Reaction of Hypercoordinate Dichlorosilanes Bearing 8-(Dimethylamino)-1-naphthyl Group(s) with Magnesium: Formation of the 1,2-Disilaacenaphthene Skeleton[**]

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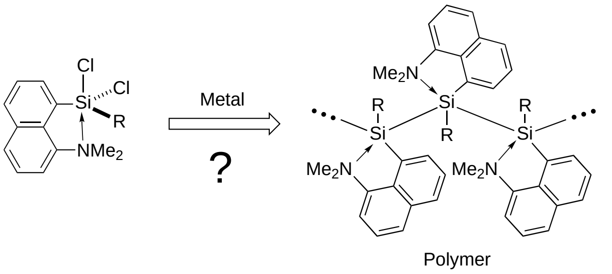
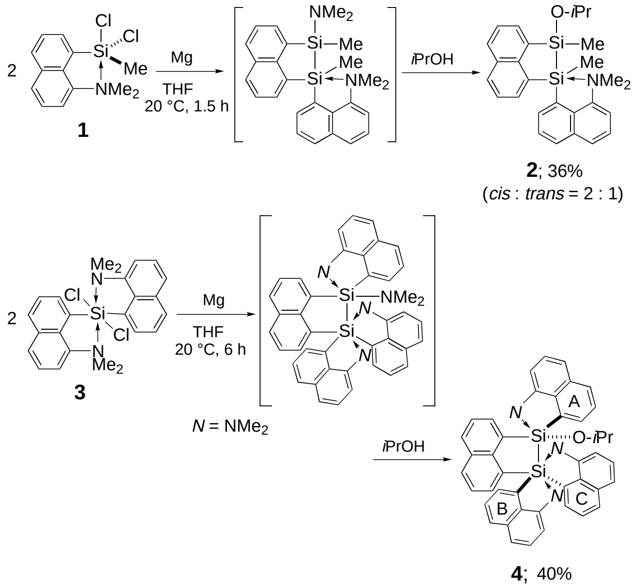
Recently, we found that a pentacoordinate monochlorosilane containing the 8-dimethylamino-1-naphthyl group undergoes reductive coupling with magnesium to form an Si–Si bond, which provided a new procedure for the direct interconnection of pseudo-pentacoordinate silicon atoms.[1] We anticipated that a similar magnesium reduction of a pentacoordinate dichlorosilane containing the same aminonaphthyl group would give polysilanes in which all the silicon atoms are pentacoordinate[2] [Eq. (1)]. However, contrary to our expectation, the reaction actually afforded no polysilanes but only a dimeric product that contained a 1,2-disilaacenaphthene skeleton arising from Si–Si and Si–C bond formation and amino group migration from the naphthyl carbon atom to a silicon atom (Scheme 1).



(1)

The pentacoordinate dichlorosilane **1** bearing an 8-(dimethylamino)-1-naphthyl group was treated with two equivalents of magnesium. After quenching with isopropyl alcohol, the dimerized product 1-isopropoxy-1,2-disilaacenaphthene (**2**) bearing only one 8-(dimethylamino)-1-naphthyl group was obtained as a mixture of stereoisomers (*cis*:*trans* = 2:1). The structure of this unexpected product was confirmed by X-ray crystallography on *cis*-**2** (Figure 1)[4a] and by ^{1}H, ^{13}C, and ^{29}Si NMR spectra of *cis*- and *trans*-**2**. It is noteworthy that the coordination number of one of the two silicon atoms is lowered from five to four.

Hexacoordinate dichlorosilane **3** bearing two 8-(dimethylamino)-1-naphthyl groups also reacted with magnesium to afford, after treatment with isopropyl alcohol, 1-isopropoxy-1,2-disilaacenaphthene (**4**), which bears three 8-(dimethylamino)-1-naphthyl groups, as the major product (Scheme 1). The structure of this crowded molecule was also determined by X-ray crystallography (Figure 2).[4b] One silicon atom is again pentacoordinate while the other is hexacoordinate.[2] Compound **4** is the first disilane composed of hexacoordinate and pentacoordinate silicon centers.



