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Notes

Synthesis and Structure of Aryllithium Compounds Containing *ortho*-Directing (Dimethylamino)methyl and Trimethylhydrazino Substituents†

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*Summary: The ortho-lithiated aryl compounds [2-Me_2NCH_2-4,6-$(Me)_2C_6H_2]_2Li_2\cdot OEt_2$ (**2**) and [2-$Me_2N(Me)N$-$C_6H_4]_2Li_2\cdot$TMEDA (**6**) have been prepared by metalation of the corresponding precursors **1** and **5**. **6** is the first aryllithium derivative bearing a hydrazino group as coordinating ortho-substituent. Both organolithium compounds form in the solid a dimeric aggregate as shown by X-ray diffraction. The seven-line ^{13}C NMR signal ($^1J(^7Li-^{13}C) = 20$ Hz) of the ipso-carbon atoms of **6** is in agreement with a dimeric structure of this compound in solution (C_6D_6) as well.*

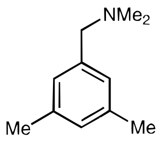
Introduction

Lithiation of aromatic compounds is markedly facilitated by *ortho*-directing groups such as NR_2, OR, CH_2NR_2, or $CONR_2$.[1] Ease and selectivity of these metalation reactions was assumed to originate from a precoordination of the attacking organolithium reagent to the donor center of the substrate as well as from an effective stabilization of the resulting aryllithium compound by an intramolecular coordination of the heteroatom to the lithium center. An alternative, more general, model stresses the importance of transition state stabilizing effects.[1f] The last years have seen a pronounced interest in solid state and solution structures of *ortho*-metalated compounds, and these have been shown to exist in a variety of oligomeric aggregates such as dimers,[2] trimers,[3] or tetramers.[2b,4]

Our interest in highly coordinated organosilicon compounds led us to search for new substituents which can be introduced to silicon via the corresponding aryllithium or Grignard compound and are suitable for intramolecular coordination to the silicon center. Here we will report on the synthesis and the structure of *ortho*-lithiated 1-((dimethylamino)methyl)-3,5-dimethylbenzene (**1**) and *N, N′,N′*-trimethylhydrazinobenzene (**5**).

Results and Discussion

Starting compound **1**[5] was obtained by reaction of ω-bromomesitylene with aqueous dimethylamine; in order to suppress quaternization of the initially formed **1**, a large excess of dimethylamine had to be used. The deprotonation of **1** was originally described by Hauser et al.,[5] and the degree of metalation was determined by reaction with benzophenone to be 52% after 24 h at room temperature. Under slightly different conditions we observed by means of ^1H NMR spectroscopy 87% conversion after 24 h; neither extended reaction times nor use of excess *n*-butyllithium drove the lithiation to completion. It is worth mentioning that the proton signals of remaining **1** in the reaction mixture were significantly shifted compared with its signals in the absence of **2**. We assume that this phenomenon is due to a coordination of **1** to **2**. Spectroscopically pure **2** was isolated by crystallization from Et_2O/hexane in 50−56% yield. According to the ^1H NMR spectrum, **2** crystallizes



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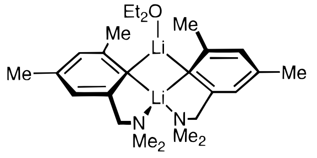

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† Dedicated to Prof. Dr. Günter Szeimies on the occasion of his 60th birthday.

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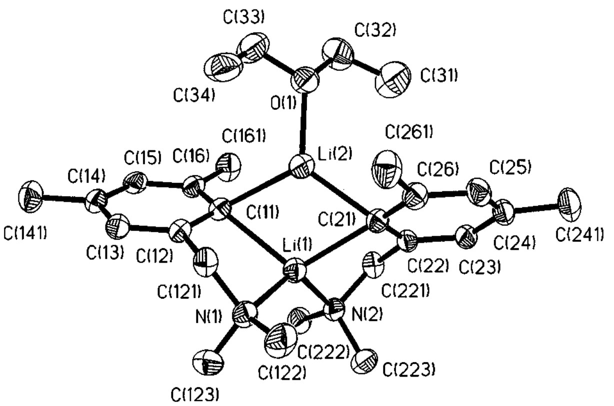


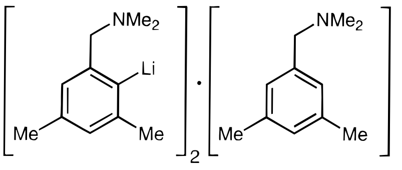
Figure 1. Crystal structure of **2**. Hydrogen atoms are omitted for clarity, and displacement ellipsoids are at the 50% probability level.

