# The First Triazatrimethylenemethane Dianion: Crystal Structure of Dilithio-triphenylguanidine $Li_2[C(NPh)_3]$ as its Tetrahydrofuran Solvate

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The dilithiation of *N,N′,N″*-triphenylguanidine with *n*-butyllithium in tetrahydrofuran provides the first example of a triazatrimethylenemethane system $[C(NPh)_3]^{2-}$, isoelectronic with both $[C(CH_2)_3]^{2-}$ and $[CO_3]^{2-}$: the X-ray crystal structure of the dilithium salt shows it to exist as a dimer with planar $CN_3$ structural units.

There has been a resurgence of interest in complexes of the trimethylenemethane (TMM) ligand recently.[1] Our interest in the possibility of substitution of one or more of the methylene groups in this ligand with isoelectronic groups such as NR, O or S to generate heterotrimethylenemethane ligands $[C(X)(Y)(Z)]^{2-}$, and the introduction of substituents on the TMM framework, led us to speculate upon the possible existence of triaza analogues of the TMM system, $[C(NR)_3]^{2-}$. Such species have never been reported, perhaps somewhat surprisingly given their relationship to the stable and well-characterised TMM and carbonate dianions. Other hetero-TMM systems have, however, attracted attention, in particular the acetone dianion (oxatrimethylenemethane),[2] its sulfur analogue (thiatrimethylenemethane)[3] and silatrimethyl enemethane systems,[4] whilst nitrogen-containing systems derived from ureas,[5] thioureas[6] and an imine[7] have also been reported.

The potentially unique electronic and steric properties of these systems as ligands and the possible formation of chiral complexes by those ligands containing bulky substituent groups on each of the TMM arms as shown in Fig. 1, suggests that this could be a most fruitful area of research. We report here the X-ray crystal structure of the first triazatrimethylenemethane system $[C(NPh)_3]^{2-}$.

The lithiation of *N,N′,N″*-triphenylguanidine with 2 molar equivalents of *n*-butyllithium in THF affords a yellow solution from which almost colourless crystals may readily be obtained by gradual cooling, after saturation by partial removal of the solvent. A single-crystal X-ray structure determination† shows the system to exist as a dimer of formula $\{Li_4[C(NPh)_3]_2(THF)_6\}$ **1** in the solid state (Fig. 2). In this structure the two dianionic units are bridged by two lithiums, each coordinated by three nitrogens and a THF molecule, whilst the remaining two lithiums are coordinated to the third nitrogen of each unit, an *ipso*C(11P)-*ortho*C(16P) C–C bond of the adjacent phenyl on N(2) and two THF molecules. There is an inversion centre at the midpoint of the central Li–Li vector. The sum of the angles around the central carbon C(2) of the dianion totals 359.9(3)° indicating the strict planarity of the $CN_3$ core and therefore significant π delocalisation through this carbon (so called Y-conjugation), whilst the geometry at the nitrogens (mean C–N–C 121.6°) suggests $sp^2$ hybridisation as would be required for such delocalisation. The C–N bond lengths within the central core of the dianion average 1.36(1) Å which compares with a value of 1.34 Å for the equivalent guanidinium system $[C(NHPh)_3][Cl_3CCO_2]$,[8] indicating some relative weakening of the π bonding in the dianion as might be anticipated. Both these bond lengths and the angles around the central carbon in **1** show significant variation which may presumably be attributed to intramolecular crowding within the dimeric structure.

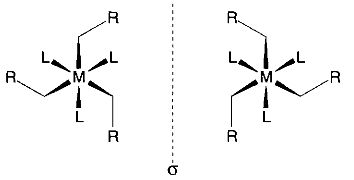

**Fig. 1** Enantiomeric pair of trisubstituted trimethylenemethane complexes (plan view). The central carbon eclipses the metal and has been omitted for clarity.

