Supplementary Material (ESI) for Chemical Communications

Supporting information (experimental details, crystal-structure determination, computational studies) belonging to the publication

Bent Phenyl Groups in Lithiosilanes – Crystall Structures and Interpretation of this Unanticipated Feature

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Experimental Details

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium and distilled prior to use.
1,2-Diphenyl-1,1,2,2-tetramethyldisilane, 1,1,2,2-tetraphenyl-1,2-dimethyldisilane and PMDTA were trading products of ABCR and Sigma-Aldrich. Bis(diethylamino)phenylchlorosilane was prepared according to a synthesis described *K. Trommer et al.*[1]

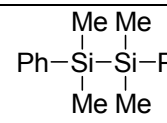
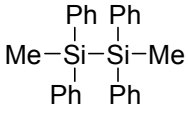
a) Synthesis of lithiobis(diethylamino)phenylsilane

1.35 g (4.74 mmol) bis(diethylamino)phenylchlorosilane were added to a suspension of 98.7 mg (14.2 mmol, 3 eq.) lithium in 15 ml thf at −20 °C and then stirred for 6 h at this temperature. Afterwards the leftover lithium was removed and the solution was divided in selected portions for subsequent reaction with the coordinating triamine PMDTA (see c).

b) General Procedure for the Preparation of Lithiosilanes by Si–Si Bond Cleavage of Disilanes

The selected disilane (cf. table 1) was added at room temperature to a threefold access of lithium suspended in a defined amount of THF. On the first occurrence of discoloration the reaction mixture was cooled to 0 °C and stirred for four hours at this temperature. Afterwards the leftover lithium was removed and the solution was divided in selected portions for subsequent reaction with the coordinating triamine PMDTA (see c).

Table 1 Selected disilanes used in the preparation of lithiosilanes **2** and **3** by Si−Si-cleavage.

disilane	$m_{disilane}$ in mg ($n_{disilane}$ in mmol)	m_{SiLi} in mg (n_{SiLi} in mmol)	m_{Li} in mg (n_{Li} in mmol)	V_{THF} in mL
	900 (3.33)	946 (6.66)	69.3 (9.99)	5.0
	750 (1.90)	776 (3.80)	39.6 (5.7)	4.0

c) General Procedure for Crystallization of Lithiosilanes in Presence of PMDTA

The solution of a selected lithiosilane was prepared as described above and used for several crystallization attempts. After removal of all volatile compounds the residue was suspended in roughly 1 ml of diethylether and then the amount of PMDTA (cf. table 2) was added. Afterwards, to support slow crystallization the reaction mixtures were stored at −30 °C. If no crystallization occurred at this temperature within several days the mixture was cooled further to −80 °C.

Table 2 Selected lithiosilanes and used additives for crystallization.

Lithiosilane	m_{SiLi} [mg] (n_{SiLi} [mmol])	m_{PMDTA} [mg]
$Ph(NEt_2)_2SiLi$	142 (0.55)	96.0
$Me_2PhSiLi$	158 (1.11)	193
$PhMe_2SiLi$	155 (0.76)	132

Crystal Structure Determination of Compounds 1, 2 and 3

Stoe IPDS diffractometer; data collection: Expose in IPDS (Stoe & Cie, 1999), cell determination and –refinement: Cell in IPDS (Stoe & Cie, 1999), integration: Integrate in IPDS (Stoe & Cie, 1999); numerical absorption correction: Faceit in IPDS (Stoe & Cie, 1999).

The crystals were mounted at –80 °C (N_2 stream), using the X-TEMP 2 device,[2] the crystal structure determination was effected at –100 °C (type of radiation: Mo-Kα, λ = 0.71073 Å). The structure was solved applying direct and fourier methods, using SHELXS-90 (G. M. Sheldrick, Universität Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, Universität Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 666392 (**1**), CCDC 666393 (**3**) and CCDC 666394 (**2**). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystallographic data for compound **1** (red blocks from diethylether): 0.40 × 0.40 × 0.20 mm^3, $C_{23}H_{48}LiN_5Si$, M = 429.69, monoclinic, space group $P2_1/c$ (no. 14), a = 14.714(4), b = 9.9895(12), c = 19.355(4) Å, β = 99.07(3)°, V = 2808.4(10) $Å^3$, Z = 4, D_c = 1.016 Mg/m^3, μ = 0.100 mm^{-1}. 28705 reflections measured with 2θ in the range 2.30-27.00°, 6091 unique reflections; 4745 with $I > 2\sigma(I)$ refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions; $R1$ = 0.0422 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1220 (all data).