Table 1. Selected Distances (Å) and Bond Angles (deg) in 2

Li(1)−C(11)	2.256(5)	Li(1)−N(2)	2.057(5)	Li(2)−O(1)	1.961(5)
Li(1)−C(21)	2.216(5)	Li(2)−C(11)	2.170(5)	Li(1)−Li(2)	2.370(6)
Li(1)−N(1)	2.071(5)	Li(2)−C(21)	2.144(5)		

C(11)−Li(1)−C(21)	111.5(2)	C(11)−Li(2)−O(1)	118.8(2)
C(11)−Li(1)−N(1)	88.0(2)	C(21)−Li(2)−O(1)	123.2(2)
C(11)−Li(1)−N(2)	123.4(2)	Li(1)−C(11)−Li(2)	64.7(2)
C(21)−Li(1)−N(1)	123.3(2)	Li(1)−C(21)−Li(2)	65.8(2)
C(21)−Li(1)−N(2)	88.4(2)	Li(2)−O(1)−C(32)	121.5(2)
N(1)−Li(1)−N(2)	125.2(2)	Li(2)−O(1)−C(33)	117.1(2)
C(11)−Li(2)−C(21)	117.9(2)	C(32)−O(1)−C(33)	112.9(2)

with 0.5 equiv of Et_2O per aryllithium unit, which could not be removed at 10^{-3} Torr/20 °C. Heating a sample of **2** to 60 °C *in vacuo* resulted in defined decomposition yielding **3**, which is made up of 1 equiv of amine per two aryllithium units, and a solid (presumably LiOEt), which is insoluble in C_6D_6. This process is interpreted as an initial deprotonotion of Et_2O by the aryllithium, which is followed by a coordination of the formed amine **1** to the lithium center. Alternatively, **3** was obtained in quantitative yield, when 1 equiv of **1** was reacted with isolated **2**.



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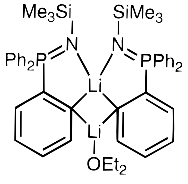
In the solid state **2** (Figure 1) adopts an approximately C_2-symmetric, dimeric structure, in which two lithium atoms are bridged by the *ipso*-carbon atoms of the aryl groups thus forming a planar Li_2C_2 ring (mean deviation: 0.015 Å). Whereas the geometry around Li(1) is distorted tetrahedral by additional coordinative interaction with two dimethylamino groups, Li(2) adopts a trigonal planar coordination . The distances of the *ipso*-carbon atoms to Li(1) are significantly elongated in comparison with the distances to Li(2) (Table 1). The central Li_2C_2 ring and O(1) are located in a plane (mean deviation: 0.014 Å), which forms tilt angles of 66.0 and 65.4°, respectively, with the plane of the aryl rings. In summary, the solid-state structure of **2** bears a strong resemblance to that of lithiated iminophosphorane **4**, which has been reported recently.[2f] Attempts to verify a dimeric bridged structure of **2** in solution as well by determining the $^7Li-^{13}C$ coupling pattern were unsuccessful. The signal of the *ipso*-carbon atoms was observed as a broad singlet at $\delta = 178.3$ in toluene-d_8 at room temperature. Cooling the solution to −90 °C resulted in a further broadening of the peak; no splitting due to $^7Li-^{13}C$ coupling was observed. However, the line width of 133 Hz is in accord with a coupling of carbon to two lithium atoms with an unresolved coupling constant of about 22 Hz, which is in the range of the coupling constants of dimeric aryllithium compounds.[2] The ^7Li NMR spectrum of **2** showed in the temperature range from 25 to −80 °C one singlet and, thus, did not reflect the inequivalence of the lithium nuclei, which was found in the solid state. Similar results were obtained with solutions of **3** in toluene-d_8.



