Deprotonation Pathway in the Reaction of Me₆Si₂ with MeLi

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Summary: A mixture of 3 mol of Me₆Si₂ and 1 mol of MeLi in the presence of P(O)(NMMe₂)₃ produced Me₆SiLi as the initial product. This then deprotonated excess Me₆Si₂ and started an unprecedented transformation leading to (Me₃Si)₂(SiMe₂H)CLi, whose quench by [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺ produced (η⁴-exo-{(Me₃Si)₂C(SiMe₂H)C₅H₅}Fe(CO)₂)₃[PPh₃] (2e). In the literature, the reaction of Me₆Si₂ and MeLi gives Me₆SiLi and/or Me₃SiMe₃Li (4). The lithium compound 3 is the major product when a previously unnoticed deprotonation pathway is enhanced by use of an excess of Me₆Si₂ and a longer reaction time.

Organosilanes have been used to enhance reactivity and selectivity in chemical transformations.¹ In one synthetic approach, the addition of silyl anions to a variety of organic electrophiles results in formation of the needed Si-C bond.² Among such silyl anions, R₃SiLi can be generated in situ by reaction of R₃SiCl with Li, or of R₃SiSiR₃ with RLi.³ We have used the electrophile [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺ to quench the generated silyl anions. The results revealed an unprecedented conversion of Me₆Si₃ to (Me₃Si)₂(SiMe₂H)CLi and gave retrochemical evidence for a deprotonation pathway in the Me₆Si₂ reaction with MeLi.

The R₃SiLi anions were generated by reaction of the respective disilane with MeLi. The resulting solutions were cooled to –78 °C and transferred dropwise by cannula to a solution of 1:1 (η⁵-C₅H₅)Fe(CO)₂[PPh₃] in THF at –78 °C, the practical equivalent to [1] [1], after chemical initiation with a trace of lithiated reagent, which in the present cases is the first few drops of R₃SiLi. The color of the solution changed gradually from black to orange-red during the addition of R₃SiLi, sometimes with formation of a yellow precipitate that redissolved as the reaction proceeded. For the silyl anions with at least one alkyl group, the Cp ring silylation products (η⁴-exo-R₃SiC₅H₅)Fe(CO)₂(PPh₃) (R₃ = Ph₃ (2a), 51%, Me₆Ph (2b), 36%, Me₅Ph (2c), 45%) were isolated as major products after column chromatography.⁴ Thus, the Si-based nucleophiles add at the Cp ring of 1, similar to what occurred with C-based nucleophiles⁵ and different from O-based nucleophiles.

(5) Manipulations were carried out under N₂ with dry degassed reagents. Preparation of 2a (typical): a 100 mL two-necked flask was charged with Ph₅SiCl (5 mmol), and fine-cut Li wire (20 mmol) and then THF (30 mL) was added. The solution became turbid after stirring for several minutes and the color changed gradually from yellow to brown. After it was stirred for 6 h, the resulting solution was cooled to –78 °C and filtered through a pad of Celite. The filtrate was added dropwise to a mixture of (η⁵-C₅H₅)Fe(CO)₂[PPh₃] (3 mmol) in THF (100 mL), also at –78 °C. The color of solution changed from black to orange-red during the addition, accompanied by the formation of a yellow precipitate, which redissolved when the addition was completed. The reaction mixture was quenched with H₂O (200 mL) and extracted with EtO (100 mL × 2) after it was stirred overnight. The organic layers were combined, dried over MgSO₄, and then evaporated to dryness under vacuum. The oily residue was purified by SiO₂ column chromatography with 1:15-20 EtOAc/hexane as eluent to give yellow-orange 2a (51%). IR (CH₂Cl₂): νₐ(CO) 1963 (s), 1902 (s), 1385 (s), 800 (s) cm⁻¹. ¹H NMR (CD₃Cl): δ 2.71 (b, 2H), 3.90 (b, 1H), 5.10 (b, 2H), 6.96–7.53 (m, 30H). ³¹P NMR (CD₃Cl): δ 71.2 (s). ²⁹Si NMR (CD₃Cl): δ −22.6 (s). FAB MS: m/z 698 (M⁺). Anal. Calcd for C₁₆H₁₇FeO₂PSi: C, 73.92; H, 5.05. Found: C, 73.60; H, 4.99. ²⁹Si NMR (CD₃Cl): δ 71.6 (s). ³¹P NMR (CD₃Cl): δ −17.3 (d, J = 10.0 Hz). FAB MS: m/z 636 (M⁺). Anal. Calcd for C₁₇H₁₉FeO₂PSi: C, 71.70; H, 5.23. Found: C, 71.58; H, 5.22. Orange side product (η⁴-C₅H₅)Fe(CO)C₆H₅(SiMe₂H)[PPh₃] yield 45%. IR (CH₂Cl₂): νₐ(CO) 1960 (s), 1901 (s) cm⁻¹. ¹H NMR (CD₃Cl): 0.32 (s, 3H), 2.57 (b, 2H), 3.51 (b, 1H), 5.18 (b, 2H), 6.97–7.52 (m, 25H). ³¹P NMR (CD₃Cl): δ 71.6 (s). ²⁹Si NMR (CD₃Cl): δ −17.3 (d, J = 10.0 Hz). FAB MS: m/z 636 (M⁺). Anal. Calcd for C₁₇H₁₉FeO₂PSi: C, 71.70; H, 5.23. Found: C, 71.58; H, 5.22. Orange side product (η⁴-C₅H₅)Fe(CO)C₆H₅(SiMe₂H)[PPh₃] yield 45%. IR (CH₂Cl₂): νₐ(CO) 1960 (s), 1901 (s) cm⁻¹. ¹H NMR (CD₃Cl): δ −0.04 (s, 6H), 2.46 (b, 2H), 3.02 (b, 1H), 5.18 (b, 2H), 6.95–7.48 (m, 25H). ³¹P NMR (CD₃Cl): δ 71.8 (s). ²⁹Si NMR (CD₃Cl): δ −11.5 (d, J = 8.0 Hz). FAB MS: m/z 574 (M⁺). Anal. Calcd for C₁₇H₁₆FeO₂PSi: C, 69.00; H, 5.44. Found: C, 69.16; H, 5.33.

