Lithium-Bridged Bis(silyl anion) of 9,10-Dimethyl-9,10-disilaanthracene

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In a low temperature ^{29}Si NMR spectrum measurement of 9,10-dimethyl-9,10-disilaanthracene dilithium (**1**), ^{29}Si-^{7}Li scalar coupling was observed. The ^{7}Li NMR spectrum showed the two different environments for these two lithium atoms in **1** at 168 K. The spectral analysis strongly suggests a structure which has singly bridged lithium for two silicon atoms (**1d**).

There are current interests in the synthesis, structural characterization, and chemical reactivity of molecules containing two or more silyl anions. Nevertheless, only few bis(silyl anion) derivatives have actually been isolated and characterized.[1-3]

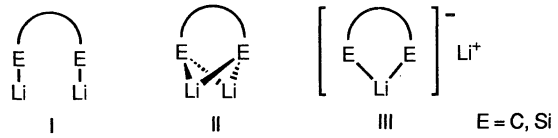
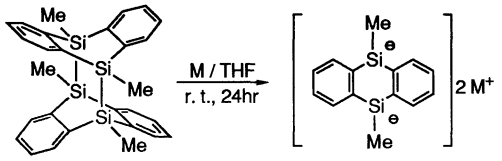


Figure 1. Bond styles of dianion compounds.

These bis(silyl anion) derivatives favored a structure containing single contact between the lithium and silicon atom (I). In the cases of bis(carbanion)s, double bridged (II)[4] and single bridged structures (III)[5] are well known. However, an example of a lithium atom bridging two silicon atoms has not yet been observed. In this paper, we wish to report the first example of a lithium bridged bis(silyl anion).



3 **1** : M = Li
2 : M = K

Scheme 1. Preparation of dianions (**1**, **2**).

Bis(silyl anion) compounds of 9,10-disilaanthracene (**1**, **2**) were prepared from the reduction of 9,10-dimethyl-9,10-disilaanthracene dimer (**3**) with an excess of lithium or potassium as shown in Scheme 1.[6] The ^{13}C NMR spectra of these dianions at 298 K showed four signals, consistent with C_{2v} symmetry, and ^{29}Si NMR spectra have only one resonance at -45.4 (**1**: M=Li) and -42.8 ppm (**2**: M=K), a large upfield shift compared to -17.9 ppm for a 9,9,10,10-tetramethyl-9,10-disilaanthracene (**4**). Typically, such upfield shifts are observed for ^{29}Si nuclei when neutral organosilanes are converted to the respective silyl anions (Table 1).[7-9]

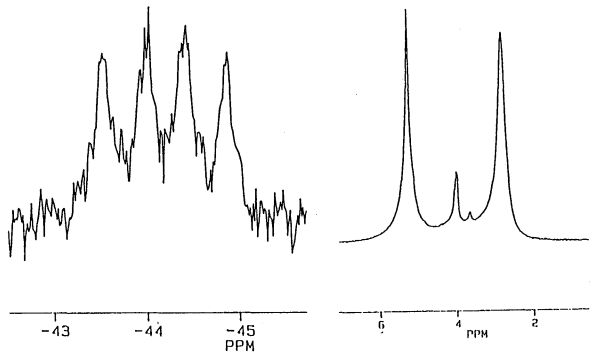


Figure 2. ^{29}Si NMR (left) and ^{7}Li NMR (right) spectra of **1** in THF-*d8* at 168 K.

Above results strongly support that 9,10-disilaanthracene dilithium and dipotassium certainly have a single product.[10] In order to shed light on the structure of **1**, a low temperature measurement of ^{29}Si-^{7}Li scalar coupling was carried out.[3, 11-14] In the ^{29}Si NMR spectrum of dilithium compound (**1**) at 168 K in THF-d_8, a quartet with ^{1}J [^{29}Si-^{7}Li]=34 Hz was observed (Figure 2). This implies that two silicon atoms in the molecule are magnetically equivalent and one lithium atom binds to the silicon atom at low temperature. The ^{7}Li NMR signal appears at 3.7 ppm as a singlet at 298 K. Dramatic change was observed at the low temperature ^{7}Li NMR measurements which yielded two different singlets at 2.8 and 5.2 ppm; unfortunately no satellite signals due to ^{29}Si scalar coupling were observed. However, it is clear from the ^{29}Si NMR spectrum that **1** has a covalent bond between ^{29}Si and ^{7}Li at low temperature. The results of ^{7}Li NMR studies reveal that different two environments exist for the two lithium atoms in the molecule at low temperature and these two lithium atoms turn into the magnetically equivalent by raising temperature because of rapid exchange of these lithium atoms.

