2-(lithio-^6Li)benzofuran–tmeda, 2-(lithio-^6Li)benzothiophene–tmeda, and 2-(lithio-^6Li)benzoselenophene–tmeda were prepared by dissolving crystals (prepared in the manner as described above using [(lithio-^6Li)-n-butyl]lithium[13c]) in dry 5-mm tubes in 0.5 mL of toluene-d_8.

NMR spectra were recorded on a JEOL GX400 spectrometer (^1H, 400 MHz) on a 5-mm dual $^1H/^{13}C$ probehead. The 90° pulse lengths are as follows: ^1H, 15 µs; ^{13}C, 9 µs. One-dimensional ^{13}C spectra were recorded with a 25 000 Hz frequency width, 32K data points, a 3.2-s repetition time, and 30° pulses. Zero filling to 64K and Gaussian apodization was carried out before Fourier transformation to give the spectra in Figures 6 and 9.

Selected parameters of the COLOC[17] spectrum in Figure 8 are as follows: ^1H frequency width, 363 Hz; ^{13}C frequency width, 6353 Hz; 1024 data points in t_2 with zero filling to 2048; 16 increments in t_1 with zero filling to 64; Gaussian apodization in t_2 (GF 12, BF-5) and in t_1 (GF 25, BF-15); 512 scans per t_1 increment; Δ_1 = 25 ms, Δ_2 = 30 ms.

Supplementary Material Available: Tables of thermal parameters, fractional coordinates, bond distances, bond angles, and torsion angles (11 pages); listings of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

Crystal Structure of [2,6-Bis(dimethylamino)phenyl]lithium: The First Trimeric Organolithium Compound

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The X-ray structure of [2,6-bis(dimethylamino)phenyl]lithium reveals the first trimeric organolithium species. This trimer is retained in apolar solvents like benzene or toluene. On the basis of NMR data a monomer–trimer equilibrium is proposed in THF solution.

Introduction

Organolithium compounds can exist in a variety of aggregation states.[1] Monomers (1), dimers (2), tetramers, (3), and hexamers (4) are common and polymers are also known.[2,3] Since the nature of the C–Li bond is largely ionic,[4-7] high aggregation states containing a maximum of C⁻–Li⁺ contacts are favored. According to high level ab initio calculations,[7] association of methyllithium monomers into dimers, trimers, or tetramers yields 22.2, 26.3, and 30.7 kcal/mol energy per monomer, respectively.
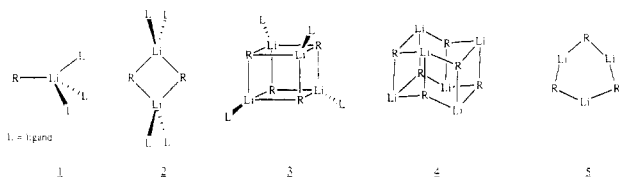
However, in solution entropy and solvation effects also are important. In the absence of solvent ligands, dissociation of tetramers into trimers is calculated to be favored over dissociation into dimers, but this preference reverses when solvation is included.[7] These calculations are consistent with the numerous tetramer–dimer equilibria found in solution.[8] Two dimers may be stacked to give a tet-

ramer.[9,10] The X-ray[11a,b] and solution[11b] structure of tetrakis[(2,6-dimethoxyphenyl)lithium] show this stacking concept nicely.

Hexameric organolithium compounds (4) are formally comprised of two stacked trimers.[10,12] NMR studies of alkyllithium compounds in solution, however, show hexamer/dimer + tetramer equilibria to be present.[13,14] Although the dissociation of hexameric aggregates into trimers is not excluded,[10,14,15] the existence of trimeric aggregates in solution has never been proven. This work reports the first trimeric organolithium compound in the solid state as well as in solution.

Results and Discussion

X-ray Structure. The X-ray structure of [2,6-bis(dimethylamino)phenyl]lithium (7) reveals a trimeric aggre-

(1) Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1985, 24, 353.
(2) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* 1985, 4, 2117.
(3) Köster, H.; Weiss, E. *Chem. Ber.* 1982, 115, 3422.
(4) Streitwieser, A.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* 1987, 98, 4778.
(5) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* 1987, 109, 5909.
(6) Bushby, R. J.; Steel, H. L. *J. Organomet. Chem.* 1987, 336, C25.
(7) Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* 1988, 7, 1597.

