NMR Investigation on the Solution Structure and Dynamic Behaviour of 1,2-Diphenyl-1,2-bis(trimethylsilyl)ethanediyldilithium

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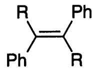
Received June 6, 1998

Keywords: Dianions / Organolithium compounds / Reductive metallation / HOESY / Lithium NMR

1,2-Diphenyl-1,2-bis(trimethylsilyl)ethene (**5**) undergoes a smooth reductive metallation with metallic lithium to yield the corresponding dilithioethane derivative (Li_2·**5**). The structure of this new compound in [D_8]THF solution was determined by NMR spectroscopy (^1H, ^{13}C, ^6Li, ^7Li NMR and ^6Li,^1H-HOESY). It is shown that the phenyl rings have a high quinoid character and that the lithium cations are relatively mobile.

Introduction

It has been known since 1928 that stilbene (**1**, R = H) and related aryl-substituted ethene derivatives (**1**, R = alkyl, aryl) react readily with alkali metals to afford π-delocalized benzylic carbanions[1][2]. Similar reductive metallations can be achieved with ethenylsilanes **2a−c**[3], in which the negative charges are stabilized by the adjacent silyl substituents. In compounds such as **3a−c**, both stabilizing effects are present[4].



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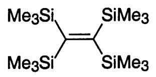

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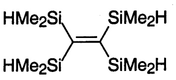

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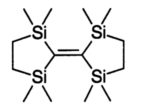

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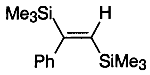

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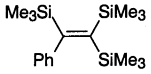

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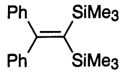


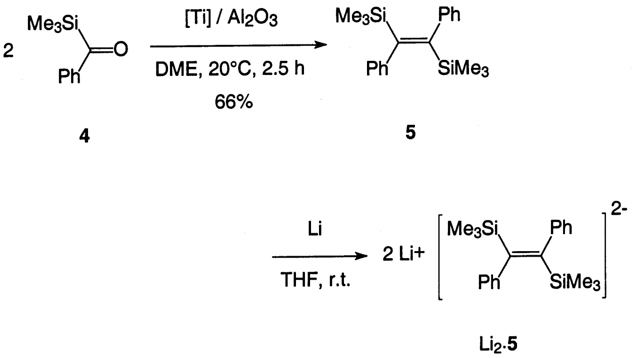
3c

These metallations proceed in a stepwise fashion: a first single electron transfer (s.e.t.) leads to short-lived radical anions which rapidly undergo a second s.e.t. to afford the corresponding dianions[5]. The latter have attracted considerable attention in recent years as stabilized analogues of the still elusive 1,2-dilithioethane[6]. Several in-depth studies employing X-ray crystallography or NMR have provided a detailed − but rather static − picture of the bonding situation in such dimetallic compounds[1][2][3][4]. In the following we describe not only the solution structure of a further missing congener of this series, i. e. the dilithio derivative of 1,2-diphenyl-1,2-bis(trimethylsilyl)ethene (Li_2·**5**), but also show that within this molecule the metal cations are highly mobile.

Results and Discussion

Recently, McMurry-type coupling reactions have been extended to substrates other than aldehydes and ketones[7]. We found that aromatic acylsilanes react reasonably well with low-valent titanium [Ti] to afford the corresponding 1,2-disilylethene derivatives as the major products.

Scheme 1



Specifically, treatment of benzoyltrimethylsilane **4** with [Ti] formed from $TiCl_3$ and “high surface sodium” (Na/Al_2O_3)[8] as the preferred coupling agent provides compound **5** in 66% yield as colorless crystals[9]. This product undergoes a smooth reductive metallation on exposure to an excess of lithium metal in thoroughly dried and degassed THF, leading to a dark-red solution of the corresponding dianion Li_2·**5**. This derivative is thermally stable for prolonged periods of time and can be isolated as a dark-red solid upon removal of the THF. However, Li_2·**5** is extremely sensitive in solution as well as in the solid state towards

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traces of air which immediately re-convert it into the starting disilylethene **5**.

Although various conditions have been used to crystallize the compound, no crystals of $Li_2 \cdot$**5** suitable for an X-ray analysis have been obtained. Therefore the structure of this compound was studied by NMR spectroscopy. A complete and unambiguous assignment of the ^1H and ^{13}C spectra (Table 1) was achieved using 2D-NMR techniques.

