The Sesquimetallated Lithium Cluster Resulting from the Reaction of a Diprotonic NH/OH Acid with *n*-Butyllithium

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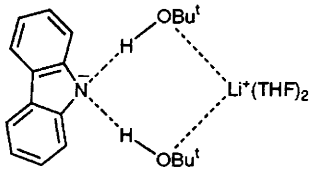
X-Ray analysis reveals that the metallation of carbazol-1-yldiphenylmethanol (H_2cdpm) with one equivalent of Bu^{n}Li in tetrahydrofuran gives a 1 : 1 complex of monolithiated and dilithiated H_2cdpm instead of the monolithiated derivative.

Recently we reported two X-ray structures of lithiated CH- and NH-acidic compounds which are complexed by ROH ligands: a water-solvated lithiomalononitrile–tetramethylethylene diamine complex **1**[1] and a lithiocarbazolide complexed with two *tert*-butyl alcohol molecules **2**.[2] Both can be regarded as intermediates during lithiation reactions. Seeking to study a complex of a lithioamine with an alcoholic side arm, we lithiated the diprotonic NH/OH-acid, carbazol-1-yldiphenylmethanol **3** (H_2cdpm),[3] with one equivalent of Bu^{n}Li. The solid-state structure of the sesquimetallated **4** [$(cdpm)_2HLi_3$] which resulted is the subject of this report.

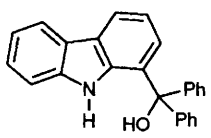
Surprisingly, the lithiation of **3** in tetrahydrofuran (THF) with 1.0 equiv. of Bu^{n}Li [eqn. (1)] [or better with 1.5 equiv. eqn. (2)] gave a sesquimetallated complex with the $(cdpm)_2HLi_3{\cdot}THF_3{\cdot}6THF_{cryst}$ (**4**$\cdot 6THF_{cryst}$) stoichiometry rather than pure cdpmHLi.† The X-ray analysis of **4**$\cdot 6THF_{cryst}$ (Fig. 1)‡ shows an aggregate consisting formally of doubly metallated cdpmLi$_2$ and of monometallated cdpmHLi. In the latter, the nonmetallated hydrogen is in an OH group.

$$[\text{---NC–CH–CN---Li}^+\text{---OH}_2\text{---NMe}_2[\text{CH}_2]_2\text{NMe}_2]_n$$

1



2



3

$$\underset{\mathbf{3}}{3\,H_2cdpm} + 3\,Bu^nLi \xrightarrow{THF} \underset{\mathbf{4}}{(cdpm)_2HLi_3} + H_2cdpm + Bu^nH \quad (1)$$

$$\underset{\mathbf{3}}{2\,H_2cdpm} + 3\,Bu^nLi \xrightarrow{THF} \underset{\mathbf{4}}{(cdpm)_2HLi_3} + Bu^nH \quad (2)$$

The quite similar acidities of carbazole (pK = 17.06 in Me_2SO–H_2O[4]) and of Bu^{t}OH (pK = 16.54 in EtOH[5]) indicate that the NH and OH acidities in **3** should be of comparable magnitude.§ Hence, monolithiated cdpmHLi (at nitrogen as well as at oxygen) as well as dilithiated cdpmLi$_2$ may be in the reaction mixture. The cdpmHLi and the cdpmLi$_2$ could aggregate to give the sesquimetallated cluster **4**. At least in the solid state, **4** is more stable than either cdpmHLi or cdpmLi$_2$.

