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1,3-Migration of Trimethylsilyl Group from Carbon to Oxygen in Highly Sterically Hindered Silanol of the Type $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeOH}$ and Reaction of the Related Iodide with Iodine Monochloride and Iodine Monobromide

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1,3-MIGRATION OF TRIMETHYLSILYL GROUP FROM CARBON TO OXYGEN IN HIGHLY STERICALLY HINDERED SILANOL OF THE TYPE (Me₃Si)₃CSi(C₆H₄Me-*p*)MeOH AND REACTION OF THE RELATED IODIDE WITH IODINE MONOCHLORIDE AND IODINE MONOBROMIDE

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The silanol (Me₃Si)₃CSi(C₆H₄Me-*p*)MeOH has been shown to isomerize to (Me₃Si)₂CHSi(C₆H₄Me-*p*)(Me)(OSiMe₃) when it was kept at room temperature for 10 h in 0.2 M NaOMe/MeOH. Corresponding isomerizations of the above silanol (to give (Me₃Si)₂CHSi(C₆H₄Me-*p*)(Me)(OSiMe₃)) are complete after 26 h under reflux in pyridine. The reaction involve 1,3-migration from carbon to oxygen within a silanolate ion to give a carbanion, which rapidly acquires a proton from the solvent. Treatment of (Me₃Si)₃CSi(C₆H₄Me-*p*)MeOH with MeLi in Et₂O/THF give, by the same rearrangement, the organolithium reagent (Me₃Si)₂CLiSi(C₆H₄Me-*p*)(Me)(OSiMe₃) which on treatment with Me₂SiHCl gives (Me₃Si)₂C(SiMe₂H)Si(C₆H₄Me-*p*)(Me)(OSiMe₃) and (Me₃Si)₂CHSi(C₆H₄Me-*p*)(Me)(OSiMe₃). When the experiment was repeated, but with Me₃SiCl in place of Me₂SiHCl, it gives exclusively (Me₃Si)₂CHSi(C₆H₄Me-*p*)(Me)(OSiMe₃). Treatment of the organolithium reagent (Me₃Si)₂CLiSi(C₆H₄Me-*p*)(Me)(OSiMe₃) with MeI gives exclusively (Me₃Si)₂CMeSi(C₆H₄Me-*p*)(Me)(OSiMe₃). The related iodide (Me₃Si)₃CSi(C₆H₄Me-*p*)MeI reacts with ICl and IBr to give rearranged (Me₃Si)₂C(SiMe₂X)Si(C₆H₄Me-*p*)Me₂ and unrearranged products (Me₃Si)₃CSi(C₆H₄Me-*p*)MeX, (X = Cl, Br) respectively. The rearranged bromide (Me₃Si)₂C(SiMe₂Br)Si(C₆H₄Me-*p*)Me₂ reacts with a range of silver [I] salts AgY (Y = OOCCH₃, SO₄²⁻) and Mercury [II] salt HgY₂ (Y = OOCCH₃, SO₄²⁻) in glacial CH₃COOH to give the corresponding species (Me₃Si)₂C(SiMe₂OOCCH₃)Si(C₆H₄Me-*p*)Me₂. The reaction of the bromide with AgBF₄ in MeOH or i-PrOH give the

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corresponding rearranged products $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Y})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$ ($\text{Y} = -\text{OMe}, -\text{OPr}^i$).

Keywords: Silicon; steric hindrance; trisyl

Several novel aspects of organosilicon chemistry have been revealed by studies of highly sterically hindered compounds of the type TsiSiR_2X ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$).¹⁻⁶ The novel chemistry in most cases arises from the inhibition of the normally great ease of nucleophilic attack at the functional silicon center, which allows observation of other mechanisms that are not normally competitive. One example of this is provided by the elimination reaction that occurs when a compound of the type TsiSiRRX , $\text{X} = \text{halogen}$, is treated with NaOMe in MeOH .⁷

A preliminary report appeared some years ago on the base-catalyzed 1,3-migration of organosilyl groups from carbon to oxygen in the silanol $\text{TsiSiMe}_2\text{OH}$.⁸

