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Lithiation of *N,N,N′,N′*-Tetramethylethylenediamine and the Structure in a Mixed Organolithium Aggregate

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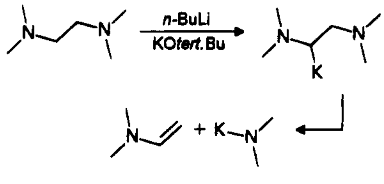
Summary: The dilithiation of 2-methyl-6-tert-butylphenol with 2 equiv of BuLi/tmeda in refluxing hexane results in low yields of the dilithiated product due to formation of lithiated tmeda as a side product. Excess BuLi/tmeda yields good conversion and crystals of a mixed aggregate consistent with the dilithiated product, lithiated tmeda, and tmeda. The structure of the mixed aggregate, revealed by single crystal X-ray diffraction, shows the first structural data for a lithiated tmeda molecule.

Introduction

The deprotonation of C−H bonds usually requires the use of strongly basic organoalkali compounds.[1] Undoubtedly, commercially available *n*-butyllithium in hexane is the most frequently used metalating reagent, but as such it lacks power to deprotonate the weaker "organic C−H acids". Besides the increase of the temperature and concentration of the metalating reagent, efficient means for gaining deprotonating power are use of the following: polar solvents (*e.g.* THF)[2] or metal-chelating cosolvents (*e.g. N,N,N′,N′*-tetramethylethylenediamine = tmeda),[3] breaking the butyllithium hexamer in smaller more reactive species;[4] stronger bases, *e.g. t*-BuLi;[5] superbase mixtures such as BuLi/MO-*t*-Bu (M = Na, K, Cs).[6]

These methods have been proven to be effective, but combinations should be used carefully. These can form very powerful metalating systems which easily attack solvents and (or) cosolvents and result in side products and loss of base.[7] Thus, combining *t*-BuLi and tmeda at low temperature and warming up to room temperature results in lithiation of the tmeda ligand mainly in the methyl group (eq 1).[8] Mixing of BuLi/KO-*t*-Bu and tmeda results in methylene metalation of the tmeda ligand followed by elimination of dimethylamide (eq 2).[8]

(1)



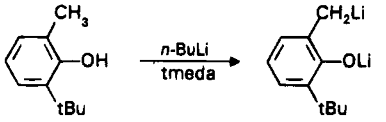
(2)

The mixture BuLi/tmeda in hexane at room temperature is commonly regarded to be stable, but it has been reported that warming to +50 °C completely deprotonates the tmeda cosolvent within several hours.[9] Despite its unstability at higher temperature, BuLi/tmeda in refluxing hexane has been used as an effective metalating reagent for the weaker "organic C−H acids", giving the desired lithium compound in good yields.[10]

We here report a lithiation reaction with BuLi/tmeda in refluxing hexane where substantial amounts of lithiated tmeda are found as a side product and describe the crystal structure of a mixed aggregate which incorporates the lithiated tmeda.

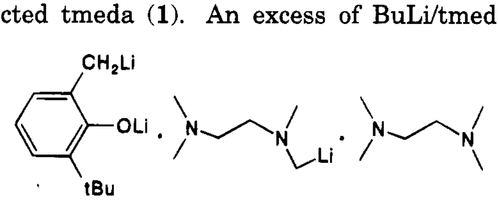
Results and Discussion

We generally use BuLi/tmeda in refluxing hexane as a metalating reagent for syntheses of polymetalated systems. Low yields were found when 2.2 equiv of BuLi/tmeda was used in the dilithiation of 2-methyl-6-*tert*-butylphenol (eq 3).[11]



(3)

The low yields of the dilithiated species correspond well with the observation of substantial amounts of lithiated tmeda as a side product. Crystals obtained from this reaction mixture consist of the dilithiated species, lithiated tmeda (methyl group lithiation), and unreacted tmeda (**1**). An excess of BuLi/tmeda (3.3



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[10] Lithiation of *N,N*-dimethylaniline or dilithiation of benzyl alcohol in refluxing *n*-BuLi/tmeda/hexane (10% excess) gives after functionalization the desired isolated products in high yields of 95% and 86%, respectively: see ref 1c, p 202.