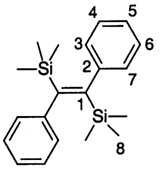

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Table 1. ^1H- and ^{13}C-NMR data for **5** and Li_2·**5** in [D$_8$]THF at 303 K; arbitrary numbering as shown

Position	^{13}C NMR **5**	Li$_2$·**5**	Δδ[a]	$^1J_{(C,H)}$	**5**	^1H NMR Li$_2$·**5**	Δδ[a]
1	159.1	69.4	−89.7				
2	145.8	153.1	7.3				
3	128.0	107.4	−20.6	159.3	7.04	5.89	−1.15
4	127.6	127.0	−0.6	159.9	7.27	6.05	−1.22
5	125.6	97.9	−27.7	160.0	7.18	4.93	−2.25
6	127.6	130.5	2.9	159.9	7.27	6.27	−1.00
7	128.0	117.6	−10.4	159.3	7.04	6.18	−0.86
8	0.2	2.3	2.1	120.0	−0.36	0.00	0.36

[a] $\Delta\delta_n = [\delta_n(Li_2\cdot\mathbf{5}) - \delta_n(\mathbf{5})]$.

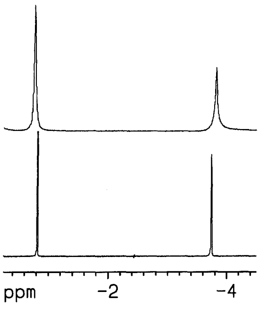
As can be seen from Table 1, five proton and six ^{13}C signals are observed at 303 K for the phenyl groups. Detailed analysis of these spectra and further experiments including COSY revealed that the two arene groups are equivalent but that within each group all the carbon atoms and protons are different. The number of signals in the ^1H- and ^{13}C-NMR spectra is unchanged when the sample is cooled to 193 K and no broadening of any of these signals is observed (cf. Experimental Section). Thus, the phenyl groups remain equivalent on the NMR time scale over the range 300 K to 193 K.

The inequivalence of the *ortho* positions (3 and 7) and of the *meta* positions (4 and 6) within each phenyl group indicates that the barrier to rotation about the C-1,C-2 bond in Li$_2$·**5** must be high. No exchange cross peaks could be detected in a ^{13}C 2D-EXSY spectrum recorded at 303 K. Taking into account the relatively high signal-to-noise ratio of this 2D spectrum and that the cross peaks due to exchange were not larger than the peak-to-peak noise, the barrier to rotation of the arene ring is estimated to be at least 90 kJ/mol.

The resonance of C-1 is observed at $\delta = 69.4$, i. e. an upfield shift of 89.7 ppm relative to the olefin **5** ($\delta = 159.1$). Moreover, the ^{13}C data indicate that the negative charges are also delocalized to a large extent over the arene rings. Specifically, the *para*-^{13}C signal of C-5 resonates at $\delta = 97.9$, corresponding to a low-frequency shift of ca. 27.7 ppm by comparison with the signal of **5**. Similarly, the *ortho* signals ($\delta = 107.4$ and 117.6) are shifted to lower frequency by 20.6 and by 10.4 ppm. These observations and the high barrier to rotation indicate that the phenyl substituents have a strong quinoid character, a conclusion which is in accordance with previous studies on related ethylene anions[3][4].

Further structural information was gained from the lithium-NMR spectra. Both the ^7Li-NMR spectra of the natural abundance compound and ^6Li spectra of a ^6Li-enriched sample were measured. Surprisingly, the temperature dependence of the ^6Li- and ^7Li-NMR spectra contrasts strongly with that observed for the ^1H- and ^{13}C-NMR spectra. At 293 K a single, broadened signal is observed in the ^6Li spectrum (88.3 MHz) at $\delta_{Li} = -2.4$ (linewidth 500 Hz), which on lowering the temperature splits into two well-resolved lines at $\delta_{Li} = -0.8$ and -3.8 (Figure 1). The separation of these signals (3.0 ppm) is large as compared to the usual range of lithium chemical shifts[10], suggesting that the environments of the lithium cations are rather different. This result is in contrast to previous investigations on dilithioethane derivatives, in which the Li signals either coincide or resonate within a narrow shift range[3][4].

Figure 1. ^7Li-NMR (233.3 MHz) spectrum (top) and ^6Li-NMR (88.3 MHz) spectrum (bottom) of Li$_2$·**5** recorded at 193 K