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which react at the CO ligand. The single-crystal X-ray structure of 2b confirmed that the MePh2Si group is exo to Fe (Figure 1), indicative of a direct silyl attack. Compounds 2a–c were desilylated upon acidification with HBF4(aq) or HCl(aq) to re-form the cationic compound [Fe(CO)4][X] (X = BF4, Cl), as shown by IR and 1H and 31P NMR spectroscopic studies.

Me3SiLi was prepared by treating Me6Si2 with MeLi in the presence of P(O)(NMe2)3 for 15 min at 0 °C. The reagent solution was then quenched with 1:1 (v/v) EtOAc/hexane to give Me3SiLi (6% yield) as a yellow-orange precipitate that redissolved by the formation of a yellow precipitate that redissolved when the addition was completed. The solution was warmed to room temperature and stirred overnight before the mixture was quenched with H2O (200 mL) and extracted with EtO (200 mL × 2). The combined organic layers were dried over MgSO4 and then evaporated to dryness under vacuum. The oil-like residue was purified by SiO2 column chromatography with 1:12 (v/v) EtOAc/hexane as eluent to give Me3SiLi (60%).

Data for 2b: C34H45FeO2PSi3, [Me3SiSiMe3(C34H45FeO2PSi3)]+, 389 parameters, 13 restraint(s), R = 0.14 (s), 18H, 0.21 (d, 3H). Me3SiSiMe3 (5 mmol) in anhydrous P(O)(NMe2)3 (12 mL) with MeLi (4 mmol) and stirring for 2 h (otherwise the same procedure as above) resulted in 2b (60%); IR (CH2Cl2): νCO 1967 (s) 1908 cm−1. 1H NMR (C6D6): δ 1H: 76.70(1)°, 374 parameters, 13 restraint(s), R = 0.14 (s), 18H, 0.21 (d, 3H). Me3SiSiMe3 (5 mmol) in anhydrous P(O)(NMe2)3 (12 mL) with MeLi (5 mmol) and stirring for 2 h (otherwise the same procedure as above) resulted in 2b (60%); IR (CH2Cl2): νCO 1967(s), 1908(s) cm−1. 1H NMR (CDCl3): δ 0.14 (s, 18H), 0.21 (d, 3H, J = 4 Hz, 6H), 2.58 (b, 2H), 3.65 (b, 3H); 4.30 (hept, 3H, J = 7 Hz, 1H), 5.03 (b, 2H), 6.98 (s). 29SiNMR (C6D6): δ 19.3 (s), 15.9 (s), 16.5 (s). 1H NMR (CDCl3): δ 0.14 (s, 18H), 0.21 (d, 3H, J = 4 Hz, 6H), 2.58 (b, 2H), 3.65 (b, 3H); 4.30 (hept, 3H, J = 7 Hz, 1H), 5.03 (b, 2H), 6.98 (s). 29SiNMR (C6D6): δ 19.3 (s), 15.9 (s), 16.5 (s).

The negative charge on the silicon atom is stabilized by the second silicon atom which reacts with the CO ligand. The single-crystal X-ray structure of 2b confirmed that the MePh2Si group is exo to Fe (Figure 1), indicative of a direct silyl attack. Compounds 2a–c were desilylated upon acidification with HBF4(aq) or HCl(aq) to re-form the cationic compound [Fe(CO)4][X] (X = BF4, Cl), as shown by IR and 1H and 31P NMR spectroscopic studies.