The details of the structure of **4** also are surprising: note the crystallographic C_2 symmetry with the C_2 axis through Li(1) and O(3). The proton H(0) located at the alcoholic oxygen, is disordered with 50 : 50 occupation probability at the O(1) and the O(1a) sites. While two of the three lithium cations [Li(2) and Li(2a)] have a pseudo-tetrahedral coordination sphere

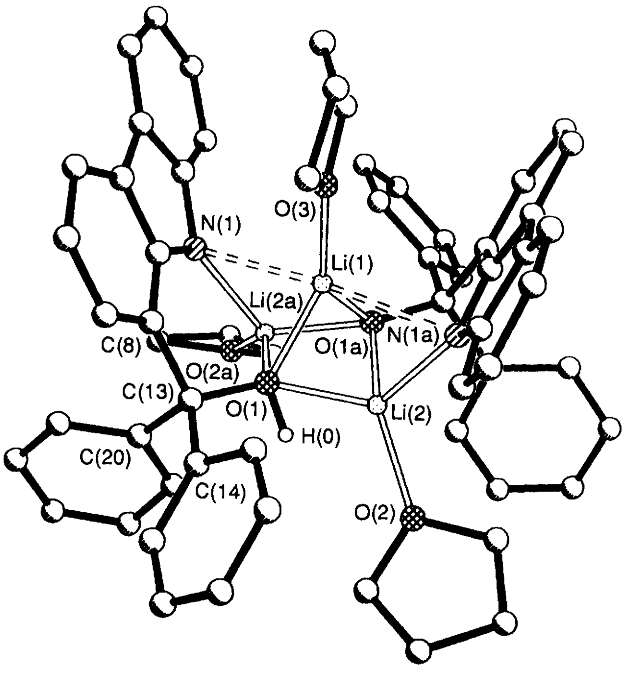


Fig. 1 Structure of **4** in the solid state. H(0) is disordered (50 : 50) at O(1) and O(1a). Only one position of H(0) is shown. Selected bond lengths (Å) and angles (°): Li(1)–O(3) 1.935(22), Li(1)–N(1) 2.526(8), Li(1)–O(1) 1.939(16), O(1)–Li(2) 1.904(15), O(1)–Li(2a) 1.995(16), Li(2)–O(2) 1.981(16), Li(2)–N(1a) 2.061(16), O(1)–H(0) 0.938. Li(2)–O(1)–Li(2a) 93.3(6), O(1a)–Li(2)–O(1) 83.0(6), O(1)–Li(1)–O(1a) 83.6(9), O(1)–Li(1)–O(3) 138.2(4), N(1)–Li(1)–N(1a) 172.9(10), C(13)–O(1)–H(0) 97.7(6).

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† Complex **4** can be prepared from carbazol-1-yl diphenylmethanol **3** in better yields by using 1.5 equiv. of Bu^{n}Li. Carbazol-1-yldiphenylmethanol **3** (153 mg, 0.44 mmol) was dissolved in 2.4 ml of THF. To this solution 1.5 equiv. of Bu^{n}Li (0.53 ml of a 1.24 mol l^{-1} solution in hexane) was added at 0 °C. A white precipitate formed which dissolved upon boiling. The solution was allowed to cool to room temperature. Colourless crystals (205 mg, 68%) of **4**$\cdot 6THF_{cryst}$ formed within 1 h which were suitable fo X-ray analysis.

‡ *Crystal data*: $C_{86}H_{107}Li_3N_2O_{11}$, M = 1365.6, monoclinic, space group $C2/c$, a = 26.63(4), b = 11.12(2), c = 25.84(2) Å, β = 90.49(8)°, V = 7647(12) Å^3, Z = 4, D_c = 1.186 Mg m^{-3}, 15 308 collected ($3.0° < 2\theta < 54.0°$), 8403 independent and 2372 observed [$F > 3.0\sigma(F)$] reflexions, 461 refined parameters, R = 0.0924, R_w = 0.0690, GOF = 1.25; all data were collected on a Nicolet-R3m/V four-circle diffractometer at 201 K using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXTL +). All nonhydrogen atoms were refined anisotropically, the hydrogens isotropically in fixed idealized positions (riding model). H(0) was located *via* a electron density difference map and refined in the located positions [50 : 50 disordered at O(1) and O(1a)] with fixed isotropic displacement parameters. There are three THF molecules in the lattice which do not interact with the cluster **4**. Near these THF molecules a high residual electron density was located which indicates a strong disorder of the THF molecules. These disorders could not be solved which is certainly responsible for the modest R values. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The acidity of Bu^{t}OH should be similar to that of the OH group in **3**, since alcohols in general span only a small range of acidities (pK *ca.* 15–17[5]). The lithium ion-pair acidity of carbazole (13.8 in THF, A. Streitwieser, C. Lambert and M. Stratakis, unpublished) should also be similar to that of the NH group in **3**.

