the 1,4-SiMe$_3$ groups.

An additional aspect of interest with respect to the different behavior of similar alkyl substituted systems, where only reductive dimerization was observed,[5] is the observation that the reaction **1** → **4** is reversible. If the mixture **3**/**4** is filtered off from the lithium and new educt **1** is added in excess, the dianion is removed through the reaction sequence **3** + **1** → 2 x **2** → **4**. Excess of **1** is converted to **5**. Adding labelled educt [D$_6$]-**1**, the ^{1}H NMR signals of **4** are reduced in intensity and those of **5** increase. Thus, radical anion **2** from the cleavage of **4** attacks deuteriated **1** whereby [D$_6$]-**2** and non-deuteriated **5** are formed. Dimerization of [D$_6$]-**2** and reaction with **2** yields deuteriated and partially deuteriated **4**. This type of mechanism has been established for the reaction of 1,1-diphenylethene with alkali metal.[23]

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Experimental. **1** was synthesized according to the literature.[24] Lithium metal was washed with n-hexane and reduction carried out in [D$_8$]THF under argon atmosphere in a Schlenk tube. The resulting reaction mixture was filtered into an NMR tube, which was sealed. NMR measurements were performed with a Bruker AMX 400 spectrometer operating at 400.1 MHz (^{1}H), 100.6 MHz (^{13}C), 79.5 MHz (^{29}Si), and 58.88 MHz (^{6}Li).

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