374 *Organometallics* **2000,** *19,* 374−376

Deprotonation Pathway in the Reaction of Me_6Si_2 with MeLi

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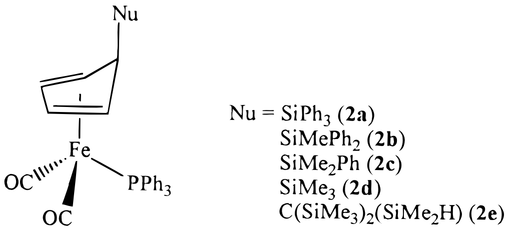
*Summary: A mixture of 3 mol of Me_6Si_2 and 1 mol of MeLi in the presence of $P(O)(NMe_2)_3$ produced Me_3SiLi as the initial product. This then deprotonated excess Me_6Si_2 and started an unprecedented transformation leading to $(Me_3Si)_2(SiMe_2H)CLi$ (**3**), whose quench by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$ produced $\{\eta^4\text{-}exo\text{-}[(Me_3Si)_2C(SiMe_2H)]C_5H_5\}Fe(CO)_2(PPh_3)$ (**2e**). In the literature the reaction of Me_6Si_2 and MeLi gives Me_3SiLi and/or $Me_3SiSiMe_2Li$ (**4**). The lithium compound **3** is the major product when a previously unnoticed deprotonation pathway is enhanced by use of an excess of Me_6Si_2 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, R_3SiLi can be generated in situ by reaction of R_3SiCl with Li, of $(R_3Si)_2Hg$ with Li, or of R_3SiSiR_3 with R′Li.[3] We have used the electrophile $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$ (**1**) to quench the generated silyl anions. The results revealed an unprecedented conversion of Me_3SiLi to $(Me_3Si)_2(SiMe_2H)CLi$ and gave retro-chemical evidence for a deprotonation pathway in the Me_6Si_2 reaction with MeLi.

The R_3SiLi 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 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/PPh_3$ in THF at −78 °C, the practical equivalent to [**1**][I], after chemical initiation with a trace of lithiated reagent,[4] which in the present cases is the first few drops of R_3SiLi. The color of the solution changed gradually from black to orange-red during the addition of R_3SiLi, sometimes with formation of a yellow precipitate that redissolved as the reaction proceeded. For the silyl anions with at least one aryl group, the Cp ring silylation products $(\eta^4\text{-}exo\text{-}R_3SiC_5H_5)Fe(CO)_2(PPh_3)$ (R_3 = Ph_3 (**2a**, 51%), $MePh_2$ (**2b**, 36%**)**, Me_2Ph (**2c**, 45%)) were isolated as major products after column chromatography.[5] Thus, the Si-based nucleophiles add at the Cp ring of **1**, similar to what occurred with C-based nucleophiles[6] and different from O-based nucleophiles



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(1) (a) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, E., Ollis, W. E., Eds.; Pergamon Press: Oxford, U.K., 1979. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworth: Boston, 1981. (c) Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer-Verlag: New York, 1983. (d) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989. (e) Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599. (f) Rappoport, Z.; Apeloig, Y., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1998; Vol. 2.

(2) Oshima, K. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1991; Vol. 2, pp 101−141.

(3) (a) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1998**, *38*, 1 and references cited herein. (b) Wiberg, E.; Stecher, O.; Andrascheck, H. J.; Kreubichler, L.; Staude, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 507. (c) Fujita, M.; Hiyama, T. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 293. (d) Vyazankin, N. S.; Razuvaev, G. A.; Gladyshev, E. A.; Korneva, S. P. *J. Organomet. Chem.* **1967**, *7*, 353. (e) Gladyshev, E. N.; Fedorova, E. A.; Yuntila, L. A.; Razuvaev, G. A.; Vyazankin, N. S. *J. Organomet. Chem.* **1975**, *96*, 169.

(4) Gipson, S. L.; Liu, L.-K.; Soliz, R. U. *J. Organomet. Chem.* **1996**, *526*, 393.