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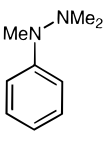

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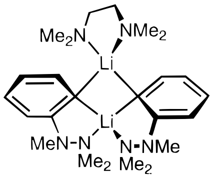
To the best of our knowledge, nothing has been reported about the *ortho*-metalation of hydrazino-substituted aromatic compounds. Having in mind the smooth deprotonation of *N*,*N*-dimethylbenzylamine or amine **1** by *n*-BuLi in Et_2O, one would expect that **5**, due to the more nucleophilic trimethylhydrazino substituent, would be more easily deprotonated than **1** under similar conditions. Surprisingly, **5** was not metalated by *n*-BuLi/Et_2O but was cleanly converted to **6** by use of the *n*-BuLi/TMEDA complex; anisole has been reported to exhibit a similar behavior toward *n*-BuLi.[6] Eventually, ^1H NMR spectroscopically pure **6** was isolated in about 50% yield by filtering off the precipitated solid; another 10−30% was obtained from the concentrated filtrate. Crystals suitable for X-ray structure analysis were grown from an *n*-pentane solution.



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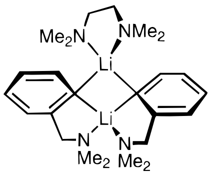

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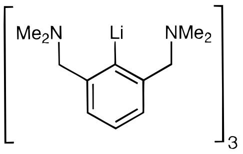

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Dimeric **6** adopts C_2 symmetry in the solid, thereby forming the Li_2C_2 quadrangle, which is characteristic of dimeric organolithium compounds (Figure 2). Li(1) is chelated by one TMEDA molecule, whereas Li(2) undergoes coordination to both dimethylamino groups. The different environments of Li(1) and Li(2) are reflected by the bond lengths to these atoms, which differ much more than in structurally analogous **7**[2e]

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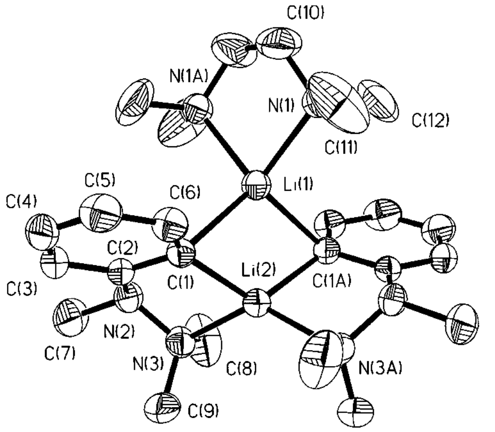

Figure 2. Crystal structure of **6**. Hydrogen atoms are omitted for clarity, and displacement ellipsoids are at the 50% probability level.

Table 2. Selected Distances (Å) and Bond Angles (deg) in 6

Li(1)−C(1)	2.284(4)	Li(2)−C(1)	2.114(4)	Li(1)−Li(2)	2.393(9)
Li(1)−N(1)	2.172(5)	Li(2)−N(3)	2.074(3)		

C(1)−Li(1)−C(1a)	107.4(3)	C(1)−Li(2)−C(1a)	121.0(3)
C(1)−Li(1)−N(1)	129.7(1)	C(1)−Li(2)−N(3)	84.2(1)
C(1)−Li(1)−N(1a)	104.0(1)	C(1)−Li(2)−N(3a)	120.8(1)
N(1)−Li(1)−N(1a)	84.0(2)	N(3)−Li(2)−N(3a)	130.7(3)
		Li(1)−C(1)−Li(2)	65.8(2)

(Table 2). The Li(1)−C and Li(1)−N distances compare well with the corresponding distances found in [PhLi·TMEDA]$_2$.[7] In contrast, the Li(2)−C and Li(2)−N bond lengths are significantly shorter and much more close to the bond lengths of the N-coordinated lithium atom in iminophosphorane **4**.[2f]

6 is only sparingly soluble in aliphatic or aromatic hydrocarbons. More polar solvents such as Et$_2$O or THF are more effective; however, **6** is rapidly protonated by these ethers. In C$_6$D$_6$, only one ^{7}Li NMR signal was observed at room temperature thus reflecting the occurrence of fast *inter*- or/and *intra*aggregate exchange processes in solution. However, the splitting of the ^{13}C-NMR signal of the *ipso*-carbon atoms into seven lines at 25 °C shows that *inter*aggregate exchange is slow on the NMR time scale at this temperature in a noncoordinating solvent such as C$_6$D$_6$. The multiplicity of the signal as well as the magnitude of the $^1J(^7\text{Li}-^{13}\text{C})$ coupling constant (20 Hz) is in agreement with a dimeric structure of **6** in solution but does not exclude the formation of trimeric aggregates as it was reported for **8**.[3]