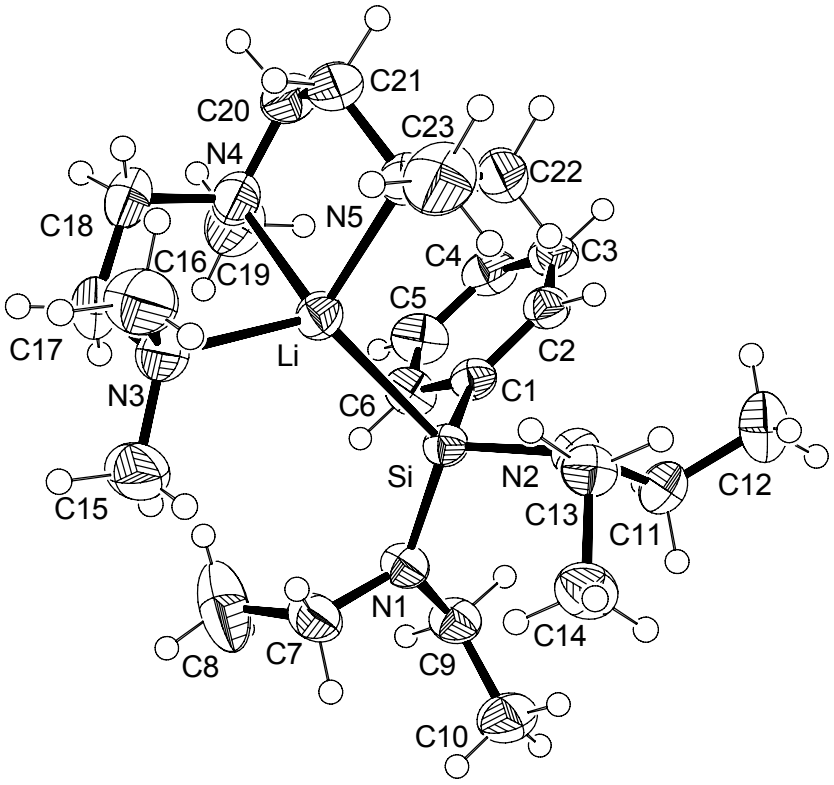


Fig. 2 ORTEP plot of **1** at 50 % probability level.

Crystallographic data for compound **2** (light brown blocks from diethylether): 0.40 × 0.30 × 0.20 mm^3, $C_{17}H_{34}LiN_3Si$, M = 315.50, monoclinic, space group $C2/c$ (no. 15), a = 17.245(3), b = 8.9641(17), c = 27.585(4) Å, β = 102.091(17)°, V = 4169.6(12) $Å^3$, Z = 8, D_c = 1.005 Mg/m^3, μ = 0.113 mm^{-1}. 12084 reflections measured with 2θ in the range 2.42-25.00°, 3674 unique reflections; 2011 with $I > 2\sigma(I)$;

refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions; $R1$ = 0.0510 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1168 (all data).