(8) (a) Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* 1966, 88, 4625. (b) Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Corby Young, T. *Organometallics* 1980, 5, 1851. (c) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* 1984, 107, 1805. (d) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* 1985, 68, 1848.
(9) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* 1982, 104, 5490.
(10) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* 1986, 295.
(11) (a) Dietrich, H.; Mahdi, W.; Storck, W. *J. Organomet. Chem.* 1988, 349, 1. (b) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1988, 110, 7802.
(12) Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* 1974, 96, 6048.
(13) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M. *J. Am. Chem. Soc.* 1984, 106, 256.
(14) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* 1980, 102, 3345.
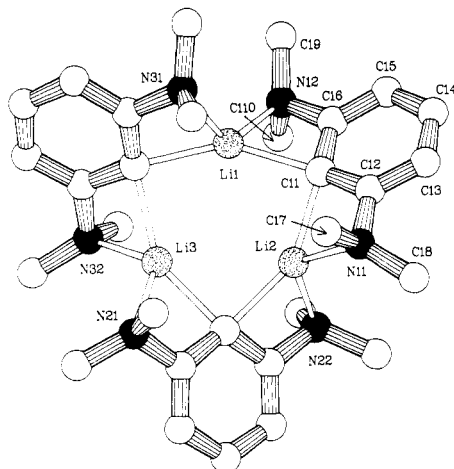(15) Darensbourg, M. Y.; Kimura, B. Y.; Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* 1970, 92, 1236.

Figure 1. Plot of the trimeric [2,6-bis(dimethylamino)-phenyl]lithium. Hydrogen atoms have been omitted for clarity.

Table I. Positional and Equivalent Thermal Parameters for the Non-Hydrogen Atoms in [2,6-Bis(dimethylamino)phenyl]lithium

atom	x/a	y/b	z/c	U_{eq}, Å^2
N(11)	0.9667 (2)	0.2220 (2)	0.0509 (1)	0.067 (1)
N(12)	0.8960 (2)	0.2181 (1)	-0.2066 (1)	0.059 (1)
N(21)	1.4408 (3)	0.3596 (1)	0.0350 (1)	0.060 (1)
N(22)	1.2303 (3)	0.1030 (1)	0.0129 (1)	0.074 (1)
N(31)	0.9527 (3)	0.4266 (1)	-0.1593 (1)	0.065 (1)
N(32)	1.3968 (2)	0.3290 (2)	-0.1518 (1)	0.060 (1)
Li(1)	1.0104 (5)	0.3061 (3)	-0.1416 (2)	0.061 (2)
Li(2)	1.1215 (5)	0.2071 (3)	-0.0070 (2)	0.066 (2)
Li(3)	1.3129 (5)	0.3169 (3)	-0.0625 (2)	0.066 (2)
C(11)	0.9287 (3)	0.2218 (2)	-0.0782 (1)	0.054 (1)
C(12)	0.8756 (3)	0.2040 (2)	-0.0186 (1)	0.057 (1)
C(13)	0.7515 (3)	0.1700 (2)	-0.0226 (2)	0.066 (1)
C(14)	0.6719 (3)	0.1511 (2)	-0.0898 (2)	0.072 (1)
C(15)	0.7166 (3)	0.1662 (2)	-0.1512 (2)	0.064 (1)
C(16)	0.8415 (3)	0.2007 (2)	0.1440 (1)	0.053 (1)
C(17)	0.9669 (3)	0.3063 (2)	0.0674 (1)	0.093 (2)
C(18)	0.9421 (3)	0.1758 (2)	0.1114 (1)	0.112 (2)
C(19)	0.7936 (3)	0.2335 (2)	-0.2732 (1)	0.089 (1)
C(21)	1.3359 (3)	0.2316 (2)	0.0241 (1)	0.053 (1)
C(22)	1.4457 (3)	0.2776 (2)	0.0587 (1)	0.052 (1)
C(23)	1.5539 (3)	0.2501 (2)	0.1118 (1)	0.061 (1)
C(24)	1.5534 (3)	0.1711 (2)	0.1324 (1)	0.070 (1)
C(25)	1.4489 (3)	0.1218 (2)	0.1012 (2)	0.067 (1)
C(26)	1.3434 (3)	0.1529 (2)	0.0478 (1)	0.058 (1)
C(27)	1.3508 (3)	0.4071 (2)	0.0673 (2)	0.086 (1)
C(28)	1.5720 (3)	0.3979 (2)	0.0451 (2)	0.104 (2)
C(29)	1.1914 (4)	0.0435 (2)	0.0607 (2)	0.124 (2)
C(31)	1.1770 (3)	0.3795 (2)	-0.1539 (1)	0.051 (1)
C(32)	1.0801 (3)	0.4374 (2)	-0.1800 (1)	0.056 (1)
C(33)	1.0975 (4)	0.5007 (2)	-0.2234 (2)	0.075 (1)
C(34)	1.2188 (4)	0.5074 (2)	-0.2423 (2)	0.087 (2)
C(35)	1.3202 (3)	0.4524 (2)	-0.2192 (2)	0.074 (2)
C(36)	1.2957 (3)	0.3899 (2)	-0.1763 (1)	0.056 (1)
C(37)	0.9574 (3)	0.4625 (2)	-0.0891 (2)	0.103 (2)
C(38)	0.8334 (3)	0.4538 (2)	-0.2127 (2)	0.112 (2)
C(39)	1.5366 (3)	0.3517 (2)	-0.1496 (2)	0.088 (2)
C(110)	0.9861 (3)	0.1545 (2)	-0.2184 (1)	0.085 (2)
C(210)	1.2570 (4)	0.0647 (2)	-0.0510 (2)	0.119 (2)
C(310)	1.3619 (3)	0.2558 (2)	-0.1937 (2)	0.083 (1)