Scheme 1. Formation of the disilaacenaphthenes **2** and **4** from **1** and **3**.

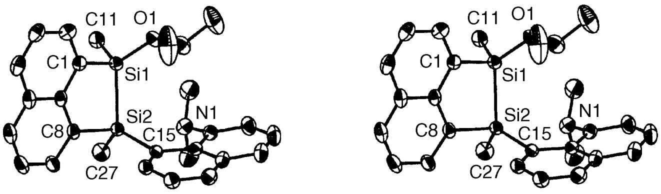


Figure 1. X-ray structure of *cis*-**2** drawn in stereoview at 30% probability level. All hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Si1–Si2 2.3469(8), Si2···N1 2.828(2); N1···Si2-C8 177.16(8) Si1-Si2-C8 89.43(8), Si1-Si2-C15 113.56(7), Si1-Si2-C27 119.14(9), Si2-Si1-O1 122.01(7), Si2-Si1-C1 93.75(7), Si2-Si1-C11 114.07(9).

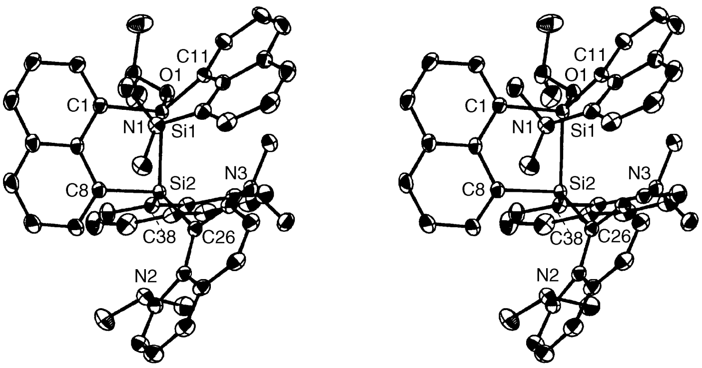


Figure 2. X-ray structure of **4** drawn in stereoview at 30% probability level. All hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Si1–Si2 2.3641(6), Si1···N1 3.078(2), Si2···N2 3.147(2), Si2···N3 2.970(2); O1-Si1···N1 168.06(6), Si2-Si1-O1 107.17(5), Si2-Si1-C1 94.35(6), Si2-Si1-C11 127.54(6), Si1-Si2···N2 171.97(4), N3···Si2-C8 175.84(7), Si1-Si2-C8 89.14(6), Si1-Si2-C26 122.15(6), Si1-Si2-C38 104.17(6).

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[**] Financial support by a Grant-in-Aid for Scientific Research on Priority Areas of "The Chemistry of Inter-element Linkage" (No. 09239103) from Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged.

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Interestingly, in these reactions, one silicon atom became bonded to the naphthyl carbon atom that bore the amino group. The amino group migrated to the coordinated silicon atom to afford an aminosilane with a lower coordination number and was finally substituted by the isopropoxyl group during workup with isopropyl alcohol.

Two types of reactions of hypercoordinate dihalosilanes with alkali or alkali earth metals have been reported. One is the conventional silicon–silicon bond formation observed by Belzner et al. in the reaction of a hypercoordinate dichlorosilane bearing 2-[(dimethylamino)methyl]phenyl group(s) with magnesium to afford the corresponding cyclic trisilane.[5] The other is cyclization by Si–C_{benzyl} bond formation and migration of the amino group from the benzyl carbon atom to the silicon atom without silicon–silicon bond formation. Thus, Corriu, Auner et al. reported the reaction of a pentacoordinate difluorosilane bearing the 8-[(dimethylamino)methyl]-1-naphthyl group with lithium or lithium naphthalenide to afford a 1-silaacenaphthene derivative.[6] Both silicon–silicon bond formation and amino-group migration proceeded concomitantly and selectively in the reaction of **1** and **3** with magnesium to afford 1-amino-1,2-disilaacenaphthene derivatives. These results indicate that the course of the reaction depends on the structure of the aminoaryl groups and suggest the possibility of developing new types of reactions by the introduction of new intramolecular coordinating groups.

