{Tris[(dimethylamino)dimethylsilyl]methyl}magnesium Iodide. A Grignard Reagent without a Carbon−Magnesium Bond?

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Received October 22, 1996⊗

Summary: Reaction of $(Me_2NMe_2Si)_3CI$ with Mg gives the Grignard reagent $(Me_2NMe_2Si)_3CMgI$, in which all three N atoms are coordinated to Mg and there is a planar carbanionic center, suggesting the absence of C···Mg bonding.

After using the very bulky ligands $(Me_3Si)_3C$ and $(PhMe_2Si)_3C$ for some years to make unusual compounds of a range of metals,[1] we recently turned to use of related ligands with similar bulk around the central carbon atom but containing one or more functional substituents on silicon potentially able to act as electron donors in intra- or intermolecular coordination. This approach has given novel compounds such as the following: (a) the internally solvated compounds $(THF)_2LiCR_2SiMe_2OMe$ (THF = tetrahydrofuran),[2] $Mg(CR_2SiMe_2OMe)_2$,[2] and $\{Yb(\mu\text{-}I)(CR_2SiMe_2OMe)(OEt_2)\}_2$,[3] where R = $SiMe_3$; (b) the cage compound $\{LiC(SiMe_2OMe)_3\}_2$, in which each Li atom is coordinated by one OMe group from its own monomer and by two from the other;[4] (c) the polymeric-ionic species $\{(Me_2NMe_2Si)_3CLi\}_n$, **1**, in which each Li atom is coordinated by two Me_2N ligands from the carbanion on one side and by one from that on the other side.[5] In **1** there is a planar carbanionic center well removed (by 3.52 Å) from the planar 3-coordinate Li center (see Figure 1); reactions of **1** with Me_3SnCl and $HgBr_2$ gave $Sn\{C(SiMe_2NMe_2)_3\}Me_3$ and $Hg\{C(SiMe_2NMe_2)_3\}_2$, **2**, respectively.[5]

$\{(Me_2NMe_2Si)_3CLi\}_n$ **1**

$Hg\{C(SiMe_2NMe_2)_3\}_2$ **2**

$(Me_2NMe_2Si)_3CMgI$ **3**

Tertiary amines have for some time been used to assist formation of organomagnesium halides in hydrocarbon solvents,[6] and a few such species (and rather more diorganomagnesium compounds) containing coordinated amines have been structuraly characterised.[7] It thus seemed of interest to make the Grignard reagent $(Me_2NMe_2Si)_3CMgI$, **3**, and this we did by treating Mg in Et_2O−light petroleum with the iodide $(Me_2NMe_2Si)_3CI$, itself obtained by reaction of **1** with ICH_2CH_2I.[8]

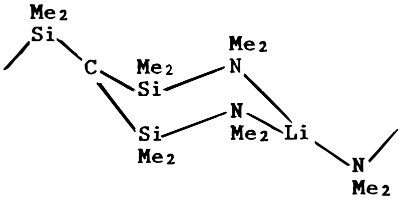

Figure 1. Monomer unit in the polymeric **1**.

An X-ray diffraction study showed **3** to have the unprecedented structure depicted in Figure 2.[9] In **1** and **3**, and also in the free anion $[(FMe_2Si)(Bu^tMe_2Si)(Me_3Si)C]^-$,[10] the sum of the angles at the central carbon C1 is ca. 360° and the C1−Si bonds are exceptionally short (mean 1.818(6) in **3**, 1.792(6) in **1**, and 1.80 Å in $[(FMe_2Si)(Bu^tMe_2Si)(Me_3Si)C]^-$), Si−C($sp^3$) bonds usu-

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⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1997.