gate with a pseudo threefold rotation axis (Figure 1). Fractional atomic coordinates, selected bond lengths and angles, and the lithium coordination geometry are given in Tables I, II, and III, respectively. The structure consists of a triangle of lithium atoms bridged along the sides by carbanions of which the NMe₂ substituents are intramolecularly coordinated to the lithium atoms. Although the same type of bonding is found in dimeric organolithium species of type **2**, C-Li and Li-Li' distances in the trimer are somewhat different from those found in dimeric aryllithium compounds. The C-Li bond distances in all structurally known dimeric aryllithium compounds vary from 2.19 to 2.28 Å (average 2.24 Å) whereas for the trimer these distances are in the range 2.130 (5)-2.228 (5) Å (average 2.170 (3) Å). The Li-Li' distances in these dimeric aryllithium compounds vary from 2.37 to 2.66 Å (average 2.48 Å) whereas the trimer shows Li-Li' distances ranging from 3.059 (6) to 3.113 (7) Å (average 3.081 (7) Å).

The C(ipso) and lithium atoms are positioned in a plane (the maximum least-squares deviation is 0.07 (2) Å) which defines angles of 40.6 (1), 33.2 (1), and 34.4 (1)° with the planes of the three phenyl rings. The six-membered CLiC'Li'C''Li'' ring is distorted from the regular hexagonal form: the average Li-Li' distance is 3.081 (7) Å whereas the average C-C' distance is 4.192 (4) Å. The bonding geometry around lithium is far from tetrahedral: the average CLiC' angle, 149.4 (3)°, is nearly linear. The average LiCLi' angle, 90.3 (2)°, is large compared to similar angles in dimeric aryllithium compounds which range from 64.2 to 67.4°. This is directly related to the longer Li-Li' distances observed in the trimer.

The structure of trimeric N-lithiohexamethyldisilazane[16] shows a striking resemblance to that of the trimer reported here. The alternating nitrogen and lithium atoms are arranged in a planar six-membered ring. The NLiN' and LiNLi' angles, 147 (3)° and 92 (2)°, respectively,[16b] are nearly equal to the C-Li-C' and Li-C-Li' angles found in **7**.

The Structure in Apolar Solvents (Benzene/Toluene). [2,6-Bis(dimethylamino)phenyl]lithium (**7**) is only slightly soluble in toluene-d_8. At -64 °C, the ¹H spectrum consists of a sharp triplet at δ = 7.25 ppm and a sharp doublet at 6.86 ppm (J = 7.6 Hz) assigned to H4 and H3-H5, respectively. The NMe₂ signal appears as a very broad singlet ($\Delta\nu_{1/2}$ = 70 Hz) at δ = 2.48 ppm. This is an indication of the presence of diastereotopic methyl groups

of which the signals are close to coalescence under these conditions.

The ¹³C NMR spectrum of **7** in toluene-d_8 shows only one set of signals at temperatures varying from -85 to +50 °C. The chemical shifts of the aromatic ring carbon atoms (Table V) are constant within 0.3 ppm over the whole temperature range. Thus, only one aggregate must be present. Compared to the protonated compound, the signal of the lithiated carbon has a downfield shift of 70.1 ppm, which is typical for organolithium compounds.[17-19] When **7** is isotopically enriched with ⁶Li, this signal splits into five lines with an approximate intensity ratio of 1:2:3:2:1 (J = 6.5 Hz), indicating coupling of ¹³C with two ⁶Li nuclei. However, this allows no discrimination between a dimer (**2**) and a trimer (**5**) as in both species the lithiated carbon is similarly bonded. The splitting is still observed at +50 °C. Thus, the interaggregate C/Li exchange must be slow on the NMR time scale.[20] Cryoscopic measurements on **7** dissolved in benzene show a degree of association of 2.92 ± 0.15 (at variable concentrations ranging from 0.11 to 0.178 m), indicating that trimeric species are present in apolar solvents like benzene or toluene.

At -85 °C the signal of the NMe₂ carbon atoms is split into two singlets ($\Delta\delta$ = 8 ppm = 800 Hz). This must arise

(16) (a) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem.* 1969, *81*, 398. (b) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* 1978, *157*, 229.

(17) Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* 1988, *7*, 552.

(18) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* 1987, *6*, 2371.