Some structural aspects of the new 1,2-disilaacenaphthene derivatives **2** and **4** are as follows: The Si1–Si2 bond lengths (2.3469(8) in **2** and 2.3641(6) Å in **4**) are shorter than expected and comparable to that of 2.338(2) Å in 1,1,2,2-tetramethyl-1,2-disilaacenaphthene, which contains two tetravalent silicon centers,[7] presumably because the Si–Si bonds are incorporated in the rather rigid five-membered ring of the acenaphthene skeleton.

One of the silicon atoms in **2** (Si2) is pentacoordinate, as indicated by the Si2$\cdots$N1 distance of 2.828(2) Å, the N1$\cdots$Si2-C8 angle of 177.16(8)°, and the pentacoordinate character %TBP_e and %TBP_a of 77 % and 54 %, respectively (see ref. [8] for details of definitions of %TBP_e and %TBP_a). Although Si2 in **2** bears no electronegative ligand, these parameters are similar to those of pentacoordinate silicon compounds bearing the same aminoaryl group and a fluorine or oxygen atom.[9] The Si1-Si2-C8 bond angle of 89.43(8)° in the 1,2-disilaacenaphthene skeleton[7] of **2** seems suitable to occupy the axial/equatorial positions in the trigonal bipyramidal geometry and thus favors the coordination of the amino group.

In **4**, two aminonaphthyl groups *cis* to each other (labeled A and B in Scheme 1) are highly distorted, as evidenced by the large Si-C1$\cdots$C8-N and C1-C2-C3/C6-C7-C8 dihedral angles[10] of 29.3 and 13.1°, resectively, in group A, and of 34.1 and 14.7°, resectively, in group B. The coordination of the nitrogen atoms to the silicon centers is weak, as shown by Si$\cdots$N distances of 3.078(2) at the pentacoordinate silicon center bearing group A and 3.147(2) Å at the hexacoordinate silicon center bearing group B. These structural features may be ascribed to steric hindrance. In contrast, aminonaphthyl group C is free of distortion,[11] as shown by the small Si-C1$\cdots$C8-N and C1-C2-C3/C6-C7-C8 dihedral angles[10] of 4.5 and 5.8°, respectively. Regardless of the hexacoordination of this silicon center, the Si2$\cdots$N3 distance (2.970(2) Å) is shorter than that of the pentacoordinate silicon center (Si1$\cdots$N1 3.078(2) Å) described above.

Mechanistic studies on this reaction are now in progress.[12]