(5) Manipulations were carried out under N_2 with dry degassed reagents. Preparation of **2a** (typical): a 100 mL two-necked flask was charged with Ph_3SiCl (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 to black. 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 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (3 mmol) and PPh_3 (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 H_2O (200 mL) and extracted with Et_2O (100 mL × 2) after it was stirred overnight. The organic layers were combined, dried over $MgSO_4$, and then evaporated to dryness under vacuum. The oily residue was purified by SiO_2 column chromatography with 1/15−20 EtOAc/hexane as eluent to give yellow-orange **2a** (51%). IR (CH_2Cl_2): ν_{CO} 1962 (s), 1903 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 2.71 (b, 2H), 3.90 (b, 1H), 5.10 (b, 2H), 6.96−7.53 (m, 30H). ^{31}P NMR (C_6D_6): δ 72.1 (s). ^{29}Si NMR (C_6D_6): δ −22.6 (s). FAB MS: *m/z* 698 (M^+). Anal. Calcd for $C_{43}H_{35}FeO_2PSi$: C, 73.92; H, 5.05. Found: C, 73.60; H, 4.99. **2b**: yield 36%. IR (CH_2Cl_2): ν_{CO} 1963 (s), 1902 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 0.32 (s, 3H), 2.57 (b, 2H), 3.51 (b, 1H), 5.18 (b, 2H), 6.97−7.52 (m, 25H). ^{31}P NMR (C_6D_6): δ 71.6 (s). ^{29}Si NMR (C_6D_6): δ −17.3 (d, J_{PSi} = 10.0 Hz). FAB MS: *m/z* 636 (M^+). Anal. Calcd for $C_{38}H_{33}FeO_2PSi$: C, 71.70; H, 5.23. Found: C, 71.58; H, 5.22. Orange side product $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)SiMePh_2(PPh_3)$: yield 12%. IR ($CH_2Cl_2$): ν_{CO} 1906 (s), 1574 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 1.22 (s, 3H), 4.07 (s, 5H), 6.96−7.77 (m, 25H). ^{31}P NMR (C_6D_6): δ 75.7 (s). ^{29}Si NMR (C_6D_6): δ −36.5(s). Anal. Calcd for $C_{38}H_{33}FeO_2PSi$: C, 71.70; H, 5.23. Found: C, 71.87; H, 5.15. **2c**: yield 45%. IR (CH_2Cl_2): ν_{CO} 1960 (s), 1901 (s) cm^{-1}. ^1H NMR (C_6D_6): δ −0.04 (s, 6H), 2.46 (b, 2H), 3.02 (b, 1H), 5.18 (b, 2H), 6.95−7.48 (m, 20H). ^{31}P NMR (C_6D_6): δ 71.8 (s). ^{29}Si NMR (C_6D_6): δ −11.5 (d, J_{PSi} = 8.0 Hz). FAB MS: *m/z* 574 (M^+). Anal. Calcd for $C_{33}H_{31}FeO_2PSi$: C, 69.00; H, 5.44. Found: C, 69.16; H, 5.33.

(6) (a) Liu, L.-K.; Luh, L.-S. *Organometallics* **1994**, *13*, 2816. (b) Luh, L.-S.; Liu, L.-K. *Bull. Inst. Chem., Acad. Sin.* **1994**, *41*, 39. (c) Liu, L.-K.; Luh, L.-S.; Chao, P.-C.; Fu, Y.-T. *Bull. Inst. Chem., Acad. Sin.* **1995**, *42*, 1. (d) Luh, L.-S.; Eke, U. B.; Liu, L.-K. *Organometallics* **1995**, *14*, 440.

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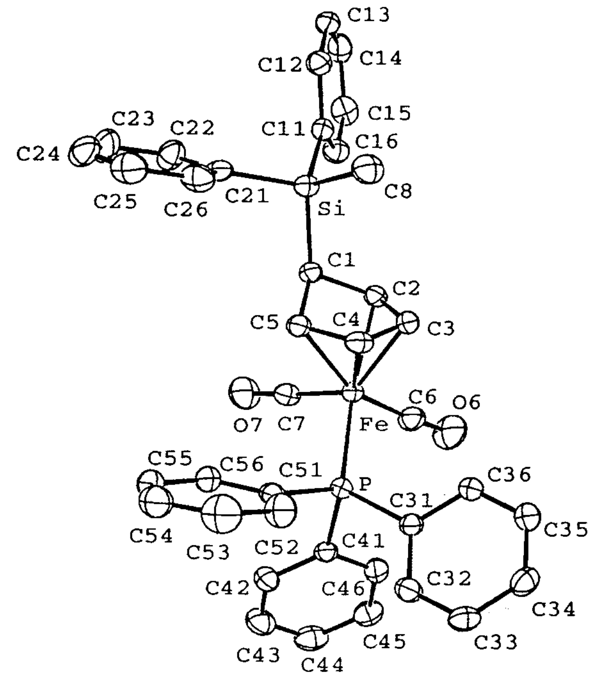

Figure 1. Molecular plot of **2b**.

which react at the CO ligand.[7] The single-crystal X-ray structure of **2b** confirmed that the $MePh_2Si$ group is *exo* to Fe (Figure 1),[8] indicative of a direct silyl attack. Compounds **2a**−**c** were desilylated upon acidification with HBF_4(aq) or HCl(aq) to re-form the cationic compound [**1**][X] (X = BF_4, Cl), as shown by IR and ^1H and ^{31}P NMR spectroscopic studies.