(19) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* 1983, *66*, 308.

(20) Thomas, R. D.; Clarke, M. T.; Jensen, R. M.; Young, T. C. *Organometallics* 1986, *5*, 1851.

Table II. Selected Bond Distances (Å) and Angles (deg)

C(11)–C(12)	1.410 (3)	C(21)–C(22)	1.398 (4)	C(31)–C(32)	1.400 (4)
C(12)–C(13)	1.381 (5)	C(22)–C(23)	1.393 (4)	C(32)–C(33)	1.394 (5)
C(13)–C(14)	1.387 (5)	C(23)–C(24)	1.395 (5)	C(33)–C(34)	1.380 (6)
C(14)–C(15)	1.385 (5)	C(24)–C(25)	1.376 (5)	C(34)–C(35)	1.386 (5)
C(15)–C(16)	1.383 (5)	C(25)–C(26)	1.401 (4)	C(35)–C(36)	1.399 (5)
C(11)–C(16)	1.406 (3)	C(21)–C(26)	1.404 (5)	C(31)–C(36)	1.394 (4)
N(11)–C(12)	1.464 (3)	N(21)–C(27)	1.467 (4)	N(31)–C(32)	1.464 (4)
N(11)–C(17)	1.461 (5)	N(21)–C(28)	1.463 (4)	N(31)–C(37)	1.467 (4)
N(11)–C(18)	1.470 (4)	N(21)–C(22)	1.458 (4)	N(31)–C(38)	1.468 (4)
N(12)–C(19)	1.469 (4)	N(22)–C(29)	1.479 (5)	N(32)–C(36)	1.457 (4)
N(12)–C(110)	1.470 (4)	N(22)–C(210)	1.468 (4)	N(32)–C(310)	1.473 (5)
N(12)–C(16)	1.469 (3)	N(22)–C(26)	1.460 (4)	N(32)–C(39)	1.474 (4)
C(12)–C(11)–C(16)	112.8 (3)	C(22)–C(21)–C(26)	113.5 (2)	C(32)–C(31)–C(36)	113.4 (3)
C(11)–C(12)–C(13)	124.9 (2)	C(21)–C(22)–C(23)	124.7 (3)	C(31)–C(32)–C(33)	124.8 (3)
C(12)–C(13)–C(14)	118.5 (3)	C(22)–C(23)–C(24)	118.1 (3)	C(32)–C(33)–C(34)	118.1 (3)
C(13)–C(14)–C(15)	120.4 (3)	C(23)–C(24)–C(25)	120.9 (3)	C(33)–C(34)–C(35)	120.9 (3)
C(14)–C(15)–C(16)	118.6 (3)	C(24)–C(25)–C(26)	118.3 (3)	C(34)–C(35)–C(36)	118.0 (3)
C(11)–C(16)–C(15)	124.8 (3)	C(21)–C(26)–C(25)	124.5 (3)	C(31)–C(36)–C(35)	124.7 (3)
C(12)–N(11)–C(17)	111.6 (2)	C(22)–N(21)–C(27)	111.6 (2)	C(32)–N(31)–C(37)	111.2 (2)
C(12)–N(11)–C(18)	114.5 (2)	C(22)–N(21)–C(28)	114.8 (3)	C(32)–N(31)–C(38)	114.8 (2)
C(17)–N(11)–C(18)	109.9 (2)	C(27)–N(21)–C(28)	110.6 (2)	C(37)–N(31)–C(38)	110.4 (3)
N(11)–C(12)–C(11)	114.0 (3)	N(21)–C(22)–C(21)	114.8 (2)	N(31)–C(32)–C(31)	114.7 (2)
N(11)–C(12)–C(13)	121.0 (2)	N(21)–C(22)–C(23)	120.5 (3)	N(31)–C(32)–C(33)	120.5 (3)
C(16)–N(12)–C(19)	114.4 (2)	C(26)–N(22)–C(29)	114.3 (2)	C(36)–N(32)–C(39)	115.8 (3)
C(16)–N(12)–C(110)	110.7 (2)	C(26)–N(22)–C(210)	110.6 (3)	C(36)–N(32)–C(310)	111.0 (2)
C(19)–N(12)–C(110)	109.9 (2)	C(29)–N(22)–C(210)	110.3 (2)	C(39)–N(32)–C(310)	110.0 (2)
N(12)–C(16)–C(11)	113.4 (3)	N(22)–C(26)–C(25)	120.4 (3)	N(32)–C(36)–C(31)	114.6 (3)
N(12)–C(16)–C(15)	121.8 (2)	N(22)–C(26)–C(21)	115.1 (2)	N(32)–C(36)–C(35)	120.7 (3)

Table III. Geometry of the Lithium Coordination[a]