The ^6Li-enriched samples were prepared to obtain additional information on the *location* of the cations using $^6Li,^1H$ heteronuclear Overhauser effects, which were measured using the 2D HOESY (HOESY = heteronuclear Overhauser effect spectroscopy) technique[10][11]. The HOESY spectrum reveals strong cross peaks between the lithium signal at $\delta_{Li} = -3.8$ and the TMS group, the *ortho* proton at $\delta_H = 5.89$ (3-H) and the adjacent *meta* proton (4-H). Additional, but weaker, cross peaks are found to the *para* proton (5-H) and the other *ortho* proton (7-H). The HOESY cross peaks of the second lithium signal at $\delta_{Li} = -0.8$ are weaker and correlate with the TMS group and both *ortho* protons (Figure 2). Since ^{6}Li,^{1}H heteronuclear Overhauser effects can only be detected over short distances[10], these results show that *both* lithium cations must be close to the organic anion and that in $Li_2 \cdot$**5** tight ion contacts are present. ^{6}Li- and ^{7}Li-NMR spectra recorded in the presence of excess TMEDA support this conclusion: although TMEDA usually dissects oligomeric organolithium compounds in solution, the lithium chemical shifts of $Li_2 \cdot$**5** are hardly affected even when 2.5 equivalents of TMEDA are added.

Figure 2. ^{6}Li,^{1}H-HOESY-NMR spectrum (contour plot) of $Li_2 \cdot$**5** recorded in [D$_8$]THF at 193 K

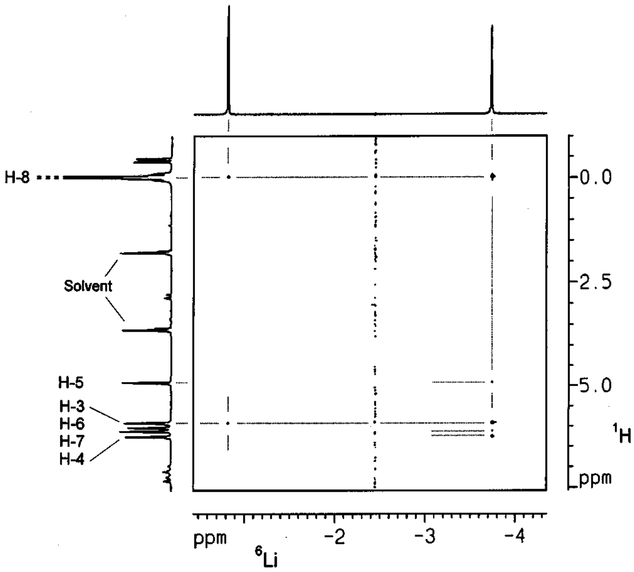
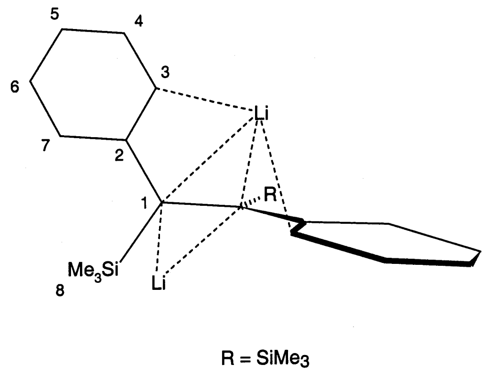


Table 1 also documents the large differences between the chemical shifts of the *ortho* carbon atoms C-3 and C-7 in $Li_2 \cdot$**5** (10.2 ppm). The signal shifted more strongly to high field arises from the *ortho* carbon atom on side of the ring having the stronger interaction with Li. Similarly, significant shift differences are found between the *meta* carbon atoms C-4/C-6 (3.5 ppm), as well as the *ortho* protons H-3/H-7 (0.29 ppm) and the *meta* protons H-4/H-6 (0.22 ppm). We interpret these data and the HOESY spectra described above as showing that the lithium cation giving rise to the resonance at $\delta = -3.8$ interacts with the phenyl groups, particularly with the sides of these groups towards the inside of the molecule (Figure 3). If the lithium atom interacts with both phenyl rings simultaneously, then the dianion cannot be planar: the torsional angle about the C-1, C-1′ bond must be reduced to ca. 90°. This is also consistent with ^{1}H-NOE data, since strong cross peaks are observed between the trimethylsilyl protons and both *ortho* protons of the arenes. Note also that the non-planar scaffold of $Li_2 \cdot$**5** implies an axially chiral environment. A schematic representation of the structure and bonding situation in $Li_2 \cdot$**5** is given in Figure 3.

Figure 3. Schematic representation of the structure and bonding situation in $Li_2 \cdot$**5**



There is evidence that additional fast exchange processes are occurring. In both, the ^{6}Li and ^{7}Li spectra, the Li signal at $\delta = -0.8$ becomes narrower when the temperature is reduced to below 250 K but the Li signal at $\delta = -3.8$ remains somewhat broadened. This is apparently caused by additional exchange phenomena involving this lithium atom alone which remain fast on the NMR time scale. It is possible that the lithium cation jumps between different sites on the phenyl groups and the observed broadening may be due to a slowing of this rate of exchange. However, we have no corroborating evidence for this from the ^{1}H- or ^{13}C-NMR spectra and this interpretation remains speculative. When TMEDA is added to the sample, this phenomenon becomes much more marked. Not only does the high-field ^{6}Li signal below 200 K split into two signals of intensities ca. 2:1 but in this case the phenyl *ortho* proton signal also shows similar behaviour.