Me_3SiLi was prepared by treating Me_6Si_2 with MeLi in the presence of $P(O)(NMe_2)_3$ for 15 min at 0 °C.[9] The reagent solution was then quenched with 1:1 (η^5-C_5H_5)-$Fe(CO)_2I/PPh_3$ at −78 °C in THF, with the expectation that $\{\eta^4$-*exo*-$(Me_3Si)C_5H_5\}Fe(CO)_2(PPh_3)$ (**2d**) would be formed. IR monitoring of the reaction solution indicated a quantitative formation of an η^4 product. However, after column chromatography, only a low-yield product (<10%) was obtained with spectroscopic data as follows (cf. **2a**−**c**): IR ν_{CO} stretching bands at 1967 (s) and 1908 (s) cm^{-1}, a ^{31}P NMR resonance (C_6D_6) at δ 76.1 (s), and ^1H NMR resonances (C_6D_6) at δ 2.58 (b, 2H), 3.65 (b, 1H), and 5.03 (b, 2H). Nevertheless, the proton integration for silyl−Me was not correct, nor was the elemental analysis. A single-crystal X-ray analysis confirmed the structure as being $\{\eta^4$-*exo*-$[(Me_3Si)_2C(SiMe_2H)]C_5H_5\}$-$Fe(CO)_2(PPh_3)$ (**2e**), which is actually a Cp ring *alkylation* product (Figure 2).[10]

It seemed possible that **2d** might have been produced as the initial product but was desilylated or decomposed, since **2a**−**c** are acid-sensitive. However, the generation of Me_3SiLi by the literature procedure[9] must have also produced, at the same time, a small amount of $(Me_3Si)_2(SiMe_2H)CLi$ (**3**) before the quench (vide infra). We suggest that the in situ generation of deep red Me_3SiLi, from MeLi and Me_6Si_2, is facile because a strong nucleophilic base easily breaks the Si−Si bond.[11] When the reaction is carried out on a larger scale, the C−Si bond in Me_6Si_2 is often observed to be cleaved in a side reaction, which leads to the formation of $Me_3SiSiMe_2Li$ (**4**)[12] (Scheme 1).[13] Obviously, the negative charge on the silicon atom is stabilized by the second silicon atom in the α-position.[14] Still another pathway that has not

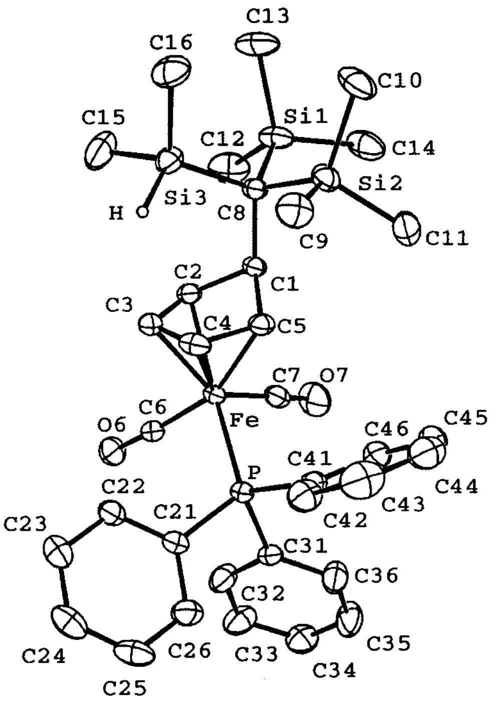

Figure 2. Molecular plot of **2e**.

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(7) Liu, L.-K.; Eke, U. B.; Mesubi, M. A. *Organometallics* **1995**, *14*, 3958.

(8) Crystal data for **2b**: $C_{38}H_{33}FeO_2PSi$, triclinic, $P\bar{1}$, $a = 9.619(1)$ Å, $b = 10.424(1)$ Å, $c = 16.566(3)$ Å, $\alpha = 87.22(1)°$, $\beta = 77.06(1)°$, $\gamma = 82.19(1)°$, $V = 1603.5(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.318$ g/cm^3, 4739 reflections ($I > 2.0\,\sigma(I)$), 389 parameters, $R = 0.031$, $R_w = 0.039$, GOF = 1.92.

(9) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.