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[8] All manipulations were carried out, with protection from light, by Schlenk techniques and/or under argon. 1,2-Diiodoethane (1.30 g, 4.6 mmol) was added dropwise with stirring during 15 min to a solution of **1** (1.50 g, 4.6 mmol)[5] in Et_2O (50 cm^3), and the mixture was then stirred for 1 h. The solvent was removed under vacuum and the solid extracted with light petroleum (bp 40−60 °C, 3 × 10 cm^3). The extract was added dropwise during 20 min to a stirred suspension of Mg turnings in Et_2O (20 cm^3) and the mixture stirred overnight. The solvent was removed under vacuum, the residue extracted with Et_2O, the extract filtered, and the solvent removed under vacuum. The solid obtained was recrystallized from benzene by slow evaporation of the solvent under reduced pressure. The crystals were washed with cold (−20 °C) light petroleum to leave compound **2**. Yield: 1.16 g, 54%. Mp: 204−209 °C (dec). Anal. Calcd for $C_{13}H_{36}IMgN_3Si_3$: C, 33.2; H, 7.7; N, 8.9. Found: C, 32.7; H, 7.6; N, 8.9. ^1H NMR (C_6D_6) (300 MHz, 25 °C): δ 0.11 (s, 18H, MeSi), 2.15 (s, 18H, MeN). ^{13}C NMR (C_6D_6, 125.76 MHz, INEPT): δ 4.3 (SiMe), 19.4, $^1J(^{13}C^{29}Si)$ 58 Hz (CSi_3), 40.2 (NMe). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 14.7. ^{15}N NMR (C_6D_6, 50.7 MHz, INEPT refocused): δ −364.9. Mass spectrum (70 eV) [*m/z* (% abundance)]: 469 (M^+, 25), 454 (M − Me, 15), 425 (M − NMe_2, 15), 275 ($(Me_2NMe_2Si)_2C{=}SiMe_2$ + H, 80), 274 ($(Me_2NMe_2Si)_2C{=}SiMe_2$, 100).

[9] Crystal data: $C_{13}H_{36}IMgN_3Si_3$; $M = 469.9$; triclinic, space group $P\bar{1}$ (No. 2); $a = 9.518(3)$, $b = 15.560(7)$, $c = 16.696(3)$ Å; $\alpha = 74.72(3)$, $\beta = 88.03(2)$, $\delta = 72.23(3)°$; $V = 2268.6(13)$ Å^3; Mo Kα radiation, $\lambda = 0.710\,73$ Å; $D_c = 1.38$ g cm^{-3}; Z = 4; $F(000) = 968$; μ(Mo Kα) = 1.60 mm^{-1}, $T = 173$ K; 7977 unique reflections measured and 6119 with $F^2 > 2\sigma(F)^2$ used. There was no absorption or decay correction, and structure solution was by direct methods with SHELXS-86. Full-matrix least-squares refinement was on F^2 (SHELXL-93) using all data, with non-hydrogen atoms anisotropic in riding mode with $U_{iso} = 1.5U_{eq}$ for the parent atoms. Final $R1 = 0.062$ and $wR2 = 0.153$ (for reflections with $F^2 > 2\sigma(F^2)$); $R1 = 0.081$ and $wR2 = 0.172$ (for all data). There are two independent molecules, and in one of them two of the NMe_2 groups are disordered such that there are two equally occupied sites for the methyl carbon atoms. Corresponding bond lengths and angles do not differ significantly between the two molecules, and data are given only for the nondisordered one.