In conclusion, we have shown that **1** and **5** undergo smoothly *ortho*-metalation with *n*-Buli/Et$_2$O and *n*-Buli/TMEDA, respectively, thereby forming dimeric aggregates in the solid. Forthcoming studies will address the utilization of this new aryllithium compounds to synthesize intramolecularly coordinated organosilicon compounds.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.9 MHz) and a Varian VXR 500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 125.7 MHz). C$_q$, CH, CH$_2$, and CH$_3$ were determined using the DEPT or APT pulse sequence. ^{7}Li NMR spectra were recorded on a Bruker MSL 400 (155.45 MHz) and a Varian VXR 500 (194.2 MHz). Chemical shifts refer to external LiCl/H$_2$O. Mass spectra were recorded on a Varian MAT 311 A. Elemental analyses were performed at Mikroanalytisches Labor der Georg-August-Universität Göttingen.

All manipulations of air- and moisture-sensitive compounds were carried out under an inert argon atmosphere using carefully dried glassware. Etheral solvents used were dried by refluxing over sodium and distilled immediately before use. Phenyltrimethylhydrazine (**5**) was prepared by upscaling and modification of a known procedure.[8]

1-((Dimethylamino)methyl)-3,5-dimethylbenzene (1). A solution of ω-bromomesitylene[9] (114 g, 0.57 mol) in 50 mL of toluene was added to a stirred aqueous solution of dimethylamine (725 mL of a 40% aqueous solution, 5.70 mol) and refluxed for 2 h. After cooling to room temperature, the mixture was acidified with 2 N hydrochloric acid, and 200 mL of EtO was added. After the suspension had been filtered to remove the quaternary ammonium bromide, the separated organic layer was extracted with three 70 mL portions of 2 N hydrochloric acid. The combined aqueous phases were made alkaline by addition of a concentrated aqueous NaOH solution and extracted with three 200 mL portions of Et$_2$O. The combined organic phases were dried over KOH and filtered, and the solvent was removed in vacuo. **1** was obtained from the remaining yellowish oil as a colorless liquid with bp 91 °C at 0.1 Torr (86.1 g, 93%). ^{1}H NMR (CDCl$_3$): δ 2.23 (s, 6 H, CH$_3$), 2.30 (s, 6 H, CH$_3$), 3.51 (s, 2 H, CH$_2$N), 6.90 (s, 1 H, ar H), 6.92 (s, 2 H, ar H). ^{13}C NMR (CDCl$_3$): δ 20.2 (CH$_3$), 45.5 (NMe$_2$), 64.5 (CH$_2$N), 126.9 (ar CH), 128.6 (ar CH), 137.7 (ar C$_q$), 138.8 (ar C$_q$). MS (EI, 70 eV): *m/z* (relative intensity) 163 (50) [M$^+$], 162 (36) [M$^+$ − H], 119 (56) [M$^+$ − NMe$_2$], 105 (27) [C$_6$H$_3$Me$_2^+$], 91 (15) [C$_7$H$_7^+$], 77 (12) [C$_6$H$_5^+$], 58 (100) [CH$_2$-NMe$_2^+$], 44 (26) [NMe$_2^+$]. Anal. Calcd for C$_{11}$H$_{17}$N: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.80; H, 10.48; N, 8.56.

[(4,6-Dimethyl-2-((dimethylamino)methyl)phenyl)-lithium]$_2$·Et$_2$O (2). To a solution of 21.50 g (131.7 mmol) **1** in Et$_2$O (200 mL) was added slowly at ambient temperature 90 mL of a 1.54 M solution of *n*-BuLi in hexane (138.6 mmol). Subsequent stirring for 22 h at room temperature afforded a red solution. The solution was concentrated in vacuo to approximately $^2/_3$ of its starting volume. On storing of the mixture overnight at −32 °C, a pale yellow precipitate was formed, which was filtered off, washed once with Et$_2$O, and dried in vacuo to yield 13.62 g (50%) of **2**. Crystals suitable for X-ray analysis were obtained by cooling a saturated solution of **2** in Et$_2$O to −15 °C. ^{1}H NMR (C$_6$D$_6$, c = 0.24 mol/L): δ 0.70 (t, ^3J = 7 Hz, 6 H, eth CH$_3$), 1.90 (s, 12 H, NMe$_2$), 2.37 (s, 6 H, CH$_3$), 2.65 (s, 6 H, CH$_3$), 2.98 (q, ^3J = 7 Hz, 4 H, eth CH$_2$), 3.0−4.1 (br s, 4 H, NCH$_2$), 6.84 (s, 2 H, ar H), 7.04 (s, 2 H, ar H). ^{13}C NMR (C$_6$D$_6$, c = 0.49 mol/L): δ 14.5 (eth CH$_3$), 21.6 (CH$_3$), 28.7 (CH$_3$), 44.8 (br, NMe$_2$), 66.1 (eth CH$_2$), 71.9 (CH$_2$N), 124.6 (ar CH), 125.8 (ar CH), 133.6 (ar C$_q$), 150.0 (ar C$_q$), 151.2 (ar C$_q$), 178.2 (br s, C$_{ipso}$). ^{7}Li NMR (C$_6$D$_6$): δ 3.25.

