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Reaction of silylpentacarbonylmanganese with hydride-transfer reagents: reduction of carbonyl ligands accompanied with Si–C and C–C coupling

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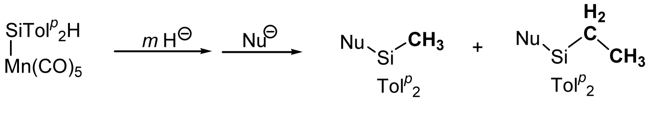
Abstract

Treatment of $\mathrm{Mn(CO)_5SiTol^{p}_{2}H}$ (**2**) with an excess of $LiAlH_4$, $NaBH_4$, or $NaBH_3(CN)$ in THF at room temperature gave hydrosilane $\mathrm{H{-}SiTol^{p}_{2}H}$ in high yield together with $Mn_2(CO)_{10}$. No reduction of CO ligands was observed. On the other hand, treatment of **2** with an excess of Red-Al ($= \mathrm{Na[(CH_3OCH_2CH_2O)_2AlH_2]}$) in toluene and subsequent addition of aqueous acidic solution afforded alkylsilanols $\mathrm{(CH_3)SiTol^{p}_{2}(OH)}$ and $\mathrm{(C_2H_5)SiTol^{p}_{2}(OH)}$. Treatment of the reaction mixture of **2** and Red-Al with $LiAlH_4$ in diethyl ether instead of hydrolysis gave alkylhydrosilanes $\mathrm{(CH_3)SiTol^{p}_{2}H}$ and $\mathrm{(C_2H_5)SiTol^{p}_{2}H}$. The methyl and ethyl groups on silicon originate from the CO ligands in **2**. These products clearly demonstrate that not only the Si–C coupling, but also C–C coupling occurs efficiently in this reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silyl complexes; Carbonyl complexes; Manganese complexes; Si–C coupling; C–C coupling; Reduction

1. Introduction

Reactions of hydride-transfer reagents with transition metal carbonyl complexes have attracted much attention in relation to the Fischer–Tropsch reaction. Although numerous reactions of this type have been reported [1–5], there are few examples in which a carbonyl ligand is not only reduced, but also coupled with another ligand [6,7]. Recently we reported a novel reaction of silyl(carbonyl)iron complexes $\mathrm{CpFe(CO)_2SiR_3}$ (**1**) ($\mathrm{Cp} = \eta^5\text{-}C_5H_5$, R = aryl, alkyl, H) with $LiAlH_4$ that resulted in Si–C coupling to give methylsilanes $\mathrm{(CH_3)SiR_3}$ as a major product in moderate to high yield [8]. The labeling experiments using $LiAlD_4$ and $\mathrm{CpFe(^{13}CO)_2SiTol^{p}_{2}R'}$ (R′ = H, Me, $\mathrm{Tol}^p = p\text{-}CH_3C_6H_4$) proved that a carbonyl ligand was reduced and coupled with the Si atom to give the methylsilane. We report herein the reaction of a silylpentacarbonylmanganese $\mathrm{Mn(CO)_5SiTol^{p}_{2}H}$ (**2**) with several hydride-transfer reagents. We found that the reaction of **2** with Red-Al ($= \mathrm{Na[(CH_3OCH_2CH_2O)_2AlH_2]}$) in toluene induces not only the Si–C, but also the C–C coupling reactions (Scheme 1).



Scheme 1.

2. Results and discussion

2.1. Reactions of 2 with several hydride-transfer reagents in THF

Treatment of $\mathrm{Mn(CO)_5SiTol^{p}_{2}H}$ (**2**) with an excess of $LiAlH_4$, $NaBH_4$, or $NaBH_3(CN)$ in THF at room temperature afforded dihydrosilane $\mathrm{HSiTol^{p}_{2}H}$ (**3**) [9] in high yield (54–91%) together with $Mn_2(CO)_{10}$ (Scheme 2) [10]. No reduction of CO ligands was observed. This is perhaps because the basic solvent THF induces the heterolysis of the Mn–Si bond in **2** prior to the reaction with the hydride-transfer reagents to give $\mathrm{[HTol^{p}_{2}Si{\cdot}THF]^+[Mn(CO)_5]^-}$ in which the THF-coordinated silyl cation is expected to be highly reactive toward hydride nucleophiles. In fact, when pale yellow **2** was dissolved

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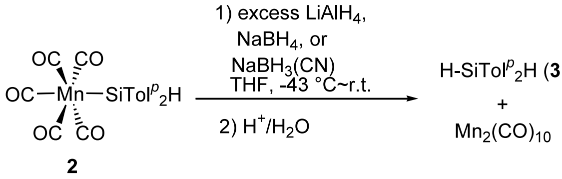


Scheme 2.

