ORGANOMETALLICS

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Organometallics, **1994**, 13 (11), 4164-4166• DOI: 10.1021/om00023a015 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Novel Fluoride Transfer and Benzyne Insertion upon Reaction of $\mathrm{ClSi(MeNCH_2CH_2)_3N}$ with $\mathrm{LiC_6F_5}$

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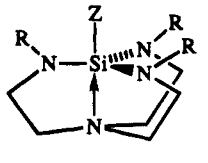
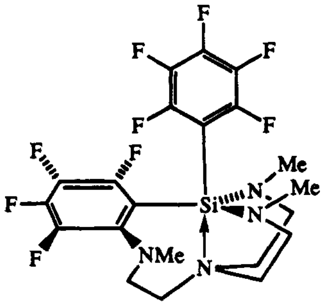
Received July 28, 1994[⊗]

Summary: Whereas $\mathrm{ClSi(HNCH_2CH_2)_3N}$ *(1) reacts with* $\mathrm{LiC_6F_5}$ *in the expected manner to give* $\mathrm{C_6F_5Si(HNCH_2CH_2)_3N}$ *(3),* $\mathrm{ClSi(MeNCH_2CH_2)_3N}$ *(2) gives a mixture of* $\mathrm{C_6F_5Si(MeNCH_2CH_2)_3N}$ *(4), the fluoride-transfer product* $\mathrm{FSi(MeNCH_2CH_2)_3N}$ *(5), and the benzyne insertion product* $\mathrm{C_6F_5Si(\textit{o}\text{-}C_6F_4NMeCH_2CH_2)(MeNCH_2CH_2)_2N}$ *(6) in the approximate ratio of 1:2:1, respectively. The structures of* ***5*** *and* ***6****, determined by X-ray means, are presented.*

Our explorations of the chemistry of a variety of azatranes[1] have recently included examples from the azasilatrane members of this class of compounds, namely, **1** and **2**. We were surprised to observe that whereas **1** allows isolation of exclusively the expected product **3** in the presence of $\mathrm{LiC_6F_5}$ formed at −50 °C,[2] **2** under the same conditions provides a 1:2:1 ratio of **4**, **5**, and **6**, respectively.[3,4] We suggest that the unprecedented fluoride to silicon transfer process that forms **5** involves an intermediate resembling **7**, in which the N→Si transannular bond may be stretched. Such an intermediate is more favored by the steric congestion to nucleophilic attack by $\mathrm{C_6F_5^-}$ in the case of R = Me than by R = H, since **1** gives only **3**. The reaction involving



	Z	R
1	Cl	H
2	Cl	Me
3	$\mathrm{C_6F_5}$	H
4	$\mathrm{C_6F_5}$	Me
5	F	Me



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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

(1) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

(2) $\mathrm{C_6BrF_5}$ (0.13 g, 0.52 mmol) was dissolved in 18 mL of pentane, and the solution was cooled to −50 °C. n-BuLi (0.26 mL, 0.52 mmol) in hexane was added, and the mixture was stirred for 30 min. A precooled (-50 °C) toluene solution (15 mL) containing 0.084 g (0.41 mmol) of **1** was added dropwise. After it was stirred at −50 °C for 1 h, the mixture was warmed slowly to room temperature and then filtered. Removal of the solvents under vacuum followed by sublimation afforded crystalline **3** in 43% yield. Mp: 102−104 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.66 (t, 6 H, $^3J_{\mathrm{HCCH}}$ = 5.7 Hz, $\mathrm{SiNC\textit{H}_2CH_2}$), 2.01 (t, 6 H, $\mathrm{SiHNCH_2C\textit{H}_2}$), 0.91 (b, 3 H, NH). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 50.76 ($\mathrm{HNCH_2\textit{C}H_2N}$), 36.79 ($\mathrm{HN\textit{C}H_2CH_2}$). The complicated pattern of the $\mathrm{C_6F_5}$ carbons caused by fluorine couplings provided barely detectable resonances. ^{29}Si NMR ($\mathrm{C_6D_6}$): δ −84.51. ^{19}F NMR: δ ($\mathrm{C_6D_6}$): δ −125.71 (dd, 2 F, *o*-F, $^3J_{\mathrm{FF}}$ = 27.4 Hz, $^4J_{\mathrm{FF}}$ = 9.0 Hz), −157.3 (t, 1 F, *p*-F, $^3J_{\mathrm{FF}}$ = 21.5 Hz), −162.26 (m, 2 F, *m*-F). MS (70 ev, EI): *m/z* (relative intensity, proposed ion) 338.1 (3.4, M$^+$), 171.1 (3.5, M$^+$ − $\mathrm{C_6F_5}$), 240.0 (33.2), 225.0 (17.3), 200.0 (16.6), 168.0 (83.3).