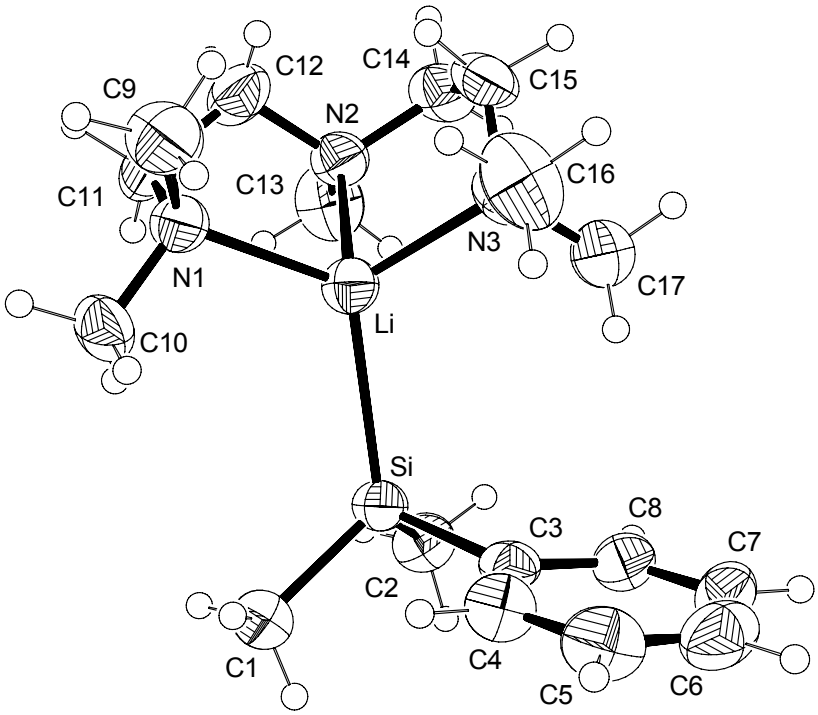


Fig. 3 ORTEP plot of **2** at 50 % probability level.

Crystallographic data for compound **3** (light brown blocks from diethylether): 0.30 × 0.30 × 0.20 mm^3, $C_{22}H_{36}LiN_3Si$, M = 377.57, orthorhombic, space group Fdd2 (no. 43), a = 18.287(14), b = 58.069(12), c = 9.1042(18) Å, V = 9668(3) $Å^3$, Z = 16, D_c = 1.038 Mg/m^3, μ = 0.107 mm^{-1}. 11024 reflections measured with 2θ in the range 2.34-26.00°, 4362 unique reflections; 3350 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions; $R1$ = 0.0572 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1501 (all data); absolute structure (Flack-) parameter 0.23 (16).

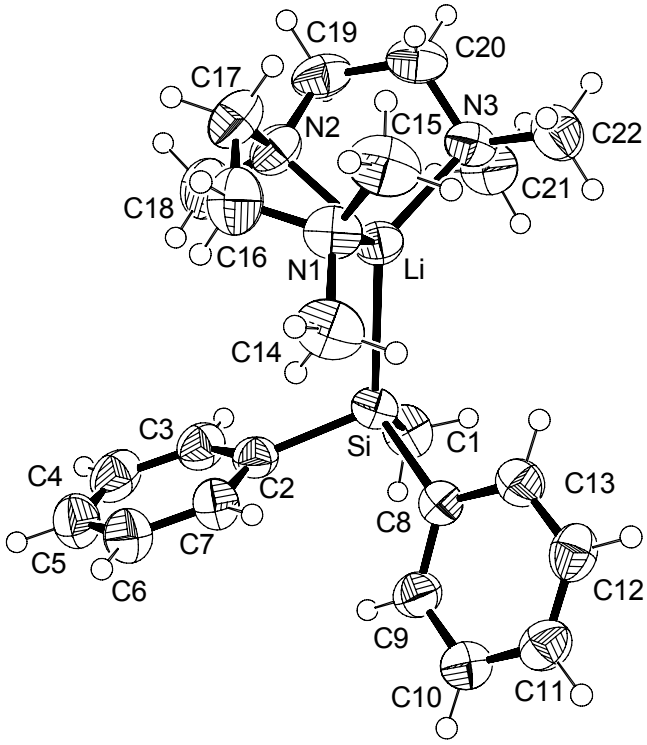


Fig. 4 ORTEP plot of **3** at 50 % probability level.

Computational Studies

All calculations were done without symmetry restrictions. Starting coordinates were taken from the crystal structure analysis of the lithiosilanes **1** (for the model systems **A** and **B**) and **2** (for the model system **C**) and modified with Chem 3D Ultra 8.0 prior to energy optimization at the B3LYP/6-31+G(d) level. Additional harmonic vibrational frequency analyses (to establish the nature of stationary point on the potential energy surface) were performed on the same level and showed no imaginary frequency. Subsequent natural bond orbital (NBO) analysis (to estimate the state of hybridization) were also performed on the same level. Table 3 lists the total and zero-point energy of the model systems **A**, **B** and **C**. Standard orientations of the model systems can be found in tables 4, 5 and 6.