[11] Addition of excess methanol-d_1 to the reaction mixture resulted in 41% deuteration of the benzylic group.

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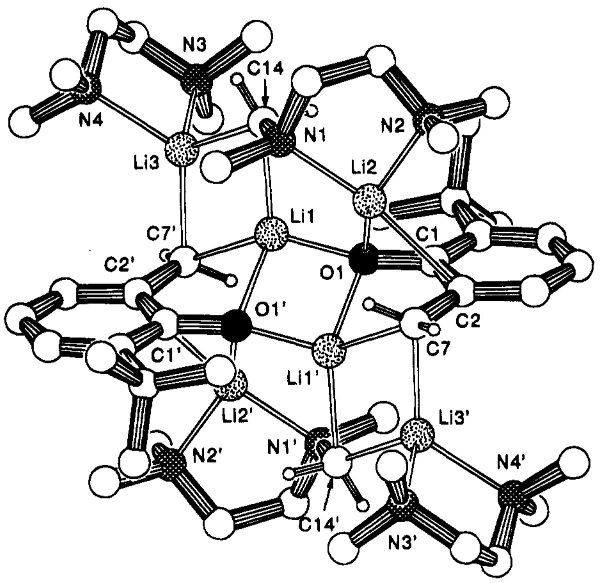

Figure 1. Plot of the dimeric structure of **1**. (Oxygen atoms are black, nitrogen atoms are checkered, and lithium atoms are speckled.)

equiv) yields practically complete conversion for this dilithiation reaction[12] and good yields of crystalline **1**. The crystal structure of this unique mixed aggregate combined from a lithium arenolate, a benzyllithium moiety, and an α-amino methyllithium species has been determined by single crystal X-ray diffraction.

Compound 1 crystallizes as a crystallographically centrosymmetric dimer (Figure 1). Li1 is bridging between the benzylic CH_2^- and the phenolic O^-. Dimerization via the Li−O bond results in an additional O−Li1 contact. Li2 completes the oxygen bonding sphere and is solvated by a tmeda ligand, which itself is lithiated in the methyl group. The NCH_2(Li3) moiety combines with the benzylic CH_2(Li1) part to form a dimeric substructure. The peripheral Li3 and Li3′ atoms are solvated by tmeda ligands which complete their coordination sphere.

Fractional atomic coordinates and selected bond distances/angles are summarized in Tables 1 and 2, respectively. The O−Li bond distances vary from 1.869(4) to 2.001(4) Å. The shorter O−Li1 bond of 1.869(4) Å is nearly collinear with the C−O bond (C−O−Li = 165.7(2)°), whereas the two longer O−Li bonds of 1.999(4) and 2.001(4) Å are approximately perpendicular to the C−O axis (C−O−Li = 86.1(2) and 107.8(2)°, respectively). A similar bonding situation is observed in the structure of {(lithium 4,6-dimethyl-2-(sodiomethyl)phenoxide)(tmeda)}$_4$.[13]

Table 1. Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)[a,b]