Li(1)–N(12)	2.109 (5)	Li(2)–N(11)	2.157 (5)	Li(3)–N(32)	2.101 (5)
Li(1)–N(31)	2.128 (5)	Li(2)–N(22)	2.071 (6)	Li(3)–N(21)	2.135 (5)
Li(1)–C(11)	2.168 (6)	Li(2)–C(11)	2.130 (5)	Li(3)–C(21)	2.170 (5)
Li(1)–C(31)	2.169 (6)	Li(2)–C(21)	2.174 (6)	Li(3)–C(31)	2.228 (5)
N(12)–Li(1)–N(31)	119.3 (2)	N(11)–Li(2)–C(11)	68.4 (2)	N(21)–Li(3)–C(21)	67.9 (1)
N(12)–Li(1)–C(31)	132.9 (2)	N(11)–Li(2)–N(22)	115.7 (2)	N(21)–Li(3)–C(31)	131.6 (3)
N(31)–Li(1)–C(11)	126.2 (3)	N(22)–Li(2)–C(11)	126.4 (3)	N(21)–Li(3)–N(32)	113.3 (3)
C(11)–Li(1)–C(31)	149.0 (2)	C(11)–Li(2)–C(21)	151.0 (3)	C(21)–Li(3)–C(31)	148.3 (3)
N(31)–Li(1)–C(31)	68.3 (2)	N(22)–Li(2)–C(21)	69.4 (2)	N(32)–Li(3)–C(31)	67.3 (2)
N(12)–Li(1)–C(11)	68.4 (2)	N(11)–Li(2)–C(21)	131.0 (2)	N(32)–Li(3)–C(21)	134.2 (3)

[a] Bond distances in Å and bond angles in deg.

Table IV. Crystal Data and the Data Collection for the Structure Determination of [2,6-Bis(dimethylamino)phenyl]lithium

|	
mol formula	$C_{30}H_{45}N_6Li_3$
cryst system	monoclinic
spacegroup	$P2_1/n$
Z	4
cell dimens	
a, Å	10.245 (1)
b, Å	16.927 (1)
c, Å	19.167 (1)
β, deg	103.84 (1)
ρ(calcd), g·cm⁻³	1.051
temp, K	295
radiatn	Cu Kα (λ = 1.541 84 Å)
scan method	ω–2θ with ω = (0.50 + 0.17 tan θ)
2θ scan range, deg	0–140
std reflctn	142
decay, %	1.1
index range	$-12 \le h \le 12, 0 \le k \le 20, 0 \le l \le 23$
no. of measd unique reflctns	6122
no. of obsd reflctns, $I \ge 2.5\sigma(I)$	3181

from the diastereotopicity of the CH₃ groups as found in the crystal structure (Figure 1; half of the methyl groups is in the Li₃C₃ plane while the others are out of this plane). Above –30 °C only one signal is found, indicating fast exchange of these methyl groups on the NMR time scale. It is probable that the trimer, which is a chiral screw, inverts via a planar transition state resulting in exchange

Table V. ¹³C NMR Data of 1,3-Bis(dimethylamino)benzene (6) and [2,6-Bis(dimethylamino)phenyl]lithium (7)

C	6[b]		7[b]		
	toluene[a]	THF	toluene[b,e]	THF[d]	
1	97.1	97.7	167.2[c]	167.5	173.9
2,6	151.6	152.3	164.0	164.4	164.4
3,5	102.4	102.7	112.0	111.8	109.7
4	129.8	129.7	128.0	127.6	125.5
CH₃	40.5	40.8	42.2/50.2	46.6	46.6

[a] Data from small amounts of hydrolysis product 6 in the spectrum of 7. [b] Dissolved crystals of ⁶Li-enriched material. [c] $^1J_{^{13}C,^6Li}$ = 6.5 Hz, quintet (at –30 °C). [d] Two sets of signals in a ratio of 1:5 at –25 °C. [e] At –85 °C.

of in-plane and out-of-plane methyl groups.
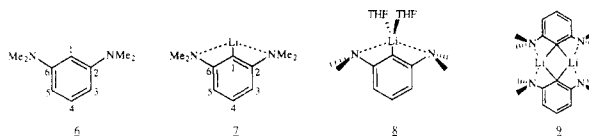
The Structure in Polar Solvents (THF). Crystals of 7 dissolve well in THF-d_8. The ¹H spectrum at +20 °C consists of a triplet at 6.99 ppm (H4) with J = 7.6 Hz, a doublet at 6.72 ppm (H3–H5), and a sharp singlet at 2.71 ppm. The ¹³C spectrum shows resonances for all carbon atoms except for the lithiated one; this signal is apparently very broad at this temperature.