(10) Preparation of **2e**. A solution of $Me_3SiSiMe_3$ (5 mmol) in anhydrous $P(O)(NMe_2)_3$ (4 mL) was cooled to 0 °C. MeLi (4 mmol) was added via syringe, and the resulting deep-red solution was stirred for 15 min. THF (30 mL) was added, and the solution was cooled to −78 °C. The solution was transferred dropwise via cannula into the mixture of (η^5-C_5H_5)$Fe(CO)_2I$ (3 mmol) and PPh_3 (3 mmol) in THF (100 mL) at −78 °C. The color of solution gradually changed from black to orange, accompanied 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 H_2O (200 mL) and extracted with Et_2O (100 mL × 2). The combined organic layers were dried over $MgSO_4$ and then evaporated to dryness under vacuum. The oil-like residue was purified by SiO_2 column chromatography with 1:12 (v/v) EtOAc/hexane as eluent to give yellow-orange **2e** (6%). *Improved procedure*: The treatment of $Me_3SiSiMe_3$ (15 mmol) in anhydrous $P(O)(NMe_2)_3$ (12 mL) with MeLi (5 mmol) and *stirring for 2 h,* (otherwise the same procedure as above) resulted in **2e** (60%). IR (CH_2Cl_2): ν_{CO} 1967(s), 1908(s) cm^{-1}. ^1H NMR (C_6D_6): δ 0.14 (s, 18H), 0.21 (d, $^3J_{HH}$ = 4 Hz, 6H), 2.58 (b, 2H), 3.65 (b, 1H), 4.30 (hept, $^3J_{HH}$ = 4 Hz, 1H), 5.03 (b, 2H), 6.98−7.53 (m, 15H). ^{31}P NMR (C_6D_6): δ 76.1(s). ^{29}SiNMR (C_6D_6): δ −15.9 (s), −16.5 (s). FAB MS *m/z*: 656 (M$^+$). Anal. Calcd for $C_{34}H_{45}FeO_2PSi_3$: C, 62.18; H, 6.90. Found: C, 61.99; H, 6.81. Crystal data of **2e**: $C_{34}H_{45}FeO_2PSi_3$, triclinic $P\bar{1}$, $a = 11.283(2)$ Å, $b = 12.591(2)$ Å, $c = 14.276(3)$ Å, $a = 66.63(1)°$, $\beta = 72.17(2)°$, $\gamma = 76.70(1)°$, $V = 1758.5(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.240$ g/cm^3, 5238 reflections ($I > 2.5\sigma(I)$), 374 parameters, $R = 0.033$, $R_w = 0.045$, GOF = 2.31.

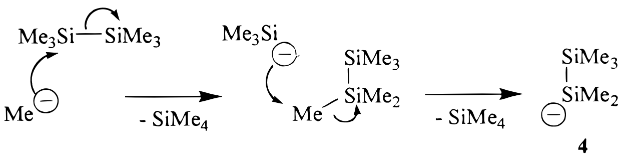
(11) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221.

(12) (a) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69. (b) Nadler, E. B.; Rappoport, Z. *Tetrahedron Lett.* **1990**, *31*, 555. (c) Allred, A. L.; Smart, R. T.; Van Beek, D. A., Jr. *Organometallics* **1992**, *11*, 4225. (d) Hwu, J. R.; Wetzel, J. M.; Lee, J. S.; Butcher, R. J. *J. Organomet. Chem.* **1993**, *453*, 21. (e) Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99.

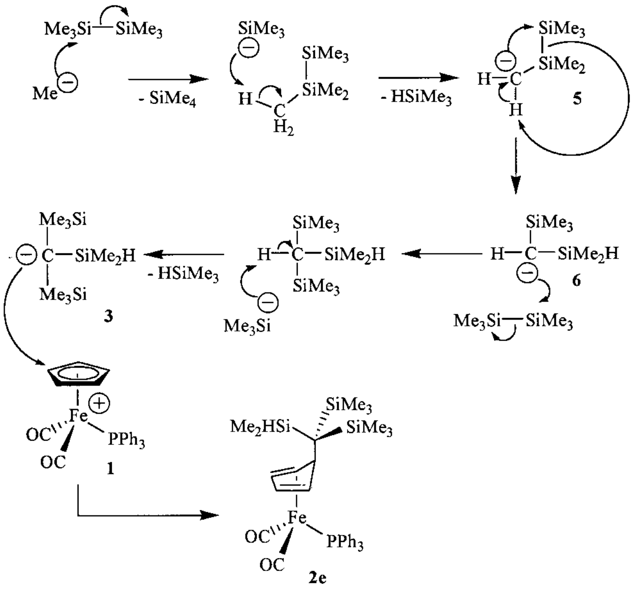
(13) It is believed that the C-based nucleophile MeLi is transformed to the Si-based nucleophile Me_3SiLi before other second-stage reactions. As an indirect clue, the formation of **4** was only observed in large-quantity preparations.