In contrast to the structure of the isoelectronic tribenzylidenemethane, $[C(CHPh)_3]^{2-}$, in which the orientation of the phenyl groups generates a structure of pseudo $C_{3h}$ symmetry,[9] the phenyls of **1** are disposed around the Y-shaped core of the dianion in the alternative fashion giving a less symmetric structure of local pseudo $C_s$ symmetry (Fig. 3). Such an arrangement of phenyl groups is in effect similar to that observed for the dibenzylidene-ethylene dianion (diphenyltrimethylenemethane).[10] To what extent this arrangement of the phenyl groups is dictated by electronic factors and the

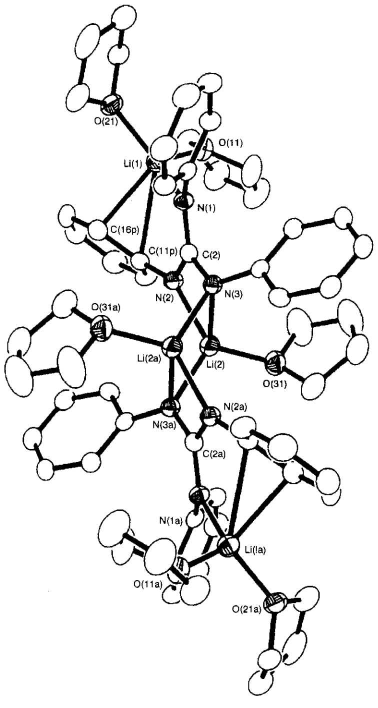

**Fig. 2** The molecular structure of $\{Li_4[C(NPh)_3]_2(THF)_6\}$ **1**. Selected bond distances (Å) and angles (°): N(1)–C(2) 1.342(4), N(2)–C(2) 1.358(4), C(2)–N(3) 1.378(4), N(1)–C(31P) 1.395(4), N(2)–C(11P) 1.388(4), N(3)–C(21P) 1.391(4), N(1)–C(2)–N(2) 121.5(3), N(1)–C(2)–N(3) 126.6(3), N(2)–C(2)–N(3) 111.8(3), C(2)–N(1)–C(31P) 122.2(2), C(2)–N(2)–C(11P) 122.3(3), C(2)–N(3)–C(21P) 120.2(3), Li(1)–C(11P) 2.740(6), Li(1)–C(16P) 2.435(7), Li(1)–N(1) 1.949(6), Li(2)–N(2) 2.004(6), Li(2)–N(3) 2.057(6), Li(2)–N(3a) 2.133(6). For numbering scheme see both Figs. 2 and 3.

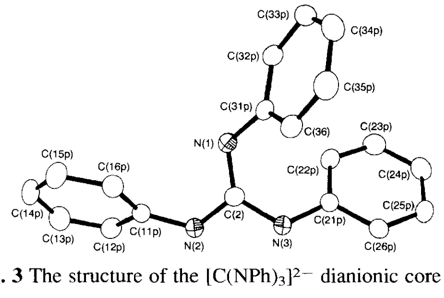

**Fig. 3** The structure of the $[C(NPh)_3]^{2-}$ dianionic core of **1**

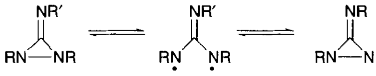

**Fig. 4** The isomerism of diaziridineimines *via* a dehydroguanidine

intramolecular coordination of one of them to a lithium is not at this stage clear: however, a theoretical study is being undertaken in order to clarify this and the electronic structure of **1**. It is interesting to note that in both triphenyl guanidine and the triphenyl guanidinium ion,[8] the phenyls are arranged in a similar fashion. It would appear that if the substituents were significantly more bulky (*tert*-butyl, trimethylsilyl, cyclohexyl) such an arrangement would not be possible without considerable torsion angle distortion across the Y-shaped core and the $C_{3h}$ structure would result.

The $^{13}$C NMR spectrum of **1** in [$^2$H$_8$]THF at 293 K[‡] shows the three phenyls to be equivalent indicating either the adoption of the symmetrical $C_{3h}$ structure in solution, rapid inversion at the nitrogens or rapid rotation about the central carbon–nitrogen bonds. Unfortunately, the low solubility of **1** prevents the acquisition of a low-temperature limiting spectrum. The central carbon of **1** gives rise to a resonance at δ 169.4 which is to considerably higher frequency than that in the isoelectronic tribenzylidenemethane dianion (δ 145.9),[11] and compares with a value of δ 144.8 for triphenylguanidine itself.