Table 3 Results from Quantum Chemical Studies on the model systems **A**, **B** and **C**.

model	method/basis	total energy (Hartree)	zero point energy (Hartree)
A	B3LYP/6-31+G(d)	−790.3470243	−790.094105
B	B3LYP/6-31+G(d)	−1318.954219	−1311.432613
C	B3LYP/6-31+G(d)	−1129.612507	−1123.181641

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Table 4 Standard Orientation of **A** [B3LYP/6-31+G(d)].

atomic symbol	X	Y	Z
C	–3.142364	1.206707	–0.025486
C	–1.757384	1.200811	–0.220503
C	2.604496	2.193045	–0.557703
C	1.243053	1.804035	1.379994
C	–3.842648	0.000160	0.072093
N	1.441797	1.501299	–0.031856
C	–1.025145	–0.000155	–0.318872
C	–3.142643	–1.206573	–0.025903
Si	0.836520	–0.000243	–0.791356
C	–1.757650	–1.200932	–0.220963
N	1.440907	–1.502391	–0.032228
C	1.243135	–1.804182	1.379962
C	2.605483	–2.191960	–0.557315
H	–3.674995	2.152671	0.053430
H	–1.227667	2.149087	–0.293602
H	2.494839	3.286230	–0.453413
H	3.545009	1.912448	–0.044894
H	2.730161	1.969129	–1.624360
H	1.135957	2.890813	1.535828
H	2.090180	1.467588	2.006769
H	0.334259	1.325299	1.755738
H	–4.919769	0.000235	0.224315
H	–3.675523	–2.152395	0.052811
H	–1.228183	–2.149290	–0.294438
H	0.332973	–1.327731	1.755116
H	2.089189	–1.464786	2.006516
H	1.139142	–2.891114	1.536765
H	3.545478	–1.908207	–0.045231
H	2.730230	–1.969447	–1.624394
H	2.498504	–3.285219	–0.451192

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Table 5 Standard Orientation of **B** [B3LYP/6-31+G(d)].

atomic symbol	X	Y	Z
H	2.957138	2.889385	–2.894223
H	1.802392	–3.436927	–2.602050
H	3.855978	–2.086985	–2.480561
H	–2.175300	–0.027917	–2.855841
H	2.246151	0.575255	–2.407859
H	–0.892213	1.744014	–2.334908
C	2.771119	2.587389	–1.864551
H	–1.620655	3.267901	–1.762529
H	–3.906226	–0.382982	–2.846321
H	–3.585657	1.917729	–2.112390
H	3.254851	4.529315	–1.037958
H	2.123436	–4.029822	–0.959484
H	–2.754685	–2.755328	–2.910598
C	–3.037308	–0.170349	–2.196011
C	2.371492	1.276702	–1.584228
C	–1.173934	2.309241	–1.443405
H	–1.160455	–2.035478	–2.522770
C	1.649917	–3.206196	–1.531507
C	3.623666	–1.869944	–1.422536
C	2.940965	3.509545	–0.825581
C	–3.290504	1.117964	–1.410383
H	–0.258358	2.505788	–0.882214
C	–2.099408	–2.395679	–2.096670
H	0.575630	–3.239307	–1.323798
H	4.167928	–2.619303	–0.815178
H	4.035833	–0.884798	–1.188281
N	2.186711	–1.901719	–1.190598
H	–4.139151	0.976132	–0.734957
N	–2.109482	1.521928	–0.621542
N	–2.738638	–1.320938	–1.319131
H	–1.870094	–3.236059	–1.435993
H	–4.680643	–2.216685	–1.432072