and form a Li(2)–O(1)–Li(2a)–O(1a) 'dimeric' subunit, the third lithium cation [Li(1)] is fivefold coordinated (trigonal bipyramidal) and caps the Li_2O_2 four-membered ring. The coordination spheres of the three lithium cations share four anionic centres [N(1), N(1a), O(1a)] and one neutral ligand [O(1)]. The lithium cluster which is formed has no precedent. Owing to the crowded arrangement, the Li(2a)–Li(1) and Li(2)–Li(1) separations (2.29 Å) are rather short (as observed in other lithium cluster compounds[6]), but this does not imply metal–metal bonding.[7]

While most Li–N and Li–O distances in **4** are in the normal range (1.9–2.1 Å[8]), the apical Li(1)–N(1) and Li(1)–N(1a) separations are considerably longer (2.53 Å). These long Li–N distances result from the steric constraints of the carbazolyl moiety and of the fifth Li(1) ligand (THF): the sum of the van der Waals radii of N(1) and O(3) is 2.9 Å whereas the N(1)–O(3) distance is 3.277 Å. Thus, shorterning the N(1)–Li(1) separation to the 'normal' Li–N distance (*ca.* 2.1 Å[8]) would increase the steric repulsion among the carbazolyl moieties and the THF ligand. As in the dimeric lithiocarbazole **5**,[9] the N(1)–Li bonds in **4** involve the N(1)-σ-lone pair orbital [N(1)-Li(2a); angle pyrrole-ring-centre–N(1)–Li(1) 168.3°] on the one hand and the N(1)-π-lone pair orbital [N(1)–Li(1); angle pyrrole-ring-centre–N(1)–Li(1) 109.5°] on the other.

Hydrogen bonding of the ROH ligand in **1**, in **2**, and in other water or alcohol complexed alkali metal compounds[10] is an essential, stabilizing feature. In contrast, the ROH proton in **4** does not hydrogen bond {*d*[H(0)–O(1a)] 2.855 Å and *d*[H(0)–O(2)] 2.544 Å} but interacts with the Li(2a) cation instead! The very short Li···H separation, 1.622 Å, is only slightly longer than the Li–H distance in the isolated lithium hydride molecule (1.596 Å[11]). Although the location of H(0) is not very precise in our X-ray structure, an *ab initio* calculation of a model compound[¶] essentially confirms this unusual hydrogen position {*d*[H(0)–Li(2)] 1.769 Å, *d*[O(1)–H(0)] 0.955 Å, ∠[C(13)–O(1)–H(0)] 103.1°}. H(0) is located in a minimum energy position which is determined by the steric requirements [preferred staggered conformation around the C(13)–O(1) bond], the electrostatic repulsions [maximum distances of H(0) to the lithium cations] and attractions [minimum distances of H(0) to the O(1a) and O(2) atoms].

Unfortunately, **4** cannot be investigated by NMR spectroscopy since it is only sparingly soluble in THF and inhomogeneous mixtures of different species are formed both in Me_2SO and in toluene solutions. Nevertheless, the X-ray structure of **4** demonstrates that the metallation of diprotonic acids with similar p*K* values can yield mixed lithiated species rather than uniform aggregates.

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[¶] The *ab initio* calculated model compound consisted of all heteroatoms (Li, O, N) as well as C(8), C(13), C(14) and C(20) in the fixed positions derived from the X-ray structure of **4**. The atoms were saturated by hydrogen atoms in idealized positions (riding model) and water was used as a ligand for Li^+ instead of THF. Only H(0) was fully optimized at the HF/6-31G* level using the GAUSSIAN 92 program: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, R. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.

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