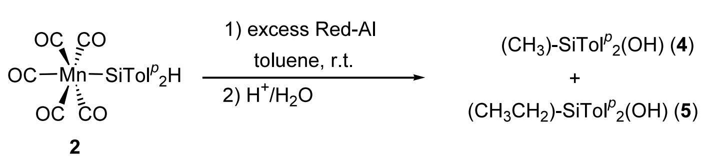
in THF, the solution changed to red instantaneously. The IR spectrum of the solution showed two weak but distinct bands assigned to ν_{CO} at extremely low wavenumber region (1900 and 1865 cm^{-1}) in addition to strong ν_{CO} bands of **2** (2092, 1998 and 1983 cm^{-1}). The intensity ratio of the former bands and those of **2** did not change in the course of time. The former values are almost identical with those of $Na^+[Mn(CO)_5]^-$ (1898 and 1863 cm^{-1}) [11]. These facts suggest that when **2** is dissolved in THF, it quickly reaches to equilibrium with $[HTol^p_2Si\cdot THF]^+[Mn(CO)_5]^-$ where **2** is the major component.

2.2. Reactions of **2** with Red-Al in toluene

By contrast, treatment of **2** with excess Red-Al *in toluene* at room temperature for 1 day and subsequent addition of aqueous acidic solution gave silanols $(CH_3)SiTol^p_2(OH)$ (**4**) and $(C_2H_5)SiTol^p_2(OH)$ (**5**) in 43 and 33% yields, respectively (Scheme 3). Neither formation of dihydrosilane **3** nor that of methylsilane **6** and ethylsilane **7** (vide infra) was observed by GC/MS. The formation of **4** and **5** clearly demonstrates that not only the Si–C coupling, but also the C–C coupling occurred efficiently in this reaction.

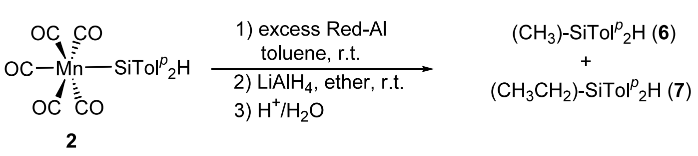
Before hydrolysis, silanols **4** and **5** were not detected in the reaction mixture by GC/MS. Thus the OH group of **4** and **5** originated from water. Actually, treatment of the reaction mixture of **2** and Red-Al with DCl/D$_2$O gave deuteriosilanols $(CH_3)SiTol^p_2(OD)$ (**4-d**) (ca. 80 atom% D) and $(C_2H_5)SiTol^p_2(OD)$ (**5-d**) (ca. 80 atom% D) in 40 and 25% yields, respectively. Although isolation of the primary products was unsuccessful, we infer that the primary products were neutral silyl manganese complexes containing $SiTol^p_2(CH_3)$ and $SiTol^p_2(C_2H_5)$ ligands in which the methyl and ethyl groups on silicon originate from the CO ligands in **2**. These complexes were then hydrolyzed through heterolysis of the Mn–Si bonds [12] to give **4** and **5**. In fact, acid hydrolysis of the model complex $Mn(CO)_5SiTol^p_2(CH_3)$ proceeded smoothly at room temperature to give $(CH_3)SiTol^p_2(OH)$ (**4**) in 90% yield. This primary formation of neutral silyl manganese complexes was further supported by the following experiment. Treatment of the reaction mixture of **2** and Red-Al with excess LiAlH$_4$ in diethyl ether instead of hydrolysis gave methylsilane $(CH_3)SiTol^p_2H$ (**6**) and ethylsilane $(CH_3CH_2)SiTol^p_2H$ (**7**) in 41 and 28% yields, respectively (Scheme 4). Use of excess LiAlD$_4$ instead of LiAlH$_4$ gave deuteriosilanes $(CH_3)SiTol^p_2D$ (**6-d**) (ca. 55 atom% D) and $(CH_3CH_2)SiTol^p_2D$ (**7-d**) (ca. 53 atom% D) in 41 and 28% yields, respectively. The yields of methylsilane **6** and ethylsilane **7** are almost identical with those of the corresponding hydrolysis products methylsilanol **4** and ethylsilanol **5**. Thus, these yields apparently reflect the proportion of the introduction of methyl and ethyl groups in the silyl ligands in primary products.