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yet been reported for Me$_6$Si$_2$ is deprotonation of a methyl substituent, which results in a lithiated carbanion Me$_3$SiMe$_2$CH$\equiv$Li ($\textit{5}$) (Scheme 2). The $\alpha$-SiMe$_2$ group stabilizes the polar C$\equiv$Li bond. The $\beta$-SiMe$_2$ group, however, destabilizes the C$\equiv$Li bond (a $\beta$-Si atom normally stabilizes a carbonium ion). Thus, intramolecular Me$_3$Si group migration$^{15}$ from the silicon atom to the carbon atom results, followed by a 1,2-proton shift. This gives the lithiated carbanion Me$_3$SiMe$_2$H$\equiv$Li ($\textit{6}$), which is isomeric with $\textit{5}$ and is stabilized by two $\alpha$-silyl groups. An extra equiv of Me$_6$Si$_2$ is attacked by $\textit{6}$ to cleave the Si$\equiv$Si bond and regenerate Me$_3$SiLi, which deprotonates the (Me$_3$Si)$_2$(SiMe$_2$H)CH thus formed to give the final lithiated species, $\textit{3}$, which is stabilized by three $\alpha$-silicon atoms. The nucleophilic alkylation of the Cp ring of $\textit{2e}$, followed by a 1,2-proton shift, affords $\textit{3}$. The characteristic deep red color of Me$_3$SiLi in solution is clearly observed, the base effecting deprotonation in Scheme 2 must be Me$_3$SiLi. Thus, it takes overall 3 mol of Me$_6$Si$_2$ in order for 1 mol of MeLi to produce 1 mol of $\textit{3}$; therefore, an increase in stoichiometric ratio between Me$_6$Si$_2$ and MeLi should favor the deprotonation pathway. The isolated yield of $\textit{2e}$ was improved to 60% when a 3:1 mixture of Me$_6$Si$_2$/MeLi was allowed to react for a longer time (2 h), resulting in a color change from deep red to orange before the quench.

To our knowledge, this is the first example of the transformation of a Me anion to a silyl anion and then back to a carbanion, starting with a simple disilane. The present deprotonation pathway in the reaction of Me$_6$Si$_2$ with MeLi is intermolecular. The known intramolecular transfer of the organolithium function in 1-Me$_2$Si-8-Li-C$_{10}$H$_6$ to form 1-Me$_2$SiCH$_2$Li-C$_{10}$H$_7$ is a similar process (C$_{10}$H$_6$ = 1,8-disubstituted naphthalene skeleton; C$_{10}$H$_7$ = 1-substituted naphthalene skeleton).

The speculative mechanism shown in Scheme 2 was tested with different organic electrophiles in order to provide evidence that $\textit{3}$ actually is formed under the reaction conditions. When a 3:1 mixture of Me$_6$Si$_2$/MeLi was quenched with Me$_3$SiCl, for instance, the expected (Me$_3$Si)$_2$CSiMe$_2$H$^{18}$ could be isolated (ca. 30%, not optimized) ($^{29}$Si NMR (C$_6$D$_6$) $\delta$ = −16.4 (SiMe$_3$) and −16.1 (SiMe$_2$H); $^1$H NMR (C$_6$D$_6$) $\delta$ 0.24 (s, SiMe$_2$, 27H), 0.29 (d, $^2$HH = 4.0 Hz, SiMe$_2$, 6H), 4.31 (hept, $^2$HH = 4.0 Hz, SiMe$_2$, 1H)). Spectroscopic evidence for the formation of Me$_3$SiH also was obtained. In a sealed NMR tube experiment, a 3:1 mixture of Me$_6$Si$_2$/MeLi with P(OMe)$_3$ in de-$\text{THF}$ gave $^1$H NMR peaks at $\delta$ 4.61 (hept, $^2$HH = 4.0 Hz), assigned to the unique SiH of $\textit{3}$, and at $\delta$ 4.00 (decatet, $^2$HH = 4.0 Hz), assigned to the unique SiH of HSiMe$_2$ in the correct molar ratios. The corresponding $^{29}$Si NMR data were $\delta$ −28.5 (SiMe$_3$) and −27.9 (SiMe$_2$H) for $\textit{3}$ and $\delta$ −16.1 for Me$_3$SiH.

In conclusion, the reaction of Me$_6$Si$_2$ and MeLi results in Me$_3$SiLi (and $\textit{4}$), plus the previously unnoticed $\textit{3}$. The latter is the more important product when excess Me$_6$Si$_2$ is used.

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Supporting Information Available: Details of the single-crystal structure analyses for $\textit{2b}$, $\textit{e}$ including tables of positional parameters and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Occasionally (p$^\pi$-co-(Me$_3$Si)CH(SiMe$_2$H)C$_6$H$_4$Fe(CO)$_2$(PPh$_3$)$_2$, the speculative Cp-ring alkylation product of $\textit{6}$ and $\textit{1}$, could be detected in trace amount in the $^1$H NMR spectrum of $\textit{2e}$. The pure complex has not been isolated for complete characterization.