Triprotic 2,4,6-tris(organoamino)-1,3,5-triazenes as precursors to multi-site triazenate ligands

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2,4,6-Tris(2-fluoroanilino)-1,3,5-triazene successively undergoes one-, two- and three-fold deprotonation in the presence of Bu^{n}Li; the dilithiated triazenate exists as the dimeric complex (thf)$_6$Li$_4$[(RN)$_2$(RNH)C$_3$N$_3$]$_2$ in the solid state (R = 2-F-C$_6$H$_4$) featuring bidentate N$_{endo}$–C–N$_{exo}$ chelation sites.

The resemblance of monoanionic amidinates [RC(NR)$_2$]$^-$ [1] and bis-imino phosphinates [R$_2$P(NR)$_2$]$^-$ [2] in reaction and coordination behaviour corroborate the diagonal relationship between carbon and phosphorus. Both are sterically demanding, electron-rich bidentate chelates, which can be obtained from the protic precursor [RC(NR)(NHR)] and [R$_2$P(NR)(NHR)], respectively. Recently, we have shown that hexakis(organoamino)cyclotriphosphazenes (RNH)$_6$P$_3$N$_3$ act as multiprotic acids in the presence of strong bases yielding trianionic [(RNH)$_3$(RN)$_3$P$_3$N$_3$]$^{3-}$ and hexaanionic phosphazenates [(RN)$_6$P$_3$N$_3$]$^{6-}$.[3] Considering the diagonal C–P relationship, analogous triprotic 2,4,6-tris(organoamino)-1,3,5-triazenes **1**H$_3$ are expected to be metallated correspondingly to give anionic triazenates (Scheme 1), which promise interesting coordination modes, due to the potential three-fold symmetry of the anticipated multi-site ligands.

Here, we present initial lithiation studies of 2,4,6-tris(2-fluoroanilino)-1,3,5-triazene (**1**H$_3$), which was generated by the reaction of cyanuric chloride with an excess of 2-fluoroaniline. We monitored the reaction of **1**H$_3$ with Bu^{n}Li in THF using ^{1}H and ^{13}C NMR spectroscopy (Fig. 1). Upon addition of Bu^{n}Li the NH signal gradually shifts up-field and decreases in intensity until it vanishes once three equivalents of Bu^{n}Li have been added. The ^{13}C NMR shift of C(1) moves down-field from 127 in **1**H$_3$ to 144 ppm in Li$_3$**1**, and that of C(6) up-field from 124 (**1**H$_3$) to 115 ppm (Li$_3$**1**) (see Fig. 1 for numbering scheme). The signal of the ^{13}C nuclei of the central triazene ring shifts only slightly from 165 (**1**H$_3$) to 169 ppm (Li$_3$**1**). Throughout lithiation the ^{19}F NMR consists of a single peak, which also shifts only marginally from 130 to 132 ppm. Both ^{1}H and ^{13}C NMR of partially deprotonated species display only one set of signals for both 2-fluoroanilino and triazene moieties, indicating rapid proton transfer at room temperature. However, two

sets of signals with an intensity ratio of 2:1 appear in the ^{13}C NMR spectrum of a THF solution containing the dilithiated species Li$_2$**1**H, which was recorded at −80 °C. The chemical shifts of the set of lower intensity are similar to the spectrum of **1**H$_3$ and can be attributed to the non-deprotonated anilino substituent, wheras those of the set of higher intensity, which resemble the pattern observed in the spectrum of Li$_3$**1**, are caused by the two deprotonated substituents. At −80 °C the ^{13}C nuclei of the triazene ring also give two resonances (at 164 and 169 ppm).

Single crystals were obtained from the reaction of **1**H$_3$ with two equivalents of Bu^{n}Li in THF. X-Ray structure determination revealed that two-fold deprotonation had occurred and the resulting Li$_2$**1**H exists as the centrosymmetric dimer (thf)$_6$Li$_4$(**1**H)$_2$ **2** in the solid state (Fig. 2).† Both ligands in **2** are linked by the two centrally arranged lithium ions (Li1, Li1a) forming an eight-membered [Li–N$_{exo}$–C–N$_{endo}$–]$_2$ ring core. In addition, Li1 and Li1a undergo weak cross-ring interactions to N$_{exo}$-sites and each is coordinated to an F-aryl atom and a thf molecule resulting in distorted trigonal bipyramidal coordination geometries. The other two lithium ions (Li2, Li2a) are accommodated in neighbouring N$_{exo}$–C–N$_{endo}$ chelates and are additionally coordinated to two thf molecules giving tetrahedral metal surroundings. **2** combines coordination modes of monomeric and dimeric lithium complexes of ligands featuring bidentate N–E–N chelates [E = (R)C,[4] (R$_2$)P,[5] (R)S[6]]. Li2
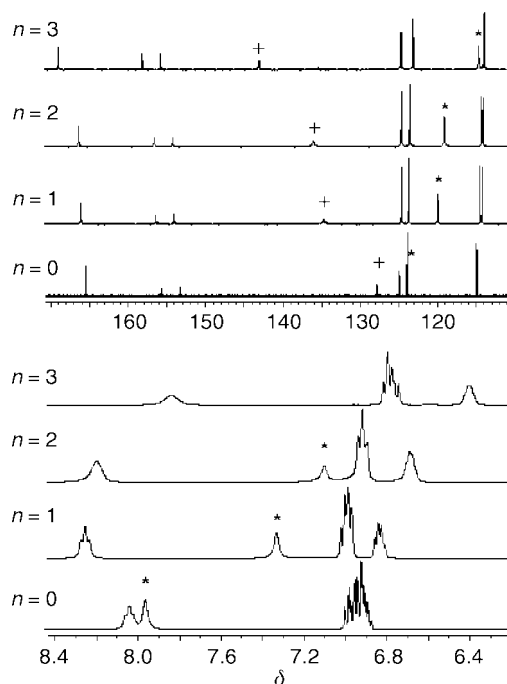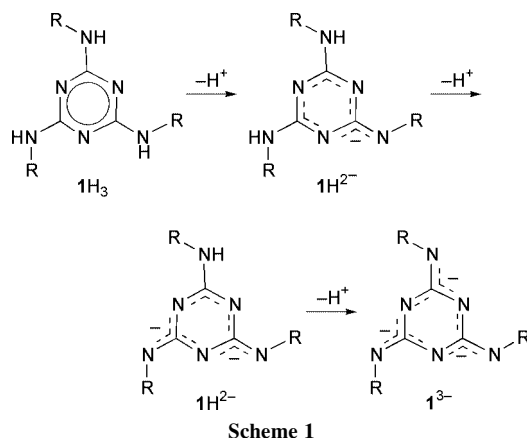
Scheme 1