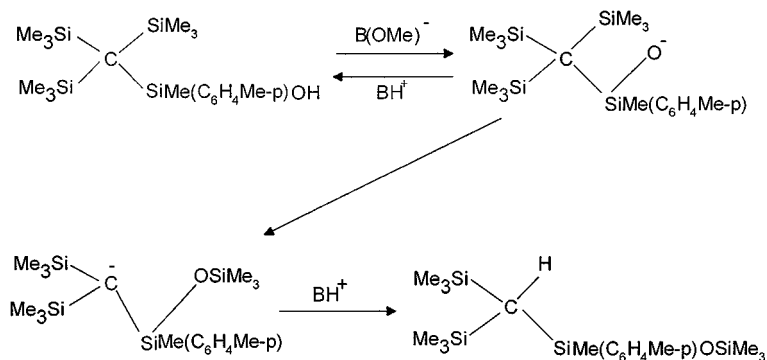
We present below details of the observation and the results of some related experiments that were carried out on highly crowded organosilanol of the type $\text{Tsi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$. We also present the results obtained from the reactions of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$ prepared by the reaction of $\text{Tsi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}$ with IBr with a range of electrophilic reagents.

RESULTS AND DISCUSSION

This type of rearrangement was first observed when $(\text{MeSi})_3\text{CSiMe}_2\text{OH}$ was treated with potassium in boiling benzene to form the siloxane $(\text{Me}_3\text{Si})_2\text{CHSiMe}_2\text{OSiMe}_3$.⁹

Rearrangement of $(\text{MeSi})_3\text{CSiMe}_2\text{OH}$ later was found to take place in MeOH containing 0.50 M NaOMe .¹⁰ The silanol $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ was found to have reacted completely within 10 h at room temperature in 0.2 M NaOMe/MeOH to give the expected siloxane $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOSiMe}_3$. Reaction in pyridine indicated that rearrangement was complete within 26 h to give the above isomeric species under reflux. The course of the rearrangement can be represented as in Scheme 1.

The formation of an Si-O bond is energetically very favorable, but this is offset by going from a negative oxygen center to a negative carbon centre. The migration is facilitated by relief of steric strain and stabilization of the forming carbanionic centre by the three attached



SCHEME 1

silyl group. The relative reactivities of the various silanols may be determined by the inherent ease of the nucleophilic attack at the relevant silicon center and at least at low base concentration, by the acidity of the silanol. In cases in which the rearranged disiloxanes are obtained fairly free from other products, the possibility of metallating the acidic CH center gives them potential for further syntheses. The oranolithium reagent $(\text{Me}_3\text{Si})_2\text{CLiSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$ formed by treatment of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ with MeLi in $\text{Et}_2\text{O}/\text{THF}$ was found to react with Me_3SiCl , but it did react with the less hindered Me_2SiHCl to give the expected $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{H})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$ and the above isomeric species $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$. When the experiment was repeated with MeI in place of Me_2SiHCl or Me_3SiCl , it gives exclusively $(\text{Me}_3\text{Si})_2\text{CMe}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$. The reaction of the iodide $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}$ with 2.5 M NaOMe in refluxing MeOH for 8 h followed by aqueous work-up was found to give the expected $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OMe})$. We also examined the corresponding reaction with 2.5 M NaOEt in EtOH , which gives $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OEt})$ after 21 h under reflux.

The iodide $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}^{11}$ was found to react with ICl in CCl_4 to give the rearranged chloride $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Cl})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$, together with the unrearranged chloride $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeCl}$. Treatment of the hydride $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeH}$ with IBr in CCl_4 gives mainly the rearranged bromide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$.

The bromide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$ was found to react with AgBF_4 in MeOH to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$. This reaction is completed after 4.5 h under reflux (may be complete at less than 4.5 h). The same bromide was refluxed with

AgBF_4 in *i*-PrOH for 6 h (6-h period used may not be necessary) to give the rearranged isopropoxide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Oi-Pr})\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$. Reaction of the bromide with Ag_2SO_4 or AgOCOCH_3 in glacial CH_3COOH gave the acetate displacement product species $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCH}_3)\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$. The reaction of bromide with HgSO_4 or $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ in glacial CH_3COOH also gave the acetate displacement product.¹¹ When the bromide was stirred with AgOCOCF_3 in CF_3COOH at room temperature for 6 h, it gave the displacement product species $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{O}_2\text{CCF}_3)\text{Si}(\text{C}_6\text{H}_4\text{Me-}p)\text{Me}_2$.