(3) To 25 mL of a pentane solution of $\mathrm{C_6F_5Br}$ (0.433 g, 1.79 mmol) at −50 °C was added 0.9 mL of a 2.01 M (1.89 mmol) hexane solution of *n*-BuLi. After the mixture was stirred at −50 °C for 3 h, 0.42 g (1.7 mmol) of **2** in 8 mL of toluene was slowly added. The mixture was stirred at ∼−50 °C for an additional 0.5 h and then warmed to room temperature, whereupon the mixture turned brownish red. After filtration and washing with 3 × 15 mL portions of toluene, a ^{1}H NMR spectrum of the filtrate revealed the three major products **4**−**6** in a ratio of approximately 1:2:1. After removal of the solvent under vacuum, **5** sublimed first at 35 °C/15 × 10^{-3} mmHg in about 90% purity. Repeated sublimation under these conditions gave pure **5** in 28% yield. Mp: 120−122 °C. The residual mixture was then sublimed at 55 °C to remove **4** together with unseparated **5** and a small amount of **6**. After removal of **4** and **5** was complete (as shown by the ^{1}H NMR spectra of the sublimed solid), a 21% yield of **6** was readily obtained by sublimation at 110 °C/15 × 10^{-3} mmHg as a white crystalline solid. Mp: 168−169 °C. Crystals of **5** and **6** suitable for X-ray studies were grown by sublimation at 60 °C in an unevacuated tube sealed under nitrogen and at 5 x 10^{-2} mmHg, respectively. Characterization for **5**: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 2.97 (s, 9 H, $\mathrm{NCH_3}$), 2.60 (dt, 6 H, $\mathrm{CH_3NC\textit{H}_2CH_2}$, $^3J_{\mathrm{HCCH}}$ = 5.7 Hz, $^4J_{\mathrm{FSiCH}}$ = 1.2 Hz), 2.03 (t, 6 H, $\mathrm{CH_3NCH_2C\textit{H}_2}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 48.32 (s, $\mathrm{CH_3NCH_2\textit{C}H_2}$), 47.05 (d, $\mathrm{CH_3N\textit{C}H_2CH_2N}$, $^3J_{\mathrm{CF}}$ = 1.5 Hz), 37.28 (d, $^3J_{\mathrm{CF}}$ = 8.0 Hz, $\mathrm{CH_3N}$); ^{19}F NMR ($\mathrm{C_6D_6}$) δ −136.19; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −99.69 (d, $^1J_{\mathrm{FSi}}$ = 191.8 Hz). Anal. Calcd for $\mathrm{C_9H_{21}FN_4Si}$: C, 46.55; H, 9.05; N, 24.14. Found: C, 46.74; H, 9.17; N, 24.37. Characterization for **6**: ^{1}H NMR (toluene-d_8) δ 2.60 (d, 3 H, $\mathrm{CH_2NC\textit{H}_3C_6F_4Si}$, $^5J_{\mathrm{FCH}}$ = 1.05 Hz), 2.56 (b, 3 H, $\mathrm{NCH_2CH_2NC\textit{H}_3Si}$), 2.14 (s, 3 H, $\mathrm{NCH_2CH_2NC\textit{H}_3Si}$), 2.78 (m, 1 H), 2.66 (m, 1 H), 2.60 (m, 1 H), 2.48 (m, 1 H), 2.38 (m, 1 H), 2.2 (m, 1 H), 1.95 (m, 1 H), 1.87 (m, H), 1.80 (m, 2 H), 1.7 (m, 1 H), 1.50 (dt, 1 H); ^{13}C NMR (toluene-d_8) δ 151.87 (m), 150.42 (m), 149.59 (m), 148.75 (m), 147.46 (m), 146.25 (m), 142.68 (m), 140.60 (m), 139.12 (m), 135.6 (m), 133.71 (m), 57.69, 56.9, 51.00, 51.44, 49.59, 48.46, 42.30 (d, $^5J_{\mathrm{CF}}$ = 7.0 Hz), 39.24 (m), 138.52 (s); ^{29}Si NMR (toluene-d_8) δ −66.06. ^{19}F NMR ($\mathrm{C_6D_6}$) δ −128.38 (b, 1 F), −129.83 (dd, $^3J_{\mathrm{FF}}$ = 27.7 Hz, 1 F, $^4J_{\mathrm{FF}}$ = 12.4 Hz), −146.01 (t, 1 F, $^3J_{\mathrm{FF}}$ = 15.2 Hz), −154.63 (t, 1 F, $^3J_{\mathrm{FF}}$ = 21.2 Hz), −155.18 (t, 1 F, $^3J_{\mathrm{FF}}$ = 18.3 Hz), −158.48 (t, 1 F, $^3J_{\mathrm{FF}}$ = 24.6), −161.98 (b, 2 F); ^{19}F NMR (toluene-d_8, −70 °C) δ −126.81 (d, 1 F, $^3J_{\mathrm{FF}}$ = 27.4), −129.03 (d, 1 F, J = 24.3 Hz), −130.00 (dd, $^3J_{\mathrm{FF}}$ = 27.4 Hz, $^4J_{\mathrm{FF}}$ = 9.0 Hz, 1 F), −146.00 (t, 1 F, J = 22.9 Hz), −158.44 (t, 1 F, $^3J_{\mathrm{FF}}$ = 21.2 Hz), −155.07 (t, 1 F, $^3J_{\mathrm{FF}}$ = 19.9 Hz), −154.26 (t, 1 F, $^3J_{\mathrm{FF}}$ = 21.2 Hz), −161.13 (m, 1 F), −162.06 (m, 1 F); HRMS for M$^+$ ($\mathrm{C_{21}H_{21}F_9N_4Si}$) calcd 528.139 18, found 528.140 39. Anal. Calcd for $\mathrm{C_{21}H_{21}F_9N_4Si}$: C, 47.73; H, 3.98; N, 10.60. Found: C, 48.19; H, 3.87; N, 10.87.