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Li1	0.0983(3)	0.0241(2)	0.0871(5)	0.031(1)
Li2	0.1421(4)	−0.0818(2)	0.0012(5)	0.033(1)
Li3	0.2478(4)	0.0999(2)	0.2116(5)	0.037(1)
O1	0.0389(1)	−0.0505(1)	0.0856(2)	0.025(1)
C1	0.0211(2)	−0.1062(1)	0.1132(3)	0.024(1)
C2	−0.0260(2)	−0.1426(1)	−0.0143(3)	0.027(1)
C3	−0.0403(2)	−0.2020(1)	0.0061(3)	0.036(1)
C4	−0.0149(3)	−0.2248(1)	0.1432(4)	0.044(1)
C5	0.0274(3)	−0.1891(1)	0.2644(3)	0.040(1)
C6	0.0470(2)	−0.1295(1)	0.2534(3)	0.030(1)
C7	−0.0621(2)	−0.1167(1)	−0.1596(3)	0.032(1)
C8	0.0995(2)	−0.0949(1)	0.3972(3)	0.036(1)
C9	0.0917(4)	−0.0290(2)	0.3830(4)	0.061(1)
C10	0.2244(4)	−0.1103(2)	0.4735(5)	0.098(2)
C11	0.0388(5)	−0.1102(2)	0.4971(5)	0.091(2)
N1	0.2602(2)	−0.0200(1)	−0.0093(2)	0.032(1)
N2	0.2662(2)	−0.1466(1)	0.0378(3)	0.035(1)
C12	0.3705(2)	−0.1112(1)	0.0837(3)	0.039(1)
C13	0.3558(2)	−0.0574(1)	−0.0079(4)	0.043(1)
C14	0.2844(2)	0.0112(1)	0.1322(3)	0.036(1)
C15	0.2358(3)	0.0229(1)	−0.1262(4)	0.049(1)
C16	0.2427(3)	−0.1759(2)	−0.0999(4)	0.055(1)
C17	0.2750(3)	−0.1903(1)	0.1485(4)	0.051(1)
N3	0.3454(2)	0.1071(1)	0.4474(3)	0.049(1)
N4	0.3697(2)	0.1674(1)	0.2040(3)	0.055(1)
C18	0.4278(3)	0.1541(2)	0.4668(5)	0.071(1)
C19	0.4654(3)	0.1578(2)	0.3398(6)	0.077(1)
C20	0.2730(4)	0.1192(2)	0.5290(4)	0.072(1)
C21	0.4052(3)	0.0521(2)	0.4945(4)	0.072(1)
C22	0.3232(3)	0.2269(2)	0.1996(5)	0.071(1)
C23	0.4039(5)	0.1623(2)	0.0810(7)	0.103(2)
H71	−0.0198	−0.0844	−0.1800	0.050
H72	−0.0706	−0.1434	−0.2400	0.050
H141	0.2911	−0.0224	0.2000	0.050
H142	0.3604	0.0281	0.1600	0.050

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Coordinates of unrefined CH_2Li and NCH_2Li are included.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1[a]

Li1−O1	1.869(4)	Li2−C1	2.289(5)	C2−C7	1.463(4)
Li1−O1′	2.001(4)	Li2−C2	2.496(5)	C7−H71	0.98
Li1−C14	2.236(5)	Li3−N4	2.207(5)	C7−H72	0.98
Li1−C7′	2.346(5)	Li3−N3	2.192(5)	N1−C14	1.502(3)
Li2−O1	1.946(5)	Li3−C7′	2.233(5)	C14−H141	1.01
Li2−N1	2.093(5)	Li3−C14	2.297(5)	C14−H142	0.97
Li2−N2	2.087(5)	O1−C1	1.344(3)		

O1−Li1−O1′	93.5(2)	N4−Li3−C14	111.9(2)
O1−Li1−C14	105.5(2)	C7′−Li3−C14	114.1(2)
O1′−Li1−C14	134.7(2)	C1−O1−Li1	165.7(2)
O1−Li1−C7′	134.9(2)	C1−O1−Li2	86.1(2)
O1′−Li1−C7′	77.5(2)	Li1−O1−Li2	90.3(2)
C14−Li1−C7′	112.1(2)	C1−O1−Li1′	107.8(2)
O1−Li2−N2	140.6(3)	Li1−O1−Li1′	86.5(2)
O1−Li2−N1	112.6(2)	Li2−O1−Li1′	104.0(2)
N2−Li2−N1	89.4(2)	Li3′−C7−Li1′	66.5(2)
O1−Li2−C1	35.9(1)	C2−C7−H71	121
O1−Li2−C2	62.2(1)	C2−C7−H72	117
N3−Li3−N4	82.9(2)	H71−C7−H72	101
N3−Li3−C7′	109.6(2)	Li1−C14−Li3	67.3(2)
N4−Li3−C7′	123.8(2)	N1−C14−H141	102
N3−Li3−C14	109.3(2)	N1−C14−H142	106
		H141−C14−H142	108

[a] Atoms designated with a prime are symmetry-related by the transformation −*x*, −*y*, −*z*.