Experimental Section

2: A solution of **1** in benzene (1.61 mmol g^{-1}, 0.62 g, 1.0 mmol) was added to a suspension of magnesium powder (49 mg, 2.0 mmol) in THF (2 mL) at 20 °C under a nitrogen atmosphere. After stirring for 1.5 h at this temperature, triethylamine (0.28 mL, 2.0 mmol) and isopropyl alcohol (0.46 mL, 6.0 mmol) were added, and the resulting mixture was stirred for 2 h. [In another experiment, the ^{1}H NMR spectrum of this mixture with triphenylsilane as internal standard indicated the presence of *cis*- and *trans*-**2** in 52 % yield (*cis*:*trans* ≈ 2:1), dimethylaminonaphthalene in about 20 % yield, and very weak signals of an unidentified compound(s).] After concentration under reduced pressure, hexane was added to the residual oil, and the precipitate thus formed was removed by filtration. The filtrate was concentrated in vacuo, and the residual oil was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1; $R_f = 0.48$) as eluent to afford crude **2**. Further purification by HPLC with hexane/ethyl acetate (50/1) as eluent afforded *cis*-**2** (49 mg, 0.11 mmol, 22 % yield) and *trans*-**2** (30 mg, 0.068 mmol, 14 % yield). *cis*-**2**: m.p. 172–173 °C (from hexane/ethyl acetate (50/1)); ^{1}H NMR (270 MHz, C_6D_6): $\delta = 0.59$ (s, 3H), 0.59 (d, $^3J(H,H) = 5.9$ Hz, 3H), 0.83 (s, 3H), 0.89 (d, $^3J(H,H) = 5.9$ Hz, 3H), 2.61 (s, 3H), 2.75 (s, 3H), 3.77 (sept, $^3J(H,H) = 5.9$ Hz, 1H), 7.15–7.24 (m, 2H), 7.34 (d, $^3J(H,H) = 7.6$ Hz, 1H), 7.50–7.59 (m, 3H), 7.67 (d, $^3J(H,H) = 7.8$ Hz, 1H), 7.82–7.91 (m, 3H), 7.96 (d, $^3J(H,H) = 6.5$ Hz, 1H), 8.15 (d, $^3J(H,H) = 7.0$ Hz, 1H); ^{13}C NMR (67.94 MHz, C_6D_6; * denotes two overlapping signals): $\delta = 0.26$, 0.44, 25.40, 25.90, 45.77, 50.61, 66.73, 117.02, 125.66, 125.92*, 126.19, 126.26, 128.52, 129.87, 130.39, 131.45, 132.67, 133.41, 134.02, 135.44, 135.60, 138.17, 141.10, 146.36, 148.32, 153.30; ^{29}Si NMR (53.67 MHz, C_6D_6, TMS): $\delta = -37.55$, 4.33; elemental analysis calcd (%) for $C_{27}H_{31}NOSi_2$: C 73.42, H 7.07, N 3.17; found: C 73.42, H 6.90, N 3.09. *trans*-**2**: m.p. 142–143 °C (from hexane/ethyl acetate (50/1)); ^{1}H NMR (270 MHz, C_6D_6): $\delta = 0.36$ (s, 3H), 0.91 (s, 3H), 1.09 (d, $^3J(H,H) = 5.9$ Hz, 3H), 1.20 (d, $^3J(H,H) = 5.9$ Hz, 3H), 2.60 (s, 3H), 2.73 (s, 3H), 4.04 (sept, $^3J(H,H) = 5.9$ Hz, 1H), 7.05 (t, $^3J(H,H) = 7.4$ Hz, 1H), 7.15 (d, $^3J(H,H) = 7.3$ Hz, 1H), 7.33 (t, $^3J(H,H) = 7.7$ Hz, 1H), 7.48 (t, $^3J(H,H) = 7.4$ Hz, 1H), 7.52–7.62 (m, 3H), 7.82–7.92 (m, 5H); ^{13}C NMR (67.94 MHz, C_6D_6; * denotes two overlapping signals): $\delta = 1.05$, 1.10, 26.12*, 47.09, 48.76, 66.83, 116.70, 125.83*, 126.01, 126.15, 126.28, 128.50, 129.71, 130.10, 131.34, 132.22, 133.23, 133.73, 135.48, 135.71, 138.01, 141.59, 146.04, 148.38, 153.05; ^{29}Si NMR (53.67 MHz, C_6D_6, TMS): $\delta = -37.35$, 6.11; elemental analysis calcd (%) for $C_{27}H_{31}NOSi_2$: C 73.42, H 7.07, N 3.17; found: C 73.44, H 7.28, N 3.16.