S0276-7333(96)00891-6 CCC: $14.00

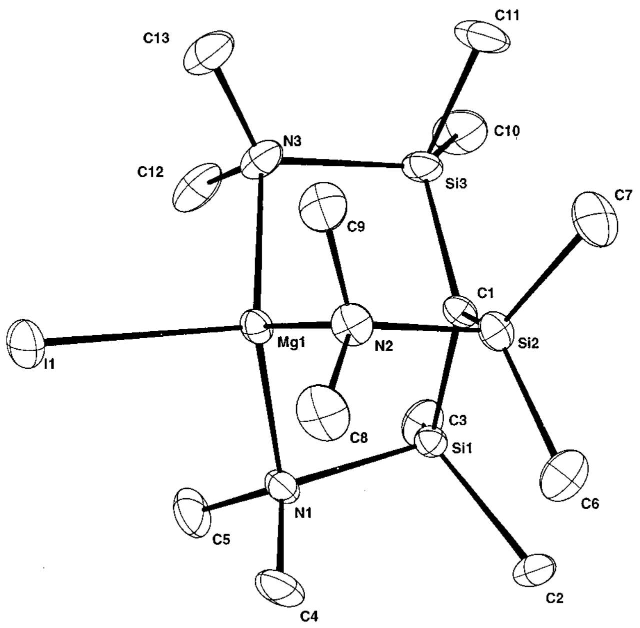

Figure 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Mg−N mean 2.196(5), Mg−I 2.741(2), C1−Si mean 1.818(5), Si−N mean 1.836(5), Mg···C1 2.418(6); N−Mg−N mean 114.9(2), Si−C−Si mean 119.6(3), Si−N−Mg mean 92.6(2), N−Mg−I mean 103.2(2).

ally having lengths in the range 1.86−1.90 Å.[11] (For comparison, the mean Si−C1−Si angle in **2** is 114.0(6)° and the mean C1−Si distance 1.90(2) Å.[12]) Both of these geometrical features are attributable to extensive delocalization of the negative charge from C1.[1a] Since either covalent or ionic bonding between C1 and Mg in **3** would be expected to result in some pyramidalization at C1,[13] we suggest that, just as there is no C···Li interaction in **1**, there can be very little, if any, C···Mg bonding in **3**, even though the C1···Mg distance of 2.418(6) Å does not greatly exceed those, viz. ca. 2.10−2.30 Å, commonly found in ordinary Grignard reagents.[7] There must, of course, be a strong electrostatic interaction between the region of negative charge dispersed over the C1 atom and its attached $SiMe_2NMe_2$ groups and the region of positive charge dispersed over the Mg atom and its attached NMe_2 groups, but this would not be regarded as a specific ionic C···Mg bond.

The Mg−I and Mg−N bond lengths are normal for four-coordinate Mg.[7] The geometry at the Mg can be regarded as that of a flattened tetrahedron (sum of angles 436.4°), with the rather wide N−Mg−N angles, mean 114.9(2)°, and narrow Mg−N−Si angles, mean 92.6(2)°, attributable to the electrostatic interaction that inhibits increase in the C1···Mg distance. Direct bonding between C1 and Mg along the C_3 I−Mg···C axis would involve a mean C−Mg−N angle of 76.8°, compared with angles of 90°, accompanied by N−Mg−N angles of 120°, expected for an ideal five-coordinate species. The Si−N bonds, mean 1.836(5) Å (cf. 1.804 Å in **1**), are much longer than those in **2**, mean 1.731(5) Å,[12] or a range of $R_3SiNR'_2$ compounds (1.71−1.72 Å);[14] this bond lengthening can be associated with the engagement of the nitrogen lone pair in coordination to the metal. (Correspondingly, there is an exceptionally long bond, of 1.86(1) Å, between silicon and quaternary nitrogen in the pyridinium salt $[C_5H_5NSiMe_3]I$.[15]) However, part of the Si−N bond lengthening in 3 could be attributable simply to the increase in the coordination number at nitrogen, and one can speculate that there may also be contributions from (a) delocalization of the electrons of the Si−N bond on to the N atom arising from the hyperconjugative stabilization of the carbanion and (b) hyperconjugative electron release of electrons from the Si−N bond to the N−Mg bond, such as was recently postulated for an $Me_3Si-Cl-Cu$ linkage.[16] However, the latter effect acting alone should give rise to short N−Mg bonds, whereas those observed are normal.

Elucidation of the detail of the bonding interactions in **3** presents an interesting challenge to theoreticians.

That **3** behaves normally as a Grignard reagent was shown by treating it with Me_3SnCl to give the compound $(Me_2NMe_2Si)_3CSnMe_3$, identical with that made previously from **1**.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council for support of this work and the Universiti Sains Malaysia for the award of a prograduate scholarship to A.F.

Supporting Information Available: Tables giving details of data collection, refinement, and the disorder, atom coordinates and *U* values, anisotropic displacement parameters, and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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