(4) To 0.64 g (2.6 mmol) of compound **2** in 25 mL of toluene was added 2.8 mmol of $\mathrm{MgBrC_6F_5}$ as a mixture prepared by mixing 0.70 g of $\mathrm{C_6BrF_5}$ with 0.70 g of Mg in 10 mL of ether at room temperature. The reaction mixture was stirred for ½ h. After filtration, all the volatiles were removed under vacuum over a period of 5 h. By sublimation at 50 °C/5 × 10^{-3} mmHg, a crystalline solid, identified as pure product **4**, was obtained in 14% yield. Mp: 105−106 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.53 (t, 6 H, $^3J_{\mathrm{HCCH}}$ = 5.7 Hz, $\mathrm{CH_3NC\textit{H}_2CH_2}$), 2.36 (s, 9 H, $\mathrm{NCH_3}$), 1.96 (t, 6 H, $\mathrm{CH_3NCH_2C\textit{H}_2}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 50.18 ($\mathrm{CH_3NCH_2\textit{C}H_2}$), 48.47 ($\mathrm{CH_3N\textit{C}H_2CH_2}$), 38.20 ($\mathrm{CH_3N}$). ^{29}Si NMR ($\mathrm{C_6D_6}$): −69.94. ^{19}F NMR ($\mathrm{C_6D_6}$): −126.46 (dd, 2 F, *o*-F, $^3J_{\mathrm{FF}}$ = 24.6 Hz, $^4J_{\mathrm{FF}}$ = 9.3 Hz), -156.32 (t, 1 F, *p*-F, $^3J_{\mathrm{FF}}$ = 19.8 Hz), −162.96 (m, 2 F, *m*-F). HRMS for M$^+$ ($\mathrm{C_{15}H_{21}N_4F_5Si}$): calcd 380.145 57, found 380.147 40.