In comparison with the iron analogue **1** that did not react with Red-Al but reacted with LiAlH$_4$ to give methylsilane $(CH_3)SiTol^p_2H$ (**6**) [8b], manganese complex **2** was reduced under milder conditions and more than one CO ligand were participated in the reaction. These differences are attributable to the following factors: (1) **2** has more CO ligands than iron analogue **1**; and (2) the CO ligands in **2** are more reactive toward nucleophiles than those in **1** because the back-donation to each CO ligand in **2** is weaker than **1**.



Red-Al = $Na[(CH_3OCH_2CH_2O)_2AlH_2]$

Scheme 3.



Red-Al = $Na[(CH_3OCH_2CH_2O)_2AlH_2]$

Scheme 4.

3. Experimental

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade hexane, Et_2O, and THF were distilled from sodium–benzophenone ketyl immediately before use. Benzene-d_6 and acetone-d_6 were dried with molecular sieves 4A. Na[$Mn(CO)_5$] [13] and Tol^p_2SiRCl (R = H, Me) [8b] were prepared according to the literature procedures. Na[$(CH_3OCH_2CH_2O)_2AlH_2$] (Red-Al) was purchased from Aldrich. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used as received. All NMR spectra were recorded in a Brucker ARX-300 spectrometer. ^{1}H-, ^{13}C- and ^{29}Si-NMR data were referenced to Me_4Si. ^{29}Si-NMR spectra were obtained by the DEPT pulse sequence. IR spectra were recorded in a Horiba FT-200 spectrometer. Mass spectra were recorded on Shimadzu GCMS-QP5050A and JEOL HX-110 mass spectrometers. The D contents in the deuterated products were determined by mass spectroscopy.

3.1. Synthesis of *$Mn(CO)_5SiTol^p_2H$* (**2**)

A THF solution of Na[$Mn(CO)_5$] (0.99 M, 20 ml, 19.9 mmol) prepared from $Mn_2(CO)_{10}$ and Na/Hg was slowly cannulated into a two-necked flask connected to a vacuum line and the solvent was removed in vacuo. Then Ar gas was introduced into the reaction vessel and the deoxygenated solution of Tol^p_2SiHCl (4.65 g, 18.8 mmol) in hexane (20 ml) was added to it by a syringe at −43 °C. The reaction mixture was stirred at room temperature (r.t.) for 12 h and filtered through a Celite pad under nitrogen. The filtrate was evaporated under reduced pressure and the residue was recrystallized from pentane to give **2** (3.33 g, 8.20 mmol, 44% yield) as pale yellow crystals. ^{1}H-NMR (300 MHz, C_6D_6) δ 7.71–7.73, 7.01–7.04 (AB q, $J = 8$ Hz, 4H × 2; p-$CH_3C_6H_4$), 5.68 (s, 1H; Si–H), 2.05 (s, 6H; p-$CH_3C_6H_4$). ^{13}C-NMR (75.5 MHz, C_6D_6) δ 213.2 (CO), 139.1, 135.1, 134.9, 129.3 (p-$CH_3C_6H_4$), 21.3 (p-$CH_3C_6H_4$). ^{29}Si-NMR (59.6 MHz, C_6D_6) δ 7.84. IR (cm^{-1}, KBr pellet): ν(Si–H) 2108, ν(CO) 2092, 1998, 1983. Mass (EI, 70 eV); m/z: 406 (M^+, 2), 378 ($M^+ -$ CO, 9), 322 ($M^+ -$ 3CO, 5), 211 ($M^+ - Mn(CO)_5$, 100). Anal. Found: C, 56.23; H, 3.59. Calc. for $C_{19}H_{15}MnO_5Si$: C, 56.16; H, 3.72%.