Table 1. Chemical shifts for 9.10-disilaanthracene dianions(**1,2**) and **4** at 298 K

		^{1}H shifts			^{13}C shifts				^{29}Si shifts	^{7}Li shift
1[a]	M=Li	7.19[c]	6.59[c]	0.58	161.1	128.2	121.1	-0.9	-45.4	3.7
2[a]	M=K	7.21[d]	6.66[d]	0.54	161.2	128.5	122.0	4.12	-42.8	
4[b]		7.68	7.41	0.47	144.5	133.4	128.3	0.0	-17.9	

[a] Me_4Si in THF-*d8* for ^{1}H, ^{13}C and ^{29}Si NMR measurements and LiCl in MeOH for ^{7}Li NMR measurement were used as external standard. [b] In $CDCl_3$, internal Me_4Si as standard. [c] 4H, AA'BB', *J*=3.3, 4.9 Hz. [d] 4H, AA'BB', *J*=3.3, 5.0 Hz.

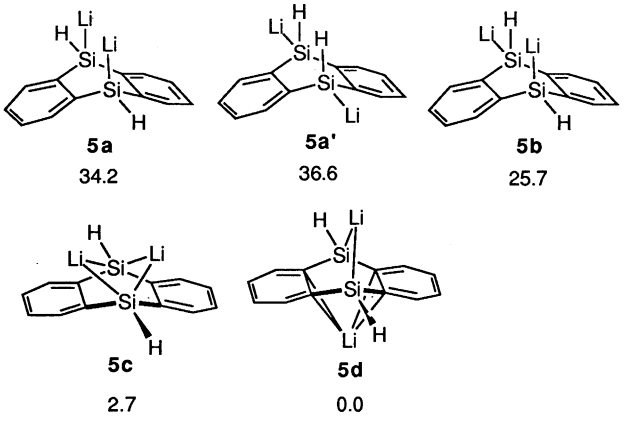


Figure 3. 3-21G(*) optimized structures for $C_{12}H_{10}Si_2Li_2$ and its relative energy (kcal/mol).

The ^{13}C-^{7}Li scalar coupling was not observed in low temperature ^{13}C NMR spectrum for **1**. The results reveal that **1** has no significant interaction between ^{13}C and ^{7}Li at low temperature.

A theoretical study on 9,10-dihydro-9,10-disilaanthracene dilithium suggests that the most stable structure is single bridged structure (**5d**); 3-21G(*) optimized results[15] showed that *cis*-dilithium (**5a, 5a'**), *trans*-dilithium compound (**5b**), and double bridged (**5c**) are 34.2, 36.6, 25.7, and 2.7 kcal/mol higher in energy than **5d** (Figure 3).

The bond form of **5b** (with slow conformational change) and **5c** are easily excluded from these candidates by the observation of a quartet in low temperature ^{29}Si NMR spectrum measurement. Bond form **5a** and **5b** (with smooth conformational change) should contain magnetically equivalent lithiums and can be ruled out from the results of low temperature ^{7}Li NMR study. Thus, the structure (**5d**) was confirmed by low temperature NMR which revealed that one lithium atom is bridging with both silicon atoms. It is supposed from the ^{7}Li NMR chemical shift of **1** that existence of **1d'** is impossible as

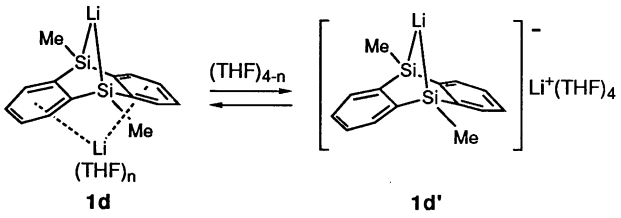


Figure 4. The equilibrium of second lithium (omit the THF molecules coordinating to bridged lithium atom).

sole product since solvent-separated lithium ion, $Li^{+}(THF)_4$, signal shall appear nearby 0 ppm in ^{7}Li NMR spectrum.[16] This implies the second lithium would be somewhat interact with π electrons (**1d**) by weakly bonding. In low temperature ^{7}Li NMR spectrum, the second lithium signal (2.8 ppm, $\nu_{1/2}$ = 41.9 Hz) is a broad compared with bridged lithium signal (5.2 ppm, $\nu_{1/2}$ = 23.9 Hz). These observations suggest that the second lithium atom may not be fixed to disilaanthracene skeleton even at 168 K and an equilibrium between **1d** and **1d'** is present as shown in Figure 4.

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