Figure 2a shows a plot of the partial structure giving a more detailed picture of the Li bonding geometry in the lithium 2-(lithiomethyl)-6-*tert*-butylphenoxide fragment. Li1′ bridges the benzylic CH_2^- and phenolic O^-. The interaction of Li1′ with the aryl ring π-electron density, a feature often observed in benzylic alkali metal compounds,[14] seems of little significance. The shortest ring contact Li1′−C1 is 2.730(5) Å, but the position of Li1′ close to the aryl ring plane (0.464(7) Å) prohibits any substantial interaction with the π-system. On the other hand, such interactions are observed in the bonding geometry for Li2 which is situated above the

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[12] Addition of excess methanol-d_1 to the reaction mixture resulted in 90% deuteration of the benzylic group.

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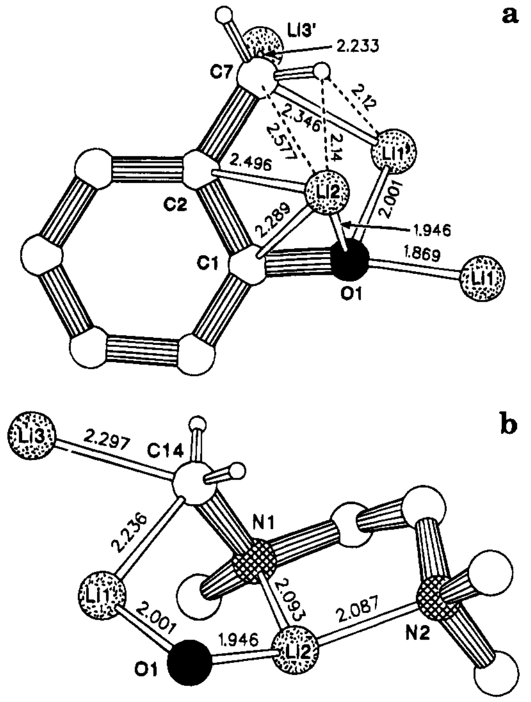
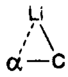


Figure 2. Plots of partial structures: (a) lithium bonding geometry for lithium 2-(lithiomethyl)-6-*tert*-butylphenoxide (viewed perpendicular on the aryl ring; distances given in Å); (b) lithium bonding geometry for the lithiated tmeda ligand.

aryl ring plane and has short bonding interactions with C1 and C2. Likewise, the distance between Li2 and the benzylic carbon (Li2−C7 = 2.577(5) Å) suggests a bonding interaction. However, the hybridization and electron density distribution at the benzylic carbon is such that electrostatic bonding is weak. From the localization of the benzylic hydrogens in the difference Fourier map it follows that the benzylic carbon is pyramidilized to a considerable extent (sum of HCH/HCC bond angles is 339.8°; for a planar sp^2-hybrid the sum of bond angles should be 360°, and for an ideal pyramidal sp^3-hybrid this should be 328.6°). Therefore, the interaction between Li2 and the "benzylic lone pair", which is pointing to the opposite direction, should be considered weak. The positions of the benzylic hydrogens also provide an explanation for the assymmetric bridging of the benzylic group between Li1′ and Li3′. The shorter C−Li bond distance to Li3′ is a consequence of the "benzylic lone pair" direction.

Very short agostic interactions between Li1′/Li2 and one of the benzylic protons are observed. This benzylic proton is bridging the atoms Li1′ and Li2 with distances of 2.12 and 2.14 Å, respectively (Figure 2a). The observed Li···H distances are comparable to the short agostic Li···H contacts of 2.2(1) Å observed between tetramers in the structure of $(MeLi)_4$[15] and agostic Li···H interactions of 2.115(8) Å in the neutron diffraction structure of $LiB(Me)_4$.[16]

The partial structure showing the lithiated tmeda molecule and its lithium coordination is depicted in Figure 2b. The lithiated methyl group bridges the atoms Li1 and Li3, whereas the ligand itself chelates Li2. Such behavior is not unexpected for organolithium compounds with a possible coordinating α-heteroatom. Intramolecular lithium coordination via a three-membered ring results in relatively strained bonding in which Li bridges the negatively charged carbon and the α-heteroatom (**2**).[17]



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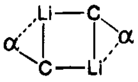

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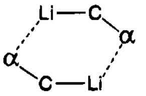

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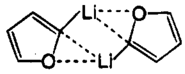