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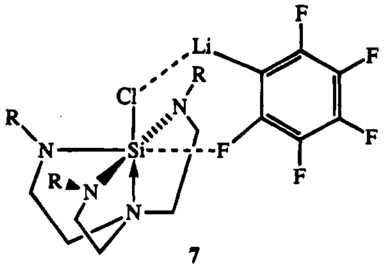

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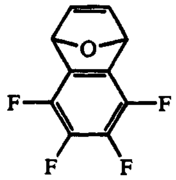

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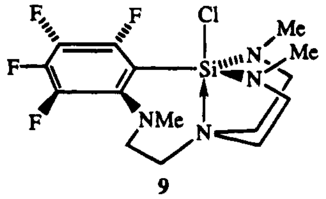
2 also produces the tetrafluorobenzyne insertion product **6**, which is rather surprising because such a transformation might have been expected to occur more readily with sterically less hindered **5**. It is also not obvious why no tetrafluorobenzyne insertion product is detected in the reaction with **1**. That **6** can arise from benzyne insertion into **4** was shown by reacting isolated **4** with a solution in which tetrafluorobenzyne was generated. That tetrafluorobenzyne was indeed generated in these reactions was shown by carrying out the reaction with **2** in the presence of furan. In that reaction the Diels–Alder adduct **8**[5] was detected by ^1H, ^{13}C, and ^{19}F NMR spectroscopy, in addition to **4**–**6**. Whether any of the tetrafluorobenzyne moiety in **8** emanated from the fluoride transfer intermediate **7** rather than from warming of the *n*-BuLi/BrC_6F_5 solution is presently inconclusive. Further support for an intermediate of type **7** to account for the formation of **5** comes from our failed attempts to fluorinate **2** by exchange with LiF in refluxing THF. Thus, it seems unlikely that **5** arises from the interaction of liberated LiF with unreacted **2**.

Tetrafluorobenzyne insertion could conceivably occur directly on **2**, giving **9**, followed by nucleophilic substitution to form **6**. If this were the case, however, then the formation of some **10** might be expected, but none was detected. Even when excess **2** was used in the aforementioned reaction, no **9** was detected.



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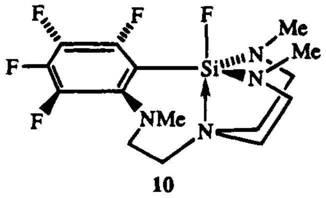

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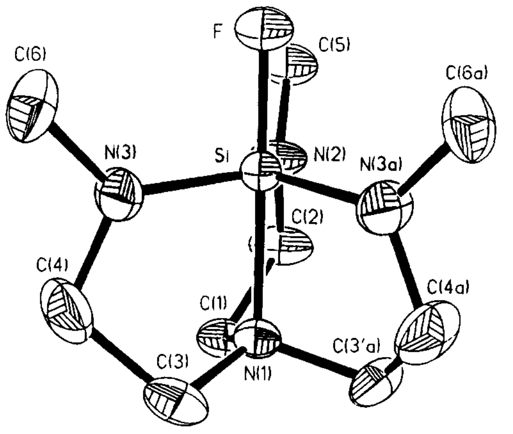
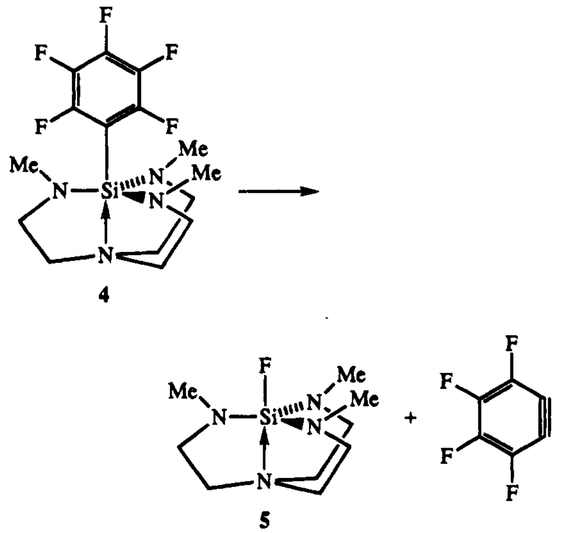


Figure 1. 1. ORTEP drawing of **5**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles: Si–N(1) = 2.034(2), Si–F = 1.643(2), average Si–N_{eq} = 1.729(2) Å; average N_{eq}–Si–N_{eq} = 119.08(9)°.