(14) Armitage, D. A. In *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 2, pp 1−203.

Scheme 1



Scheme 2



yet been reported for Me_6Si_2 is deprotonation of a methyl substituent, which results in a lithiated carbanion $Me_3SiSiMe_2CH_2Li$ (**5**) (Scheme 2). The α-$SiMe_2$ group stabilizes the polar C−Li bond. The *β*-$SiMe_3$ group, however, destabilizes the C−Li bond (a *β*-Si atom normally stabilizes a carbonium ion).[14] Thus, intramolecular Me_3Si group migration[15] from the silicon atom to the carbon atom results, followed by a 1,2-proton shift. This gives the lithiated carbanion $Me_3Si(SiMe_2H)$-CHLi (**6**), which is isomeric with **5** and is stabilized by two α-silyl groups. An extra 1 equiv of Me_6Si_2 is attacked by **6** to cleave the Si−Si bond and regenerate Me_3SiLi, which deprotonates the $(Me_3Si)_2(SiMe_2H)CH$ thus formed to give the final lithiated species, **3**, which is stabilized by three α-silicon atoms. The nucleophilic alkylation of the Cp ring of **1** by **3** affords **2e**.[16]

As the characteristic deep red color of Me_3SiLi in solution is clearly observed, the base effecting deprotonation in Scheme 2 must be Me_3SiLi. Thus, it takes overall 3 mol of Me_6Si_2 in order for 1 mol of MeLi to produce 1 mol of **3**; therefore, an increase in stoichiometric ratio between Me_6Si_2 and MeLi should favor the deprotonation pathway. The isolated yield of **2e** was improved to 60% when a 3:1 mixture of Me_6Si_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_6Si_2 with MeLi is intermolecular. The known intramolecular transfer of the organolithium function in 1-Me_3Si-8-Li-$C_{10}H_6$ to form 1-Me_2SiCH_2Li-$C_{10}H_7$[17] 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 **3** actually is formed under the reaction conditions. When a 3:1 mixture of Me_6Si_2/MeLi was quenched with Me_3SiCl, for instance, the expected $(Me_3Si)_3CSiMe_2H$[18] could be isolated (ca. 30%, not optimized) (^{29}Si NMR (C_6D_6) δ −16.4 (*Si*Me_3) and −16.1 (*Si*Me_2H); ^{1}H NMR (C_6D_6) δ 0.24 (s, Si*Me_3*, 27H), 0.29 (d, $^2J_{HH}$ = 4.0 Hz, Si*Me_2*H, 6H), 4.31 (hept, $^2J_{HH}$ = 4.0 Hz, $SiMe_2$*H*, 1H)). Spectroscopic evidence for the formation of Me_3SiH also was obtained. In a sealed NMR tube experiment, a 3:1 mixture of Me_6Si_2/MeLi with P(O)-$(NMe_2)_3$ in d_8-THF gave ^{1}H NMR peaks at δ 4.61 (hept, $^2J_{HH}$ = 4.0 Hz), assigned to the unique Si*H* of **3**, and at δ 4.00 (decatet, $^2J_{HH}$ = 4.0 Hz), assigned to the unique Si*H* of $HSiMe_3$, in the correct molar ratios. The corresponding ^{29}Si NMR data were δ −28.5 (*Si*Me_3) and −27.9 (*Si*Me_2H) for **3** and δ −16.1 for Me_3SiH.

In conclusion, the reaction of Me_6Si_2 and MeLi results in Me_3SiLi (and **4**), plus the previously unnoticed **3**. The latter is the more important product when excess Me_6Si_2 is used.

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Supporting Information Available: Details of the single-crystal structure analyses for **2b**,**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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[15] (a) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, pp 149−227. (b) Eisch, J. J.; Tsai, M.-R. *J. Organomet. Chem.* **1982**, *225*, 5.

[16] Occasionally $\{\eta^4$-*exo*-$[(Me_3Si)CH(SiMe_2H)]C_5H_5\}Fe(CO)_2(PPh_3)$, the speculative Cp-ring alkylation product of **6** and **1**, could be detected in trace amount in the ^{1}H NMR spectrum of **2e**. The pure complex has not been isolated for complete characterization.

[17] Wroczynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *J. Organomet. Chem.* **1979**, *170*, C29.

[18] Dua, S. S.; Eaborn, C.; Happer, D. A. R.; Hopper, S. P.; Safa, K. D.; Walton, D. R. M. *J. Organomet. Chem.* **1979**, *178*, 75.