4: After the reaction of magnesium powder (24 mg, 1.0 mmol) with **3** (0.23 g, 0.5 mmol) in THF (1 mL) at 20 °C for 6 h, the products were quenched with triethylamine (0.14 mL, 1.0 mmol) and isopropyl alcohol (0.23 mL, 3.0 mmol) at 20 °C for 1.5 h as described above. [In another experiment, the ^{1}H NMR spectrum of this mixture with triphenylsilane as internal standard indicated the presence of **4** in 70 % yield and dimethylaminonaphthalene in 30 % yield.] After workup as described above, recrystallization of the residual solid from hexane afforded pure **4** (74 mg, 0.10 mmol, 40 % yield). **4**: m.p. 270–271 °C (from hexane/ethyl acetate (50/1)); ^{1}H NMR (270 MHz, C_6D_6): $\delta = -0.17$ (d, $^3J(H,H) = 5.1$ Hz, 3H), 0.51 (s, 3H), 0.72 (s, 3H), 1.13 (d, $^3J(H,H) = 5.9$ Hz, 3H), 1.18 (s, 3H), 1.64 (s, 3H), 2.52 (s, 3H), 2.54 (s, 3H), 3.77 (sept, $^3J(H,H) = 5.9$ Hz, 1H), 6.56 (dd, $^3J(H,H) = 7.8$ Hz, 7.0 Hz, 1H), 6.74 (dd, $^{3,4}J(H,H) = 4.9$, 0.8 Hz, 1H), 6.90 (dd, $^3J(H,H) = 8.0$, 6.6 Hz, 1H), 7.15–7.40 (m, 6H), 7.47–7.64 (m, 7H), 7.67 (dd, $^{3,4}J(H,H) = 8.0$, 0.9 Hz, 1H), 7.72 (dd, $^{3,4}J(H,H) = 8.4$, 1.4 Hz, 1H), 7.77 (dd, $^{3,4}J(H,H) = 8.2$, 0.9 Hz, 1H), 7.83–7.94 (m, 3H), 8.22 (dd, $^{3,4}J(H,H) = 6.8$, 1.4 Hz, 1H), 9.03 (dd, $^{3,4}J(H,H) = 7.3$, 1.4 Hz, 1H,); ^{13}C NMR (67.94 MHz, C_6D_6; * denotes two overlapping signals): $\delta =$ 24.05, 26.40, 41.17, 43.28, 49.58, 50.12, 51.04, 51.29, 66.92, 117.04, 117.25, 120.42, 124.73, 125.22, 125.29, 124.45, 125.54*, 125.65, 125.72, 125.77, 126.31, 127.14, 128.74, 129.10, 129.15, 129.76, 130.75, 132.40, 133.19, 133.44, 134.04, 134.60, 135.08, 135.38, 135.74, 135.89, 136.07, 136.19, 137.09, 137.88, 139.12, 139.54, 140.81, 146.31, 147.41, 154.22, 154.38, 154.71; ^{29}Si NMR (53.67 MHz, C_6D_6, TMS): $\delta = -21.54$, -11.52; elemental analysis calcd (%) for $C_{49}H_{49}N_3OSi_2$: C 78.25, H 6.57, N 5.59; found: C 78.27, H 6.55, N 5.49.

Received: May 17, 1999 [Z13422IE]
German version: *Angew. Chem.* **1999**, *111*, 3520–3523

Keywords: heterocycles · hypervalent compounds · magnesium · silicon · rearrangements

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[2] In view of the weak coordination of the nitrogen atom of the 8-(dimethylamino)-1-naphthyl group, it may be better to describe the resulting structures as [4+1]-coordinate[3] and [4+2]-coordinate.[3] However, we prefer to refer to them as "pentacoordinate" and "hexacoordinate" for the sake of simplicity.