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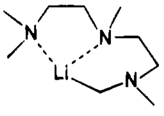

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In dimeric structures this generally leads to ring enlargement (**3** → **4**).[18] Only few examples of intramolecular lithium coordination via a three-membered ring have been observed in benzofuryllithium compounds.[19] However, also in these compounds the strained intramolecular coordination partly weakens C−Li bonds within these dimers (**5**) resulting in a structure intermediate between **3** and **4**. *Ab initio* calculations on lithiated *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (**6**) also suggest no intramolecular lithium coordination via the α-amine functionality.[20]

A comparison of the structural properties of tmeda with those of lithiated tmeda would be appropriate. Unfortunately, the well-documented disorder commonly observed for metal-chelating tmeda ligands[18b,19a] prohibits an accurate statistic database study on the structure of such ligands. However, an internal comparison of the structure of the lithiated tmeda with that of unreacted tmeda, both present in **1**, shows the following features.

The $N-CH_2Li$ bond length of 1.502(3) Å is slightly longer than the N−Me bonds (range 1.450(5)−1.480(5) Å; average 1.462(5) Å). This is most likely due to repulsive N(lone pair)−"CH_2^-(lone pair)" interactions. A similar, but more pronounced, situation has been reported for α-oxygen organolithium compounds of which structure and reactivity has been related to that of lithium carbenoids (**2**, α = halogen).[21] The small elongation of the $N-CH_2Li$ bond in lithiated tmeda indicates little carbenoid character. This corresponds well with the results of a study on structure and

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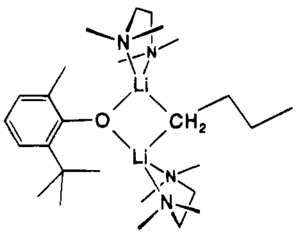
reactivity of a series of α-lithiated amines to which no significant carbenoid character could be ascribed.[22]

The lithiated tmeda ligand is chelating Li2 with relatively short N−Li distances of 2.093(5) and 2.087(5) Å. These N−Li distances are shorter than those observed in chelation of Li3 by the unreacted tmeda ligand (2.192(5) and 2.207(5) Å). Nevertheless, it is not likely that lithiation of the Me group in a tmeda ligand results in stronger lithium chelating. A Crystallographic Database search[23] shows large variance for the N−Li bond distances in tmeda−Li fragments (1.999−2.347 Å). These bond lengths seem to depend more on steric effects and coordinative saturation of the chelated lithium atom.

It is not clear why considerable amounts of **1** are formed when treating 2-methyl-6-*tert*-butylphenol with 2.2 equiv of BuLi/tmeda. Under similar reaction conditions, 2-methyl-4-*tert*-butylphenol gives good yields of the dilithiated product.[24] It is most likely that benzylic lithiation of both substrates proceeds via a mixed aggregate of butyllithium and the lithium aryloxide in which the lithiums are solvated by tmeda ligands. The steric consequence of a *tert*-Bu group at the ortho position will induce bending of one of the tmeda ligands to the reactive butyl anion (**7**) and could accelerate deprotonation of tmeda relative to that of benzylic metalation.



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Experimental Section

General Conditions. All experiments were carried out in an inert argon atmosphere using Schlenk techniques and syringes. Solvents were freshly destilled from sodium/benzophenone prior to use.

NMR spectra were recorded on Bruker AC 250 and Jeol 400 machines (^{1}H frequencies of 250 and 400 Mhz, respectively). ^{1}H and ^{13}C chemical shifts (δ) are given with respect to TMS. Internal solvent signals were used for referencing: methanol-d_4 (^{1}H, C*H*D$_2$OD, δ = 3.30 ppm; ^{13}C, *C*D$_3$OD, δ = 49.0 ppm).