In the reaction of **2** with $BrMgC_6F_5$ at room temperature,[4] only **4** was observed to form. Since $BrMgC_6F_5$ is stable up to 80 °C,[2] it is not surprising that the tetrafluorobenzyne product **6** is not seen in this reaction until it is heated above this temperature. Somewhat surprising, however, is the lack of fluoride-transfer product. Perhaps the BrMg analogue of intermediate **7** is disfavored because the Mg–Cl bond is 58 kJ/mol weaker than the Li–Cl link[6] and because the bromine atom places greater steric demands on such an intermediate. Another possible source of tetrafluorobenzyne and **5** is the decomposition reaction (1). Although we did observe such a reaction as a minor pathway in the EI mass spectrum of **4**, a toluene solution of this compound is stable from room temperature to 100 °C.



(1)

The Si–F bond length in **5**[7] (Figure 1) is comparable with the axial Si–F lengths in SiF_5^- (1.646 Å[8]) and $PhSiF_4^-$ (1.669(3) Å[9]). Despite the expansion of one of

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[5] (a) Hoffman, R. W. *Dehydrobenzene and Cycloalkyne*; Academic Press: New York, 1967. (b) Hankinson, B.; Heaney, H.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2372. (c) Gilman, H.; Gozich, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 2625.

[6] Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978.

[7] Crystallographic information for **5**: $C_{14}H_{36}FN_4Si$, M_r = 307.56, monoclinic, $P2_1/m$, a = 7.352(1) Å, b = 12.361(2) Å, c = 7.512(1) Å, α = 90.0°, β = 119.30(1)°, γ = 90.0°, V = 595.3(2) Å^3, Z = 2, D_c = 1.716 Mg/m^3, $F(000)$ = 342, T = 223 K, R = 3.48%, R^2_w = 9.26% for 805 reflections with 2θ range (Cu Kα) 6.76–56.80° and $I \geq 2\sigma I$.

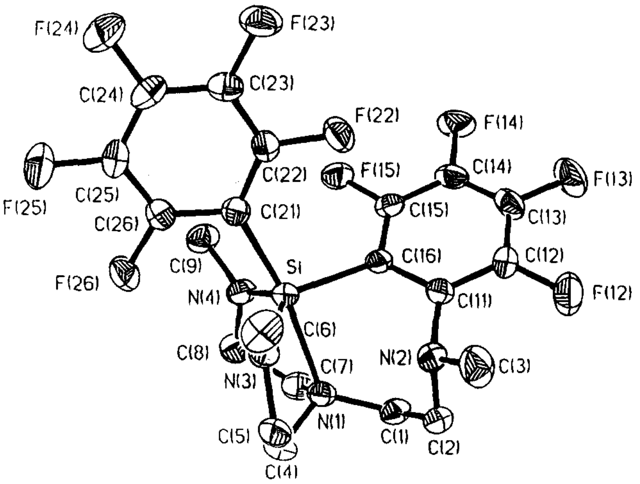

Figure 2. 2. ORTEP drawing of **6**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles: Si–N(1) = 2.246(2), Si-C(21) = 1.996(2), Si–C(16) = 1.924(2), average Si–N_{eq} = 1.733(2) Å; N(4)–Si–N(3) = 125.0(1), average C_{16}–Si–N(3) = 118.3(1), C_{16}–Si–N(4) = 112.9(1)°.

the five-membered rings in **4** by tetrafluorobenzyne insertion, the N→Si transannular bond (2.246(2) Å) is preserved in **6**[10] (Figure 2), although it is longer than that in **5** (2.034(2) Å).

Acknowledgment. This work was supported by grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Text giving details of the X-ray structure determinations, packing diagrams, and tables of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen coordinates with isotropic displacement parameters for **5** and **6** (28 pages). Ordering information is given on any current masthead page.

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(8) Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378.

(9) Schomburg, D. *J. Organomet. Chem.* **1981**, *221*, 137.

(10) Crystallographic information for **6**: $C_{21}H_{21}F_9N_4Si$, $M_r = 528.5$, triclinic, $P\bar{1}$, $a = 8.586(2)$ Å, $b = 10.215(2)$ Å, $c = 13.745(3)$ Å, $\alpha = 95.62(2)°$, $\beta = 102.25(2)°$, $\gamma = 107.74(2)°$, $V = 1104.8\ (4)$ Å^3, $Z = 2$, $D_c = 1.589$ Mg/m^3, $F(000) = 540$, $T = 223$ K, $R = 3.21\%$, $R_w = 4.66\%$ for 2679 reflections with 2θ(Cu Kα) = 4.0–115.0° and $F \geq 4.0\sigma(F)$.