Cooling the sample to −25 °C results for the ^{1}H spectrum in broadening of the aromatic signals and splitting of the NMe$_2$ signal in two broad ones at 2.70 and 2.80 ppm in a ratio of ca. 1:5; thus two species must be present. The ^{13}C spectrum at this temperature shows two sets of signals in a similar ratio (Table V; the chemical shifts of the methyl group signals as well those of the carbon 2–6 signals coincide within the resolution of 5 Hz). Since splitting of the lithiated carbon signals is not observed, no information on the aggregation states of both species is obtained. However, the signals of the species present in minor amounts show a striking resemblance to ^{13}C NMR data obtained for the trimeric 7 in toluene-d_8. This indicates that the trimer is present in small quantities, although a dimeric species cannot be ruled out.

Further cooling of the sample to −90 °C results in a gradual disappearance of minority signals (these signals disappeared completely at −80 °C), suggesting a temperature-dependent equilibrium between the two species. The splitting of the ^{13}C signal of the lithiated carbon remains unresolved at these temperatures, but cryoscopy of 7 in THF (mp −108 °C) showed that it is a monomer ($n = 0.97 ± 0.05$; $c = 0.09$ m). It is extremely likely that in THF solution the lithium is coordinated to two THF molecules (8).

Conclusions

[2,6-Bis(dimethylamino)phenyl]lithium (7) is a trimer in the crystalline state and in apolar solvents like benzene and toluene. The only aryllithium compounds with two intramolecularly chelating ortho substituents described so far are dimeric [2,3,5,6-tetrakis[(dimethylamino)methyl]phenyl]lithium[21] and tetrameric [2,6-dimethoxyphenyl]lithium[11] which is comprised of two stacked dimers. MNDO calculations on dimeric and trimeric 7 (without symmetry constraints) fail to explain the observed preference for trimeric aggregation, and only qualitative speculations can be made.

A model of a planar dimer (9; D_{2h} symmetry) was built and examined. The C–Li and Li–Li' distances in this model were assigned the values 2.24 and 2.48 Å, respectively, which are the averaged values for all structurally known dimeric aryllithium compounds. The geometry for the bis(dimethylamino)phenyl anions is taken from the averaged values for the crystal structure of 7. Since N to N distances and methyl to methyl distances between these anions are found to be 4.53 and 3.77 Å, respectively, there seems a priori no steric reasons for instability. The N–Li distance is 2.22 Å which is only slightly longer than the usual value of 2.10–2.20 Å. The intramolecular lithium coordination seems normal; however, delocalization of the nitrogen lone pair into the aromatic ring is "shut off" (the nitrogen lone pair is oriented perpendicularly to the aromatic π-system). In the trimeric compound the aromatic rings are tilted with respect to the CLiC'Li'C''Li'' plane, and some compromise is reached between delocalization and lithium coordination of the nitrogen lone pair (the averaged angle of the nitrogen lone pair with the phenyl ring plane is 25.1 (2)°). Tilting of the aromatic rings in the dimeric model results only in efficient N–Li coordination when the Li–C–Li' angle is enlarged from 60° to ca. 90°. This would result in a simultaneous decrease of the C–C' distance to ca. 3.0 Å, which is rather small for such negatively charged atoms. In order to avoid these large electron–electron repulsions, ring enlargement to a trimer seems to be the best solution. The C–C' distances

in this trimer are 4.167 (4), 4.179 (4), and 4.231 (4) Å, which is quite an improvement.

Stacking of the trimeric species is prohibited sterically (blocking methyl groups), and thus no hexamer can be formed.

Cryoscopy in THF at temperatures below −80 °C shows that 7 is a monomeric species for which we propose structure 8. At temperatures above −80 °C a second species is observed of which the NMR data closely resemble those obtained for the trimer. The relative concentration of this second species increases with rising temperature, suggesting the presence of a monomer/trimer equilibrium:

$$3[RLi\cdot2THF] \rightleftharpoons (RLi)_3 + 6THF$$
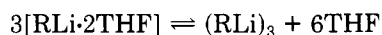
Probably the formation of this trimer goes via a short-living dimeric species.

Experimental Section

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

Synthesis. [2,6-Bis(dimethylamino)phenyl]lithium was synthesized by direct metalation of 1,3-bis(dimethylamino)benzene by butyllithium in hexane under reflux conditions. Butyllithium (20.0 mL, 1.6 M in hexane, 32.0 mmol) was added to 1,3-bis(dimethylamino)benzene (5.50 g, 30.8 mmol) dissolved in 15 mL of hexane at room temperature. The mixture was heated under reflux for 1 h. During this time a white precipitate formed, and cooling of the solution to −30 °C allows further crystallization of the product. Washing the precipitate two times with ca. 20 mL of pentane yields 3.65 g (70%) of the product as a white crystalline compound.