3.2. Reaction of *$Mn(CO)_5SiTol^p_2H$* (**2**) with *$LiAlH_4$* in THF

To a suspension of $LiAlH_4$ (298 mg, 7.83 mmol) in THF (15 ml) was added a THF solution (5 ml) of **2** (789 mg, 1.94 mmol) at −43 °C. The mixture was allowed to warm to r.t. and was stirred for 4 h. After removal of solvent in vacuo, the residue was extracted with hexane and the extract was filtered through a Celite pad under nitrogen. The solvent was removed in vacuo and the residue was subjected to silica gel flash chromatography (12 mm o.d. × 30 mm) with 1/5 toluene–hexane as eluent to give $Tol^p_2SiH_2$ (504 mg, 1.77 mmol) as a colorless liquid in 91% yield together with $Mn_2(CO)_{10}$ (87.1 mg, 223 μmol) as a bright yellow powder in 23% yield.

3.3. Reaction of *$Mn(CO)_5SiTol^p_2H$* (**2**) with *$NaBH_4$* in THF

To a suspension of $NaBH_4$ (308 mg, 8.11 mmol) in THF (15 ml) was added a THF solution (5 ml) of **2** (804 mg, 1.98 mmol) at −43 °C. The mixture was allowed to warm to r.t. and was stirred for 1 day. The reaction mixture was worked up in a manner similar to that for the reaction with $LiAlH_4$ to give $Tol^p_2SiH_2$ (475 mg, 1.67 mmol) in 84% yield together with $Mn_2(CO)_{10}$ (122 mg, 312 μmol) in 32% yield.

3.4. Reaction of *$Mn(CO)_5SiTol^p_2H$* (**2**) with *$NaBH_3(CN)$* in THF

To a suspension of $NaBH_3(CN)$ (673 mg, 8.10 mmol) in THF (15 ml) was added a THF solution (5 ml) of **2** (798 mg, 1.97 mmol) at −43 °C. The mixture was allowed to warm to r.t. and was stirred for 2 days. The reaction mixture was worked up in a manner similar to that for the reaction with $LiAlH_4$ to give $Tol^p_2SiH_2$ (302 mg, 514 μmol) in 54% yield together with $Mn_2(CO)_{10}$ (200 mg, 514 μmol) in 52% yield.

3.5. Reaction of *$Mn(CO)_5SiTol^p_2H$* (**2**) with Red-Al and subsequent hydrolysis

A toluene solution of Red-Al (3.4 M, 30 ml, 102 mmol) was added dropwise to a solution of **2** (4.09 g, 10.1 mmol) in toluene (50 ml) over a period of 30 min and then stirred for 1 day at r.t. The reaction mixture was cooled in an ice bath, and EtOAc (10 ml) was added dropwise to destroy an excess of Red-Al. Then aqueous HCl solution (1 M, 200 ml) was added and the organic layer was washed with saturated $NaHCO_3$ solution, water, and saturated NaCl solution, and then dried over anhydrous $MgSO_4$. Removal of solvent in vacuo gave a mixture of $(CH_3)SiTol^p_2(OH)$ (**4**) (1.05 g, 4.34 mmol), and $(C_2H_5)SiTol^p_2(OH)$ (**5**) (853 mg, 3.33 mmol) in 43 and 33% yields, respectively. All the products were identified by comparing the ^{29}Si-NMR and GC/MS data with those of the authentic samples. Yields were determined by quantitative analysis with GC/MS.

3.6. Reaction of $Mn(CO)_5SiTol^p_2H$ (**2**) with Red-Al and subsequent treatment with DCl/D_2O

A toluene solution of the reaction mixture of **2** (215 mg, 529 μmol) and Red-Al (3.4 M, 0.3 ml, 1.02 mmol) was added dropwise to DCl/D_2O solution (1 M, 200 ml). The reaction mixture was worked up in a manner similar to that for the reaction with HCl/H_2O to give a mixture of $(CH_3)SiTol^p_2(OD)$ (**4-d**: ca. 80 atom% D) (51.6 mg, 212 μmol) and $(C_2H_5)SiTol^p_2(OD)$ (**5-d**: ca. 80 atom% D) (34.0 mg, 132 μmol) in 40 and 25% yields, respectively.

3.7. Acid hydrolysis of $Mn(CO)_5SiTol^p_2(CH_3)$

To a Et_2O solution (50 ml) of $Mn(CO)_5SiTol^p_2(CH_3)$ (563 mg, 1.34 mmol) was added aqueous HCl (1 M, 200 ml) at r.t. and then stirred for 1 day. The mixture was placed in a separatory funnel. The organic layer was separated, washed with saturated $NaHCO_3$ solution, water, and saturated NaCl solution, and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give $(CH_3)SiTol^p_2(OH)$ (**4**) (292 mg, 121 mmol) in 90% yield.