C	2.131892	0.826858	–0.267458
H	–3.237557	3.038973	0.391138
C	2.713506	3.096099	0.491396
C	–3.956116	–1.844670	–0.684827
Si	1.346389	–0.911974	0.072581
C	–2.478562	2.262711	0.599463
H	–1.585357	2.790468	0.945215
Li	–1.270131	–0.391268	0.085433
H	2.856967	3.796304	1.313155
C	2.317631	1.779970	0.757506
H	–4.448372	–1.072478	–0.087970
H	–3.692214	–2.672088	–0.019096
H	3.922460	–0.393765	1.467855
H	2.162884	1.475295	1.791267
C	–3.938704	0.874298	1.396669
H	–3.000076	1.345567	1.710428
N	2.022438	–1.275273	1.722800
H	3.980777	–2.139100	1.805655
C	3.443631	–1.197983	2.033673
N	–2.053871	0.269192	2.054792
H	–3.242726	1.963808	2.595302
H	1.828562	–3.316523	2.355791
C	–0.892106	0.795156	2.796070
H	0.321751	–2.380424	2.267490
C	1.388170	–2.311490	2.516593
H	–0.188750	–0.014100	2.999588
H	–0.358276	1.536150	2.198757
H	–3.566028	–1.183311	2.315737
H	–1.205030	1.260330	3.748773
H	3.601400	–0.991108	3.107301
C	–2.717112	–0.762311	2.863727
H	–2.007709	–1.567168	3.077075
H	1.477168	–2.099792	3.598518
H	–3.087480	–0.362074	3.824894

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Table 6 Standard Orientation of **C** [B3LYP/6-31+G(d)].

atomic symbol	X	Y	Z
H	–4.367467	0.122044	–2.735113
H	–1.041175	4.007826	0.927762
H	–2.703278	3.505729	0.542142
H	1.419935	1.268215	–2.491902
H	–2.841185	1.653635	–1.555147
H	–0.287586	–0.100008	–2.563276
C	–3.955635	–0.166599	–1.770198
H	–0.125898	–1.844635	–2.918203
H	3.166326	1.171814	–2.794978
H	2.202613	–1.073935	–3.116906
H	–4.984351	–2.071826	–1.723278
H	1.424855	–3.396044	–0.688603
H	2.833205	3.453414	–1.376315
C	2.357811	0.849771	–2.113755
C	–3.086894	0.699257	–1.094413
C	–0.168053	–1.088602	–2.113726
H	1.152061	2.971590	–0.946618
H	–1.811268	0.591384	3.348108
H	–2.881125	1.933573	2.893339
C	–4.306581	–1.399563	–1.204284
C	2.265694	–0.683025	–2.086055
H	–1.038659	–1.262561	–1.480276
C	2.206774	2.857626	–0.688128
H	–1.217047	2.258145	3.438668
C	–1.640344	3.260639	0.383102
H	3.169179	–1.103864	–1.634750
N	1.076003	–1.113422	–1.282928
N	2.573359	1.404876	–0.735224
H	2.344901	3.223808	0.332909
H	4.680892	1.796343	–0.974465
C	–2.532803	0.381301	0.170513

H	1.656341	–3.194650	–1.353073
C	–3.796127	–1.738351	0.057134
C	3.995146	1.239496	–0.310200
Si	–1.189271	1.480739	1.018272
C	1.263699	–2.449439	–0.636871
H	0.274765	–2.796402	–0.323909
Li	1.090840	0.272619	0.329956
H	–4.086246	–2.677554	0.523796
C	–2.929713	–0.863631	0.723430
H	4.276751	0.183238	–0.323289
H	4.106579	1.620587	0.709275
H	–2.569936	–1.143781	1.711910
H	3.216336	–2.081798	0.254370
C	2.206590	–2.362093	0.574762
H	–0.306708	–1.909502	1.577171
C	–1.841542	1.570918	2.846144
N	1.750069	–1.332027	1.560924
H	2.279905	–3.357630	1.051228
C	0.516608	–1.781678	2.281890
H	0.226638	–1.006017	2.994309
H	3.724790	–0.697847	2.025121
H	0.698172	–2.730024	2.820191
C	2.825365	–1.030665	2.551781
H	2.481309	–0.228053	3.211292
H	3.077382	–1.913661	3.166679

Literature

[1] Trommer, K; Herzog, U; Georgi, U; Roewer, G *J. Prakt. Chem.* **1998**, *340*, 557.

[2] T. Kottke, D. Stalke, *J. Appl. Cryst.* **1993**, *26*, 615.

Complete reference 12 of the publication:

Gaussian 03 (Revision B.04), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda,

O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.