X-ray Data Collection. After recrystallization of 7 from a hexane/diethyl ether (4/1) mixture at −30 °C, a suitable crystal with dimensions 0.8 × 0.4 × 0.3 mm was sealed under nitrogen in a Lindemann glass capillary. An Enraf-Nonius CAD 4 diffractometer was used, and the cell constants were determined from a least-squares fit of the setting angles of 25 reflections with the θ range 15.6–21.4°. One standard reflection was measured every 50 reflections. Corrections for Lorentz–polarization effects and linear decay were applied. Details of the data collection are given in Table IV.

Solution and Refinement of the Structure. On basis of regular extinctions the space group was determined as $P2_1/n$. Direct methods using the program SHELXS-86[22] led to the location of all carbon and nitrogen atoms. After one cycle of isotropic refinement the lithium atoms were found in the difference Fourier map. Anisotropic least-squares block refinement converged to $R(F) = 0.103$. The hydrogen atoms were placed at idealized C(sp^2) and C(sp^3) positions at a distance of 1.0 Å from their carbon atoms. During further refinement the hydrogen atoms were riding on their carrier atoms with an overall variable-temperature factor. After the last cycle of refinement with 353 parameters, $R(F)$ and $R(wF)$ (with weight = $1/\sigma^2(F)$) converged to 0.056 and 0.045, respectively. The overall temperature factor of the hydrogens refined to 0.129 Å^2; the average shift to error ratio (Δ/σ) is 0.008; maximum and minimum residual electron densities are 0.16 and −0.19 e Å^{-3}, respectively.

Neutral atom scattering factors[23] were used for all atoms. Anomalous dispersion factors were taken from Cromer and Liberman.[24] Calculations were performed on the CYBER 180-855 of the University of Utrecht using the program SHELXS-86[22] (structure determination), SHELX-76[25] (structure refinement), and the EUCLID package[26] (illustrations and geometric calculations).

(21) van der Zeyden, A. A. H.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* 1986, *105*, 1.

(22) Sheldrick, G. M. *SHELXS-86*, Program for crystal structure solution; University of Göttingen: Göttingen, Germany, 1986.

(23) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* 1968, *A24*, 321.

(24) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, *53*, 1891.

(25) Sheldrick, G. M. *SHELX-76*, Program for crystal structure determination; University of Cambridge: Cambridge, England, 1976.

(26) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

NMR Analyses. NMR spectra in toluene-d_8 were recorded on a JEOL GX 400 spectrometer (^{1}H, 400 MHz). Chemical shifts are referenced to the solvent (toluene-d_8) signals: $\delta = 2.03$ ppm (^{1}H, C$_6$D$_5$-CHD$_2$) and $\delta = 125.2$ ppm (^{13}C, para-C). Crystals of 7 (130 mg, ^{6}Li-enriched material) were placed under argon in a dry 5-mm NMR tube fitted with a serum cap. Dry toluene-d_8 (0.6 mL) was added. The compound is only slightly soluble.

NMR spectra in THF-d_8 were recorded on a Bruker AC 200 spectrometer (^{1}H, 200 MHz). Chemical shifts are referenced to the solvent (THF-d_8) signals: $\delta = 1.73$ ppm (^{1}H, 3-H THF-d_7) and $\delta = 25.2$ ppm (^{13}C, β-CD$_2$). Crystals of 7 (129 mg, ^{6}Li-enriched material) were placed under nitrogen in a dry 5-mm NMR tube and dissolved readily in 0.6 mL of THF-d_8.

Cryoscopy Measurements. Cryoscopy measurements in THF and benzene were carried out in an apparatus described by Bauer

et al.[27]

Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters, bond distances, bond angles, and torsional angles (8 pages); a listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

(27) Bauer, W.; Seebach, D. *Helv. Chim. Acta* 1984, 67, 1972.

Synthesis and Reaction Chemistry of Iridium(III) Hydrides Formed by the Intramolecular N–H Addition of Hybrid Phosphine Amines to Iridium(I)