3.8. Reaction of $Mn(CO)_5SiTol^p_2H$ (**2**) with Red-Al and subsequent treatment with $LiAlH_4$

A toluene solution of Red-Al (3.4 M, 7.3 ml, 24.8 mmol) was added dropwise to a solution of **2** (912 mg, 2.25 mmol) in toluene (20 ml) over a period of 10 min and then stirred for 18 h at r.t. The reaction mixture was added dropwise to a Et_2O solution (30 ml) of $LiAlH_4$ (997 mg, 26.2 mmol) at r.t. and stirred for 3 h. Hydrolysis and workup in a manner similar to those in Section 3.5 gave a mixture of $(CH_3)SiTol^p_2H$ (**6**) [8b] (208 mg, 920 μmol) and $(CH_3CH_2)SiTol^p_2H$ (**7**) (151 mg, 629 μmol) in 41 and 28% yields, respectively.

3.9. Reaction of $Mn(CO)_5SiTol^p_2H$ (**2**) with Red-Al and subsequent treatment with $LiAlD_4$

A toluene solution of the reaction mixture of **2** (387 mg, 952 μmol) and Red-Al (3.4 M, 0.5 ml, 1.70 mmol) was added dropwise to a Et_2O solution (10 ml) of $LiAlD_4$ (339 mg, 8.07 mmol). The reaction mixture was worked up in a manner similar to that for the reaction with $LiAlH_4$ to give a mixture of $(CH_3)SiTol^p_2D$ (**6-d**: ca. 55 atom% D) [8b] (88.7 mg, 390 μmol) and $(CH_3CH_2)SiTol^p_2D$ (**7-d**: ca. 53 atom% D) (64.5 mg, 267 μmol) in 41 and 28% yields, respectively.

3.10. Preparation of $Tol^p_2SiMe(OH)$ (**4**)

To a Et_2O solution (30 ml) of $Tol^p_2SiMeCl$ (5.23 g, 20.1 mmol) and phenolphthalein was added 1 M NaOH aqueous solution until the solution was neutralized. The mixture was placed in a separatory funnel. The organic layer was separated, washed with 1 M HCl aqueous solution (10 ml × 3), saturated $NaHCO_3$ solution (10 ml), water (10 ml × 3), and saturated NaCl solution (10 ml), and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give **4** (4.50 g, 18.6 mmol) in 93% yield as a colorless oil. ^1H-NMR (300 MHz, acetone-d_6) δ 7.20–7.23, 7.59–7.62 (AB q, $J = 8.1$ Hz, 4H × 2; p-$CH_3C_6H_4$), 5.62 (br, 1H; Si–OH), 2.34 (s, 6H; p-$CH_3C_6H_4$), 0.65 (s, 3H; Si–Me). ^{13}C-NMR (75.5 MHz, acetone-d_6) δ 139.6, 135.9, 134.7, 129.1 (p-$CH_3C_6H_4$), 21.5 (p-$CH_3C_6H_4$), −0.56 (Si–Me). ^{29}Si-NMR (59.6 MHz, acetone-d_6) δ −0.84. Mass (EI, 70 eV); m/z: 242 (M^+, 37), 227 ($M^+ - Me$, 100). Exact mass found: 242.1126. Calc. for $C_{15}H_{18}OSi$: 242.1127.