[(4,6-Dimethyl-2-((dimethylamino)methyl)phenyl)lithium]$_2$·3,5-Dimethyl-1-((dimethylamino)methyl)benzene (3). To a solution of **2** (0.50 g, 1.2 mmol) in 6 mL of hexane was added 0.20 g (1.2 mmol) of **1** at ambient temperature. The mixture was stirred for 0.5 h at room temperature, the solvent was removed, and the remaining pale yellow solid was dried in vacuo for 3 h to yield ^{1}H NMR spectroscopically pure **3** (0.60 g, 100%). ^{1}H NMR (C$_6$D$_6$, c = 0.24 mol/L): δ 1.89 (s, 6 H, CH$_3$), 1.90 (s, 12 H, NMe$_2$), 2.11 (s, 6 H, CH$_3$), 2.35 (s, 6 H, CH$_3$), 2.54 (s, 6 H, CH$_3$), 3.13 (s, 2 H, NCH$_2$), 3.2−4.0 (br s, 4 H, NCH$_2$), 6.70 (s, 2 H, ar H), 6.72 (s, 1 H, ar H), 6.86 (s, 2 H, ar H), 6.99 (s, 2 H, ar H). ^{13}C NMR (C$_6$D$_6$, c = 0.24 mol/L): δ 21.2 (CH$_3$), 21.6 (CH$_3$), 29.4 (CH$_3$), 44.7 (br, NMe$_2$), 45.2

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(9) Weiler, B. *Chem. Ber.* **1922**, *33*, 339.

Table 3. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for 2 and 6

	2	6
empirical formula	$C_{26}H_{42}Li_2N_2O$	$C_{24}H_{42}Li_2N_6$
M_r	412.515	428.52
cryst size (mm)	0.8 × 0.8 × 0.5	0.8 × 0.7 × 0.2
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	10.642(5)	12.106(2)
b (Å)	11.231(7)	13.654(3)
c (Å)	12.641(6)	17.189(3)
α (deg)	76.21(3)	90
β (deg)	73.58(2)	110.22(2)
γ (deg)	70.06(2)	90
V (Å^3)	1345.4(12)	2666.2(9)
Z	2	4
D_x (g cm^{-3})	1.018	1.068
μ (mm^{-1})	0.060	0.064
F(000)	452	936
range (deg)	$3.58 \leq 2\theta \leq 24.94$	$3.59 \leq 2\theta \leq 22.50$
range of hkl	$-11 \leq h \leq 12$	$-13 \leq h \leq 13$
	$-12 \leq k \leq 13$	$-14 \leq k \leq 14$
	$-9 \leq l \leq 14$	$-18 \leq l \leq 18$
no. of rflns collcd	5109	3052
no. of indep rflns	4690	1732
R(int)	0.0922	0.0388
no. of data	4686	1738
no. of params	290	151
S_{all}	1.038	1.067
g_1	0.097	0.08
g_2	0.7	4.0
$R1$ ($F > 4\sigma(F)$)	0.0646	0.06119
w$R2$ (all data)	0.1981	0.1794
largest diff peak (e Å^{-3})	0.240	0.221
largest diff hole (e Å^{-3})	−0.257	−0.238

(NMe_2), 64.7 (CH_2N), 71.7 (CH_2N), 125.0 (ar CH), 126.0 (ar CH), 127.5 (ar CH), 129.4 (ar CH), 133.6 (ar C_q), 137.9 (2 ar C_q), 150.0 (ar C_q), 151.4 (ar C_q), 178.1 (br s, C_{ipso}). ^{7}Li NMR (toluene-d_8): δ 3.09.