In summary, the NMR data are consistent with the presence of contact ionic interactions in $Li_2 \cdot$**5** with the anion having a C_2-symmetrical twisted, axially chiral conformation with a torsional angle of about 90°. As a result of their high quinoid character, the phenyl rings cannot rotate. On time average the two lithium cations are found on the plane orthogonal to the central C−C bond and passing through its midpoint. At room temperature the lithium cations exchange locations with one another rapidly but at 193 K this exchange is slow on the NMR time scale. One of the lithium cations lies between the phenyl rings and interacts strongly with the *ortho* positions.

We thank the *Fonds der Chemischen Industrie*, Frankfurt, for generous financial support.

Experimental Section

General: All reactions as well as the sample preparations for NMR were carried out under Ar using Schlenk techniques. All glassware was thoroughly flame-dried in vacuo. Natural abundant Li and ^{6}Li powder (Aldrich, 95% ^{6}Li, dispersion in mineral oil) were repeatedly washed with pentane and dried in vacuo prior to use. $[D_8]$THF was dried by distillation from Na/K alloy and transferred under Ar. Substrate **5** was prepared by a McMurry-type coupling reaction as previously described[9a].

NMR Spectroscopy: All the NMR spectra were measured with a Bruker DMX-600 NMR spectrometer: ^{1}H (600.2 MHz), ^{6}Li (88.3 MHz), ^{7}Li (233.3 MHz), and ^{13}C (150.9 MHz). The chemical shifts were determined relative to the β-methylene signals of the solvent and converted to the TMS scale (^{1}H, β-CH_2, $\delta_H = 1.78$; ^{13}C, β-CH_2, $\delta_C = 25.2$). The sequence of proton signals 3-H to 6-H was determined in the COSY spectrum and confirmed by NOESY. These assignments were transferred to ^{13}C using data from the ^{1}H,^{13}C correlation. The strongest ^{6}Li,^{1}H cross-peaks in the HOESY spectrum were to the protons at 5.89 (*ortho*) and 6.27 (adjacent *meta*), allowing the "outer" and "inner" sides of the phenyl ring to be identified. The lithium chemical shifts are given relative to external 0.1 M LiBr in THF solution (0 ppm). The HOESY experiments were recorded using the experiment hoesytp from the standard Bruker pulse library using a mixing time of 1.8 s (256 experiments each of 64 scans, 1 K in f_2, magnitude calculation in f_1, exponential multiplication in both dimensions using lb = 2).

Preparation of Diphenyl-1,2-bis(trimethylsilyl)ethanediyldilithium (Li$_2$·**5**). To a stirred suspension of lithium powder (35 mg, 5.04 mmol) in 5 ml of $[D_8]$THF was added a solution of alkene **5** (144 mg, 0.44 mmol)[9a] in 5 ml of $[D_8]$THF. The reaction mixture turned dark-red within a few minutes and stirring was continued overnight. An aliquot of the supernatant dark-red liquid was transferred via cannula into a thoroughly dried NMR tube, the rest was filtered off and concentrated to afford a dark-red amorphous solid. − ^{7}Li NMR ($[D_8]$THF, 303 K) $\delta = -2.2$, $\Delta\nu_{1/2} = 265$ Hz. − ^{7}Li NMR ($[D_8]$THF, 193 K) $\delta = -0.78, -3.82$. − ^{1}H NMR ($[D_8]$THF, 193 K): $\delta = 6.25, 6.10, 6.02, 5.92, 4.91, -0.03$. − ^{13}C NMR ($[D_8]$THF, 193 K) $\delta = 153.0, 130.6, 127.0, 117.0, 107.4, 97.9, 68.2$. − After addition of TMEDA: ^{1}H NMR ($[D_8]$THF, 303 K): $\delta = 6.27, 6.19, 6.03, 5.90, 4.95, 0.02$. − ^{1}H NMR ($[D_8]$THF, 193 K): $\delta = 6.25, 6.17, 5.98, 5.87, 4.90, -0.02$. − ^{7}Li NMR ($[D_8]$THF, 193 K): $\delta = -2.2$, $\Delta\nu_{1/2} = 350$ Hz. − ^{7}Li NMR ($[D_8]$THF, 193 K): $\delta = -0.75, -3.68$ (br.). − For the assignment and additional data see Table 1.

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