Guanidines are found to coordinate to Lewis acids through the imine nitrogen alone thus generating guanidinium type species,[12] whilst for the guanidine monoanion a bridging mode of coordination ($\mu$-$\eta^2$–) to a platinum dimer has been reported.[13] The only example of a coordinated guanidine dianion is that generated in a mechanistically obscure reaction between $Fe(CO)_5$ and dicyclohexylcarbodiimide where the ligand is found to bridge an $Fe_2(CO)_6$ dimer.[14]

It has previously been suggested that the triplet diradical triazatrimethylenemethane $MeN{=}C(N{\cdot}CMe_3)_2$ is involved in the isomerism of the corresponding diaziridineimine in which the NR groups are permuted between the imine and aziridine nitrogen environments (Fig. 4).[15] On this basis, two-electron oxidation of **1** might be expected to lead to the triphenyl diaziridineimine. The isomerism of these diaziridineimines is found to be a lower energy process than that in the corresponding methylene cyclopropanes, and accordingly, since methylene cyclopropanes are effective precursors to coordinated TMM ligands,[16] the diaziridineimines may prove useful reagents for the introduction of triazatrimethylenemethane ligands. This, and other methods directly from the dianion **1**, are currently being explored as potential routes to triazatrimethylenemethane complexes.

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## Footnotes

[†] Owing to its anticipated sensitivity, a colourless cuboid (0.35 × 0.27 × 0.27 mm$^3$) was handled under a stream of dry nitrogen gas before being coated in a film of perfluoropolyether oil and transferred into the cold stream of an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr*, 1986, **19**, 105] operating at 150 K and mounted on a Stoe Stadi-4 four-circle diffractometer.

[‡] *Crystal data.* $C_{62}H_{78}Li_4N_6O_6$, $M$ = 1031.06, triclinic, space group $P\bar{1}$ with $a$ = 10.531(12), $b$ = 11.857(11), $c$ = 12.92(2) Å, $\alpha$ = 96.48(8), $\beta$ = 97.22(9), $\gamma$ = 112.61(7)°, $U$ = 1454(3) Å$^3$ (from setting angles of 12 reflections with $29 \leqslant 2\theta \leqslant 32°$, $\lambda$ = 0.71073 Å), $D_c$ = 1.177 g cm$^{-3}$, $Z$ = 1, $\mu$ = 0.070 mm$^{-1}$, $F$(000) = 552. Diffraction data were collected using graphite-monochromated Mo-K$\alpha$ X-radiation, $\omega$–2$\theta$ scans and on-line profile fitting (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22). During data processing a correction for linear isotropic decay (*ca.* 15%) was successfully applied. Of 3836 unique reflections collected [$2\theta_{max}$ = 50°, $-12 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 13$], 3820 were used in all calculations. Automatic direct methods [G. M. Sheldrick, SHELXS-86: *Acta Crystallogr., Sect. A*, 1990, **46**, 467] followed by iterative cycles of least-squares refinement and difference Fourier synthesis located all non-hydrogen atoms: these were then refined anisotropically. Two of the symmetry-unique phenyl rings were restrained to have $C_{2v}$ symmetry while the one having close contacts to Li(1) was unrestrained. H atoms were included in calculated positions and allowed to ride on their parent C atoms with a common $U_{iso}(H) = 1.2U_{eq}(C)$ (G. M. Sheldrick, SHELXL-93: University of Göttingen, Germany, 1993). At final convergence $R[F \geqslant 4\sigma(F)] = 0.0530$, $wR(F^2$, all data) = 0.1383, $S(F^2)$ = 1.020 for 353 refined parameters and the final Δ$F$ synthesis showed no peaks outwith ±0.25 e Å$^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] $^{13}$C NMR spectrum of **1** in [$^2$H$_8$]tetrahydrofuran at 293 K: δ 169.4, 155.4, 127.1, 120.1, 113.2.

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