Synthesis of 1. A mixture of 2-methyl-6-*tert*-butylphenol (1.0 g, 6.1 mmol), tmeda (3.0 mL, 19.9 mmol), and 20 mL of hexane is heated to reflux temperature. *n*-BuLi (1.6 M in hexane, 12.4 mL, 19.9 mmol) is slowly added via a syringe through the reflux condenser, resulting in a vigorous evolution of butane. The reaction mixture is refluxed for 1 h and turns gradually bright yellow. Slow cooling of this yellow solution and standing for 1 night at +4 °C yields yellow crystals of **1** suitable for X-ray diffraction (yield: 1.79 g, 4.3 mmol, 71%). Crystals have limited solubility in THF and toluene. An NMR study in these solvents shows at various temperatures complicated spectra with strongly broadened signals probably arising from complex dynamic processes. ^{13}C-NMR data could not be obtained due to limited solubility and extensive signal broadening. Crystals were characterized by NMR analysis of the quench products. ^{1}H and ^{13}C NMR spectra of crystals dissolved (and deuterated) in methanol-d_4 reveal their composition and the regioselectivity of the lithiation.

^{1}H-NMR data (methanol-d_4): 1.40 (s, 9H, C_4H_9); 2.16 (t, ^2J(H,D) = 2.0 Hz, 2H, CH_2D); 2.22 (t, ^2J(H,D) = 1.6 Hz, 2H, NCH_2D); 2.24 (s, 22H, NCH_3); 2.45 (s, 8H, NCH_2); 6.30 (t, ^3J(H,H,) = 7.5 Hz, 1H, aromatic CH); 6.80 (dd, ^3J(H,H,) = 7.5 Hz, ^4J(H,H) = 1.8 Hz, 1H, aromatic H); 6.90 (dd, ^3J(H,H,) = 7.5 Hz, ^4J(H,H) = 1.8 Hz, 1H, aromatic H). ^{13}C-NMR data (methanol-d_4): 18.5 (t, ^1J(C,D) = 19.0 Hz, CH_2D); 30.8 and 35.8 (*t*-Bu); 45.5 (t, ^1J(C,D) = 19.7 Hz, NCH_2D); 45.9 (NCH_3); 57.9 (NCH_2); 113.8, 124.4, 128.6, 128.7, 138.7, 164.8 (aromatic C's).

X-ray Structure Determination of 1. A single crystal with dimensions 0.4 × 0.4 × 0.5 mm³, protected by a layer of paraffin oil, was placed on top of a glass fiber and immediately mounted in the cold nitrogen stream of an Enraf-Nonius CAD4 diffractometer (λ(Mo Kα) = 0.710 69 Å). The cell constants were determined by refining the setting angles of 25 reflections with θ in the range of 12−17°. The system was checked for higher symmetry by reduced cell calculations (DELOS[25] and LePage[26]). The monoclinic space group $P2_1/c$ was fully determined by systematic absences. Crystal data: monoclinic, a = 12.648(4), b = 22.949(2), c = 9.968(3) Å; β = 113.03(1)°; V = 2663(1) Å^3; space group $P2_1/c$; formula $(C_{11}H_{14}OLi_2)(C_6H_{15}LiN_2)(C_6H_{16}N_2)$; Z = 2, d_{calcd} = 1.034 g/cm^3, μ = 0.58 cm^{-1}. A total of 6533 reflections were collected as $\omega-2\theta$ scans at T = −75 °C up to θ = 27.4° ($-16 \le h \le 15$, $-29 \le k \le 0$, $0 \le l \le 12$) of which 6024 reflections were unique. Corrections for Lorentz polarization effects were applied.[27] The hourly measurement of three standard reflections indicated a decay of 15.6% which was corrected anisotropically. The structure was solved by direct methods.[28] Full matrix least-squares refinement on F^2 with all reflections and 280 parameters converged to wR2 = 28.8% ($R(F)$ = 7.2% for 3419 observed reflections with $F \ge 4\sigma(F)$).[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 43 hydrogen atoms were found in difference Fourier syntheses. Two hydrogen atoms of a tmeda methyl group were introduced at calculated positions. The parameters of all 45 hydrogen atoms were fixed during refinement.

Neutral atom scattering factors were used for all atoms.[30] Anomalous dispersion factors were taken from Cromer and Liberman.[31] The EUCLID package has been used for illustrations.[32]

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Supplementary Material Available: For compound **1**, tables of crystal and structure refinement data, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and U(eq) values and an ORTEP plot (9 pages). Ordering information is given on any current masthead page.

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