S2: Topological analysis and geometrical parameters of [{2−(Me$_3$Si)$_2$C(Li)C$_5$H$_4$N}$_2$].

Unit	Method[a]	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å^3]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å^5]	Ellipticity ε
Li···N_a	Experiment	1.9508	0.215(2)	5.201(2)	0.02
	Theory	1.9636	0.24	4.76	0.04
Li−C1	Experiment	2.2049	0.150(2)	2.521(1)	0.12
	Theory	2.1757	0.19	2.52	0.11
C1−Si2	Experiment	1.8592(4)	0.859(14)	1.73(3)	0.13
	Theory	1.8819	0.80	3.16	0.11
C1−Si1	Experiment	1.8552(4)	0.756(15)	4.25(3)	0.19
	Theory	1.8798	0.78	3.16	0.12
C1−C11	Experiment	1.4798(5)	1.78(2)	−11.29(5)	0.12
	Theory	1.4783	1.73	−13.38	0.11
Si1−C2	Experiment	1.8804(6)	0.693(17)	4.63(3)	0.22
	Theory	1.9050	0.79	2.92	0.01
Si1−C3	Experiment	1.8930(8)	0.758(14)	2.73(3)	0.20
	Theory	1.9197	0.76	2.99	0.01
Si1−C4	Experiment	1.8781(7)	0.765(16)	4.23(3)	0.14
	Theory	1.9023	0.79	3.01	0.01
Si2−C5	Experiment	1.8811(5)	0.714(16)	5.39(3)	0.12
	Theory	1.9083	0.78	2.91	0.01
Si2−C6	Experiment	1.8888(6)	0.735(16)	4.41(3)	0.07
	Theory	1.9094	0.78	2.89	0.02
Si2−C7	Experiment	1.8947(7)	0.717(16)	3.84(3)	0.03
	Theory	1.9180	0.76	2.97	0.01

[a] the experimental values were obtained by multipole refinement of the experimental charge density (see S1), the theoretical calculations were performed at the B3LYP/6−311G(3d, 3p)//B3LYP/6−31G(d) level of theory.

Unit	Method[a]	Distance [Å]	$\rho(\mathbf{r}_c)$ [e/Å^3]	$\nabla^2\rho(\mathbf{r}_c)$ [e/Å^5]	Ellipticity ε
N−C11	Experiment	1.3636(6)	2.17(3)	−17.34(13)	0.23
	Theory	1.3729	2.16	−22.96	0.10
C11−C12	Experiment	1.4168(6)	2.06(2)	−16.48(5)	0.21
	Theory	1.4223	2.01	−18.88	0.18
C12−C13	Experiment	1.3834(7)	2.165(19)	−19.03(4)	0.23
	Theory	1.3846	2.13	−21.06	0.21
C13−C14	Experiment	1.3948(7)	2.133(19)	−18.090(0)	0.24
	Theory	1.4000	2.07	−20.04	0.17
C14−C15	Experiment	1.3821(7)	2.20(3)	−20.68(6)	0.24
	Theory	1.3858	2.13	−21.20	0.23
N−C15	Experiment	1.3454(7)	2.39(3)	−22.34(12)	0.22
	Theory	1.3450	2.27	−24.80	0.13
C7−H7c	Experiment	1.0981	1.71(4)	−12.85(11)	0.08
	Theory	1.1009	1.78	−20.03	0.03
C3−H3b	Experiment	1.1003	1.73(5)	−13.01(17)	0.05
	Theory	1.0974	1.81	−20.78	0.03
C3−H3c	Experiment	1.0919	1.65(4)	−12.64(11)	0.08
	Theory	1.1001	1.79	−20.25	0.03
C3−Li_a	Experiment	2.5107	0.082(1)	0.828(1)	0.69
	Theory	2.4793	0.06	1.30	0.98

[a] the experimental values were obtained by multipole refinement of the experimental charge density (see S1), the theoretical calculations were performed at the B3LYP/6−311G(3d, 3p)//B3LYP/6−31G(d) level of theory.

Selected angles [deg] for [{2−$(Me_3Si)_2C(Li)C_5H_4N$}$_2$].[a]

C1−Li−N_a	Experiment	145.90	Li_a−N−C11	Experiment	104.12
	Theory	142.9		Theory	110.4
Li_a−Li−C1	Experiment	65.55	Li−C1−Si1	Experiment	104.51
	Theory	70.6		Theory	105.1
Li−Li_a−N	Experiment	104.46	Li−C1−Si2	Experiment	88.92
	Theory	95.7		Theory	90.6
Li_a−N−C15	Experiment	135.39	Li−C1−C11	Experiment	123.15
	Theory	128.6		Theory	116.5

[a] the experimental values were obtained by multipole refinement of the experimental charge density (see S1), the theoretical calculations were performed at the B3LYP/6−311G(3d, 3p)//B3LYP/6−31G(d) level of theory.