Phenyltrimethylhydrazine (5). To a solution of 10.5 mL (31.5 mmol) of 3 M H_2SO_4, 12.5 mL (168 mmol) of 37% formaline solution, and 50 mL of THF was added a suspension of 2.75 mL (28 mmol) of phenylhydrazine, 9.53 g (0.25 mol) of $NaBH_4$, and 50 mL of dry THF; the temperature was maintained at 20−30 °C. When the addition was half finished, the reaction mixture was acidified by another 10.5 mL (31.5 mmol) of 3 M H_2SO_4. The addition of the $NaBH_4$ slurry was finished, and after completion the suspension was stirred for a further 30 min. A 50 mL volume of H_2O was added, and the resulting suspension was made alkaline by addition of solid NaOH until pH > 11. The organic layer was separated and the aqueous layer extracted with two 50 mL portions of Et_2O. The combined organic phases were extracted with 50 mL of a saturated NaCl solution and dried over Mg_2SO_4. After removal of solvent in vacuo, the remaining brownish oil was distilled at 45 Torr. The pale yellow fraction boiling between 130 and 133 °C was collected and further purified by flash chromatography (column 5 × 40 cm, 40:1 PE/Et_2O, $R_f = 0.26$) to yield 2.94 g (70%) of **5**. ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 6 H, NMe_2), 2.76 (s, 3 H, NMe), 6.74 (tt, $^3J = 7$ Hz, $^4J = 1$ Hz, 1 H, ar H), 7.01 (d, $^3J = 8$ Hz, 2 H, 2 ar H), 7.23 (ddd, $^3J = 8$, $^3J = 7$, $^4J = 2$ Hz, 2 H, 2 ar H). ^{13}C NMR ($CDCl_3$): δ 26.6 (NMe), 41.0 (NMe_2), 112.9 (ar CH), 117.6 (ar CH), 128.8 (ar CH), 150.3 (ar C_q). MS (EI, 70 eV): m/z (relative intensity) 150 (100) [M^+], 135 (92) [$M^+ - Me$], 106 (63) [$M^+ - NMe_2$], 77 (45) [$C_6H_5^+$].

[(2-(Trimethylhydrazino)phenyl)lithium]$_2$·TMEDA (6). A solution of 0.48 g (3.2 mmol) of **5**, 1.4 mL (3.3 mmol) of 2.36 M n-BuLi/hexane solution, and 0.49 mL (3.3 mmol) of tetramethylethylenediamine in 10 mL of pentane was stirred at ambient temperature for 2 days, during which **6** precipitated as a white solid. The solution was filtered off, and 353 mg (50%) of **6** was isolated (dec 163 °C). Another 92 mg (13%), suitable for X-ray analysis, was obtained by concentrating the filtrate in vacuo and cooling it to −5 °C (dec 165 °C). ^{1}H NMR (C_6D_6): δ 1.82 (br s, 16 H, tmeda), 2.28 (s, 12 H, NMe_2), 2.57 (s, 6 H, NMe), 6.64 (d, $^3J = 8$ Hz, 2 H, ar H), 7.13 (dd, $^3J = 6$ Hz, $^3J = 7$ Hz, 2 H, ar H), 7.32 (dd, $^3J = 8$ Hz, $^3J = 7$ Hz, 2 H, ar H), 8.15 (d, $^3J = 6$ Hz, 2 H, ar H). ^{13}C NMR (C_6D_6): δ 27.0 (NMe), 40.9 (CH_2N), 45.9 (NMe_2), 57.6 (NMe_2), 110.8 (ar CH), 120.1 (ar CH), 124.1 (ar CH), 143.2 (ar CH), 162.9 (ar C_q), 176.6 (sept, $^1J_{C^7Li} = 20$ Hz, C_{ipso}). ^{7}Li NMR (C_6D_6): δ 2.91.

X-ray Structure Determination for 2 and 6. Crystal data, data collection, and least-squares parameters are summarized in Table 3. Data for **2** and **6** were collected on a STOE-Siemens-AED four-circle-diffractometer at −120 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Both structures were solved by direct methods.[10] All non-hydrogen atoms were refined anisotropically.[11] A riding model starting from calculated positions was employed for all hydrogen atoms. The structures were refined against F^2 with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$, where $P = (F_o^2 + 2F_c^2)/3$. The R-values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

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Supporting Information Available: For compounds **2** and **6**, tables of X-ray parameters, all atomic coordinates and U values, bond lengths and angles, and anisotropic displacement parameters (10 pages). Ordering information is given on any current masthead page.

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