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Monovalent P-bonded iridium and rhodium complexes MCl(1,5-COD)(o-Ph$_2$PC$_6$H$_4$NHR) (R = CH$_2$Ph, Et) have been prepared from [M(μ-Cl)(1,5-COD)]$_2$ and o-Ph$_2$PC$_6$H$_4$NHR. New P,N-chelate complexes [Ir(1,5-COD)(o-Ph$_2$PC$_6$H$_4$NHR)]ClO$_4$ are formed upon reaction of the iridium complexes with AgClO$_4$. The amine arm of the chelate can be substituted by added ligands L to give [Ir(1,5-COD)(o-Ph$_2$PC$_6$H$_4$NHR)L]ClO$_4$ (L = pyridine, acetonitrile). Solution thermolysis of [Ir(1,5-COD)(o-Ph$_2$PC$_6$H$_4$NHCH$_2$Ph)]ClO$_4$ results in cyclometalation of the benzyl ring. The complex IrHCl(o-Ph$_2$PC$_6$H$_4$NR)(o-Ph$_2$PC$_6$H$_4$NHR) (R = CH$_2$Ph, Et) has been obtained from the reaction between [Ir(μ-Cl)(C$_8$H$_{12}$)$_2$]$_2$ and o-Ph$_2$PC$_6$H$_4$NHR. The pathway involves N–H addition to iridium(I). Reversible protonation of IrHCl(o-Ph$_2$PC$_6$H$_4$NR)(o-Ph$_2$PC$_6$H$_4$NHR) with HX gives [IrHCl(o-Ph$_2$PC$_6$H$_4$NHR)$_2$]X. The chloride ligand is replaced by CO to give two isomers of [IrH(o-Ph$_2$PC$_6$H$_4$NR)CO(o-Ph$_2$PC$_6$H$_4$NHR)]Cl. The reaction between [Rh(μ-Cl)(C$_8$H$_{14}$)$_2$]$_2$ and o-Ph$_2$PC$_6$H$_4$NHCH$_2$Ph gives the unstable complex [Rh(o-Ph$_2$PC$_6$H$_4$NHCH$_2$Ph)$_2$]Cl, which reacts with CO to give trans-RhCl(CO)(o-Ph$_2$PC$_6$H$_4$NHCH$_2$Ph)$_2$. Crystal data for [IrHCl(o-Ph$_2$PC$_6$H$_4$NHCH$_2$Ph)$_2$]Cl·2CDCl$_3$: $P2_1/n$, $a = 10.111$ (4) Å, $b = 25.886$ (3) Å, $c = 19.939$ (3) Å, $\beta = 93.03$ (2)°, $Z = 4$, refined to $R = 0.036$, $R_w = 0.054$.

Introduction

The insertion of a low-valent metal center into an N–H bond is an important reaction for the development of catalytic processes involving the carbonylation or alkylation of amines with carbon monoxide or alkenes.[1] Despite this potential significance there are very few examples of such reactions.[2] Low-valent complexes are more prevalent

for later transition metals, but such metals are likely to disfavor N–H addition because of the formation of a relatively weak metal–nitrogen amide bond.[3] The best current estimates of N–H, M–H, and M–N bond enthalpies suggest that the reaction is approximately thermoneutral for the platinum group metals.[4] Our decision to focus on these metals is based on the logic that not only is the N–H addition reaction thermodynamically feasible but also the metal–amide bond formed is sufficiently weak that subsequent insertion reactions into it are possible.

In this paper we present our results on the reactions of phosphine amines with low-valent complexes of rhodium and iridium.[5] These ligands are chosen because they can undergo intramolecular "chelate-assisted" oxidative addition of the N–H bond from a tertiary phosphine anchor to give 5-membered ring complexes.[6]

(1) Sheldon, R. A. *Chemicals from Synthesis Gas*; Reidel: Hingham, MA, 1983; Chapter 8. Fukuoka, S.; Chono, M.; Kohno, M. *Chem. Tech.* 1984, 14, 670–676. Grate, J. H.; Hamm, D. R.; Valentine, D. H. PCT Int. Appl. WO 85 01,285; *Chem. Abstr.* 1985, 103, 104735e. Waller, F. J. *J. Mol. Catal.* 1986, review issue, 43–61. Barman, T. E. *Enzyme Handbook*; Springer-Verlag: New York, 1969; Vol. II, p. 797.

(2) Roundhill, D. M. *Inorg. Chem.* 1970, 9, 254–258. Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* 1982, 907–910. Nelson, J. H.; Schmidt, D. L.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *Inorg. Chem.* 1970, 9, 2678–2681. Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 1006–1009. Goel, R. A.; Srivastava, R. C. *J. Organomet. Chem.* 1983, 244, 303–310. Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* 1974, 96, 3098–3105. Mague, J. T. *Inorg. Chem.* 1972, 11, 2558–2560. Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* 1981, 316, C56–C60. Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* 1977, 1328–1330. Fink, G. S. Z. *Naturforsch., B: Anorg. Chem. Org. Chem.* 1980, 35B, 454–457. Sappa, E.; Milone, L. *J. Organomet. Chem.* 1973, 61, 383–388. Lin, Y.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* 1984, 272, 207–229. Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* 1987, 26, 971–973. Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* 1984, 106, 5014–5016.

(3) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, England, 1980.

(4) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, 109, 1444–1456.

(5) For a preliminary communication see: Park, S.; Hedden, D.; Roundhill, D. M. *Organometallics* 1986, 5, 2151–2152.

(6) For examples, see: Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* 1975, 97, 3386–3392. Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* 1982, 1, 506–513. Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R. *J. Am. Chem. Soc.* 1984, 106, 1314–1318. Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* 1984, 106, 3054–3056. Hedden, D.; Roundhill, D. M. *Inorg. Chem.* 1986, 25, 9–15.