3.11. Preparation of $Tol^p_2SiEt(OH)$ (**5**)

A 2 l four-necked flask was equipped with a condenser, a mechanical stirrer, and a dropping funnel. $EtSiCl_3$ (78.5 g, 480 mmol) and THF (650 ml) were placed in the flask. A THF solution of Tol^pMgCl (1.00 M, 800 ml, 800 mmol) was added dropwise from the dropping funnel into the flask over a period of 1 h, and then the mixture was refluxed for an additional 5 h. After the reaction mixture was allowed to cool to r.t., it was filtered and the salt was washed with Et_2O (3 l). The filtrate was concentrated and the residue was distilled under reduced pressure to give $Tol^p_2SiEtCl$ (61.3 g, 223 mmol, 46%) as a colorless oil, b.p. 134 °C/0.3 mmHg. ^1H-NMR (300 MHz, C_6D_6) δ 7.57–7.59, 6.99–7.02 (AB q, $J = 8$ Hz, 4H × 2; p-$CH_3C_6H_4$), 2.08 (s, 6H; p-$CH_3C_6H_4$), 1.19 (quartet, $^3J(H,H) = 7$ Hz, 2H; Si–CH_2CH_3), 1.09 (t, $^3J(H,H) = 7$ Hz, 3H; Si–CH_2CH_3). ^{13}C-NMR (75.5 MHz, C_6D_6) δ 140.6, 134.8, 130.6, 129.2 (p-$CH_3C_6H_4$), 21.5 (p-$CH_3C_6H_4$), 9.10, 7.02 (Si–Et). ^{29}Si-NMR (59.6 MHz, C_6D_6) δ 13.0. Mass (EI, 70 eV); m/z: 274 (M^+, 12), 245 ($M^+ - Et$, 100).

Hydrolysis of $Tol^p_2SiEtCl$ (5.64 g, 20.5 mmol) in a manner analogous to that for **4** gave $Tol^p_2SiEt(OH)$ (**5**) (4.85 g, 18.9 mmol, 92%) as a colorless oil. ^1H-NMR (300 MHz, acetone-d_6) δ 7.50–7.52, 7.16–7.19 (AB q, $J = 8$ Hz, 4H × 2; p-$CH_3C_6H_4$), 5.52 (br, 1H; Si–OH), 2.30 (s, 6H; p-$CH_3C_6H_4$), 1.02 (br s, 5H; Si–Et). ^{13}C-NMR (75.5 MHz, acetone-d_6) δ 139.7, 135.0, 134.9, 129.1 (p-$CH_3C_6H_4$), 21.4 (p-$CH_3C_6H_4$), 7.94, 7.10 (Si–Et). ^{29}Si-NMR (59.6 MHz, acetone-d_6) δ −0.90. Mass (EI, 70 eV); m/z: 256 (M^+, 5), 227 ($M^+ - Et$, 100). Exact mass found: 256.1281. Calc. for $C_{16}H_{20}OSi$: 256.1283.

3.12. Preparation of Tol^p_2SiHEt (**7**)

To a Et_2O solution of EtMgBr (0.875 M, 120 ml, 105 mmol) was added a Et_2O solution (60 ml) of Tol^p_2SiHCl

(13.0 g, 52.4 mmol) over a period of 5 min. The mixture was stirred at r.t. for 1.5 h and then cooled in an ice bath. Water (20 ml) was added dropwise to hydrolyze an excess of EtMgBr and then 6 M HCl (100 ml) was added to dissolve the salt. The aqueous layer was extracted with two 50 ml portions of ether and the combined organic layer was washed with saturated $NaHCO_3$ solution (200 ml), water (200 ml), and saturated NaCl solution (200 ml) and then dried over anhydrous $MgSO_4$. After removal of solvent, the residue was distilled under reduced pressure to give **7** (10.9 g, 45.4 mmol, 87%) as a colorless oil, b.p. 114 °C/0.2 mmHg. ^{1}H-NMR (300 MHz, C_6D_6) δ 7.51–7.53, 7.02–7.05 (AB q, $J = 8$ Hz, 4H × 2; p-$CH_3C_6\mathit{H}_4$), 5.10 (t, ^3J(H,H) = 4 Hz, 1H; Si–H), 2.10 (s, 6H; p-$C\mathit{H}_3C_6H_4$), 1.08 (br s, 5H; Si–Et). ^{13}C-NMR (75.5 MHz, C_6D_6) δ 139.4, 135.6, 131.2, 129.1 (p-$CH_3\mathit{C}_6H_4$), 21.4 (p-$\mathit{C}H_3C_6H_4$), 8.40, 4.77 (Si–Et). ^{29}Si-NMR (59.6 MHz, C_6D_6) δ −11.6. IR (cm^{-1}, NaCl plate): ν(Si–H) 2110. Mass (EI, 70 eV); m/z: 240 (M^+, 37), 211 ($M^+ - Et$, 100), 148 ($M^+ - H - Tol^p$, 42), 119 ($M^+ - H - Et - Tol^p$, 18). Anal. Found: C, 79.79; H, 8.44. Calc. for $C_{16}H_{20}Si$: C, 79.93; H, 8.38%.

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