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[4] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120868 and 120869. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). a) Crystal data for *cis*-**2**: $C_{27}H_{31}NOSi_2$, $M_r = 441.72$, crystal dimensions $0.5 \times 0.4 \times 0.3$ mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.7570(3)$, $b = 36.023(1)$, $c = 8.8050(2)$ Å, $\beta = 118.604(2)^\circ$, $V = 2438.5601$ Å^3, $Z = 4$, $\rho_{calcd} = 1.20$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.64$ cm^{-1}, $2\theta_{max} = 50.2^\circ$. A Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) at $T = 293$ K was used. A total of 3771 reflections was collected. The data were corrected for Lorentzian and polarization effects. A correction for secondary extinction was applied (coefficient $= 4.40260 \times 10^{-7}$). The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included but not refined. The final cycle of the full-matrix least-squares refinement was based on 3271 observed reflections ($I > 3\sigma(I)$) and 281 variable parameters with the teXsan crystallographic software package. The structure was refined to a GOF of 1.47 and final residuals of $R_1 = 0.053$ and $wR_2 = 0.090$. The max./min. peaks on the final difference Fourier map corresponded to $0.50/-0.25$ e Å^{-3}. b) Crystal data for **4**: $C_{49}H_{49}N_3OSi_2$, $M_r = 752.12$, crystal dimensions $0.6 \times 0.4 \times 0.3$ mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.283(2)$, $b = 17.446(3)$, $c = 20.793(3)$ Å, $\beta = 99.562(8)^\circ$, $V = 4036.3000$ Å^3, $Z = 4$, $\rho_{calcd} = 1.238$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.29$ cm^{-1}, $2\theta_{max} = 55.2^\circ$. A Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) at $T = 293$ K was used. A total of 8250 reflections was collected. The data were corrected for Lorentzian and polarization effects. A correction for secondary extinction was applied (coefficient $= 6.56940 \times 10^{-7}$). The structure was solved by direct methods (SIR92) and expanded by using Fourier techniques (DIRDIF94). The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were isotropically refined. The final cycle of the full-matrix least-squares refinement was based on 6100 observed reflections ($I > 3\sigma(I)$) and 693 variable parameters with the teXsan crystallographic software package. The structure was refined to a GOF of 1.27 and final residuals of $R_1 = 0.038$ and $wR_2 = 0.055$. The max./min. peaks on the final difference Fourier map corresponded to $0.28/-0.27$ e Å^{-3}.

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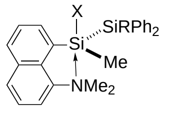
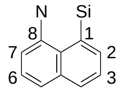


5 a; X = OEt, R = Me
b; X = F, R = Ph



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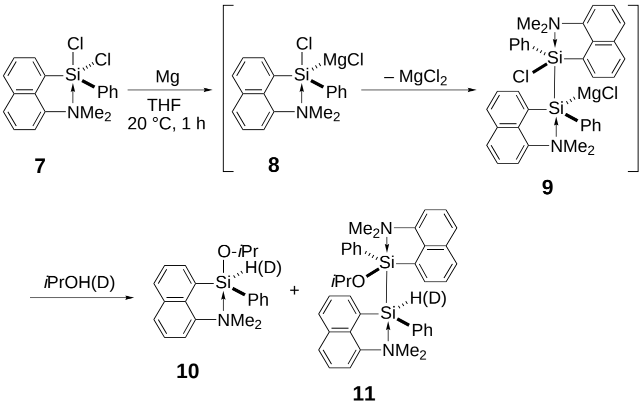
[10] For the numbering of naphthyl carbon atoms used to denote the dihedral angles, see formula **6**.

[11] Note that the aminonaphthyl group in **2** is somewhat distorted, as shown by the Si-C1···C8-N and C1-C2-C3/C6-C7-C8 dihedral angles[10] of 19.3 and 8.1°.

[12] A similar reaction of phenyl-substituted pentacoordinate dichlorosilane **7** with magnesium followed by quenching with *i*PrOH(D) afforded not the disilaacenaphthene derivative but the pentacoordinate monosilane **10** and disilane **11**, each of which bears an *i*PrO group and an H(D) atom in yields of 30 and 29%, respectively. The ^{29}Si NMR spectrum of the reaction mixture before quenching showed three signals at $\delta = -45.89$, -40.23, and -23.87, which were assigned to precursors of **10** and **11**, most probably the silylenoid **8** and its self-condensation[13] product **9**, on the basis of the high-field shift[14] of the signals relative to the dihalide **7** ($\delta = -23.22$) and the unsymmetrical structure of the precursor of **11**. Similar species may also be involved in the reactions of **1** and **3** with magnesium as well.



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