Fig. 1 ^{13}C NMR (top) and ^{1}H NMR (bottom) spectra of stepwise reaction of **1**H$_3$ with *n* equivalents of Bu^{n}Li in thf at 20 °C. In ^{13}C NMR '+' refers to the C(1) (= C–N) and '*' to the C(6) position of 2-fluoroaniline substitutents; in ^{1}H NMR '*' refers to the NH signal.
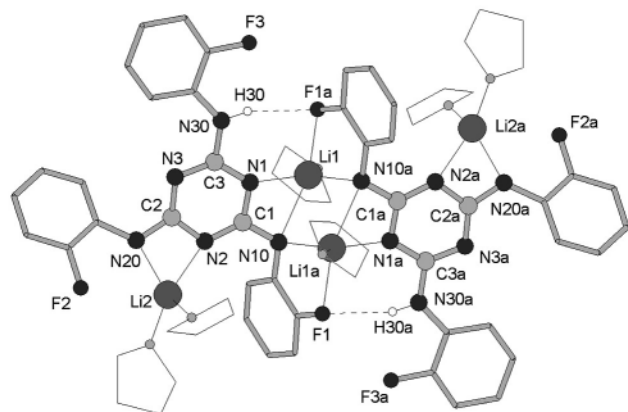
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Fig. 2 X-Ray structure of **2**. Selected bond lenghts (Å) and angles (°): N1–C1 1.339(9), N1–C3 1.351(9), N2–C1 1.343(9), N2–C2 1.359(9), N3–C3 1.336(9), N3–C2 1.341(9), C1–N10 1.353(9), C2–N20 1.334(9), C3–N30 1.374(10), Li1–N1 2.03(2), Li1–N10 2.32(2), Li1–N10a 2.07(2), Li1–F1a 2.15(2), Li2–N2 2.11(2), Li2–N20 1.99(2), Li2···F2 3.072(15); C1–N1–C3 113.1(7), C1–N2–C2 115.7(7), C2–N3–C3 114.3(7), N1–C1–N2 125.5(8), N2–C2–N3 124.0(8), N3–C3–N1 127.3(7), N1–C1–N10 111.6(8), N2–C2–N20 110.5(7), N3–C3–N30 118.5(8).

corresponds to the 'monomeric' mode, where the lithium ion is chelated by a single N–E–N unit, and Li1 to the often encountered N–E–N dimer mode, where two ligands encapsulate two lithium ions in both mono- and bi-dentate fashion. A similar motif is observed in the polymeric trilithium salt of trithiocyanuric acid.[7]

In contrast to phosphazenates, where the metallation causes a marked impact on the structural parameters of the central P_3N_9 core, bonding parameters within the central C_3N_6 ligand core of **2** are not very much affected upon metallation. The C–N$_{exo}$ bond involving the non-metallated anilino group is only marginally longer [C3–N30 1.374(10) Å] than those of the deprotonated substituents [C1–N10 1.353(9), C2–N20 1.334(9) Å], which are of similar lengths as C–N$_{endo}$ bonds ranging from 1.336(9) to 1.359(9) Å. Accordingly, in neutral 2,4,6-tris-(amino)-1,3,5-triazenes C–N$_{exo}$ bonds are on average only 0.02 Å longer than C–N$_{endo}$ bonds.[8]

1H$_3$ is deprotonated without undergoing side reactions. The lithiation is reversible as **1**H$_3$ is recovered after protolysis of Li$_3$**1**. On the other hand, 1,3,5-triazene and 2,4,6-tris(organo)-1,3,5-triazenes are prone to nucleophilic attack by organolithium reagents at C$_{endo}$ positions, which leads to either nucleophilic addition, substitution or ring cleavage.[9] F(aryl) functions in **2**, initially introduced to act as ^{19}F NMR spectator sites, are inert on lithiation. The absence of line broadening of ^{19}F signals indicates that there are no considerable ^{7}Li–^{19}F interactions in solution.

The electron deficiency of the central C_3N_3 ring in **1**$^{3-}$ is compensated for by the π-donating character of exocylic N centres, which allow delocalisation of negative charge across the entire C_3N_6 core. In contrast to the non-aromatic tri- and

hexa-anionic triphosphazenates, triazenates H**1**$^{2-}$ and **1**$^{3-}$ feature an aromatic ligand core. This enables electronic interaction between accommodated metal centres across the aromatic ligand system. In addition, the D_{3h} symmetry of the C_3N_6 ligand core and the straightforward introduction of organo amino groups with various functionalities promise the generation of metal complexes with interesting properties.

Notes and references

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