EXPERIMENTAL

Solvents

Cyclohexane, diethylether, dichloromethane, tetrachloromethane, methanol, and pyridine were dried by standard methods.

Spectra

The ^1H NMR spectra were recorded on a Perkin Elmer (80 MHz) with CDCl_3 as solvent and CH_2Cl_2 or SiMe_4 as internal standard. The IR spectra were recorded in CCl_4 on a Perkin Elmer 156G spectrometer. Mass spectra (electron impact) were obtained with Finningan-Mat model 8400, 70 eV. Melting points were determined on a 9100 electrothermal apparatus.

Reaction of the $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ with NaOMe/MeOH

A solution of the silanol (0.3 g, 0.78 mmol) in 0.2 M NaOMe/MeOH (50 ml) was kept at room temperature for 10 h. Hexane was added followed by a large excess of water. The organic layer was separated, washed several times with water (MgSO_4) and evaporated under reduced pressure at room temperature to leave an oil. The viscous residue was purified by TLC (silicagel cyclohexane as eluent) to give the main product i.e., the isomeric form of the starting silanol which was assigned the structure $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$ (80%) from its $^1\text{HNMR}$ (CDCl_3) spectrum:- 0.2 (s, 1H, CH), 0.1 (s, 18H, SiMe_3), 0.2 (s, 9H, OSiMe_3), 0.45 (s, 3H, SiMe), 2.3 (s, 3H, Me-Aryl) and 7.1–7.5 ppm (m, 4H, aryl); m/z 368 $[\text{M-Me}]^+$, 290 $[\text{M-(C}_6\text{H}_4\text{-Me-}p)]^+$, 278 $[(\text{M-MeOSiMe}_3)]^+$ and 73 $[\text{SiMe}_3]^+$. (Found: C, 56.6; H, 9.9. $\text{C}_{18}\text{H}_{38}\text{OSi}_4$ calculated: C, 56.5; H, 9.9%).

Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ with Pyridine

A solution of the silanol (0.1 g, 0.26 mmol) in pyridine (20 ml) boiled under reflux for 26 h and worked-up as above gave an oil. The viscous residue was purified by preparative TLC (silicagel 1:1 dichloromethane-hexane as eluent) to give the isomeric $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$ (40%) together with the starting silanol. The properties were identical to those described above.

Trapping of $(\text{Me}_3\text{Si})_2\text{CLiSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$

(a) A solution of 0.1 M MeLi in Et_2O (10 ml) was added to $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ (0.2 g, 0.5 mmol) in THF (10 ml) and the mixture was refluxed for 3 h. An excess of Me_2SiHCl (2.0 cm^3) was added and the mixture refluxed for a further 3 h (possibly unnecessary). The volatile materials were removed under vacuum and light petroleum (b.p. 60–80) was added, followed by water. The organic layer was separated, dried (MgSO_4), filtered and evaporated, to leave a viscous liquid. The liquid product mixture was subjected to preparative TLC (silicagel dichloromethane as eluent) to give the liquid product $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$, with properties identical to those listed in the section entitled Reaction of the $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeOH}$ with NaOMe/MeOH.

(b) When the experiment was repeated, but with Me_3SiCl in place of Me_2SiHCl , the $^1\text{HNMR}$ spectrum of the product indicated that it was exclusively $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$. The properties were identical to those described above.

(c) Treatment of the organolithium reagent $(\text{Me}_3\text{Si})_2\text{CLiSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$ with MeI gives exclusively $(\text{Me}_3\text{Si})_2\text{CMeSi}(\text{C}_6\text{H}_4\text{Me-}p)(\text{Me})(\text{OSiMe}_3)$, $^1\text{HNMR}$ (CDCl_3): -0.01 (s, 3H, CMe), 0.01 (s, 18H, $(\text{SiMe}_3)_2$), 0.1 (s, 9H, OSiMe_3), 0.45 (s, 3H, SiMe), 2.35 (s, 3H, Me-aryl) and 7.1 – 7.5 ppm (m, 4H, Aryl); m/z 381.2 $[\text{M-Me}]^+$, 367.1 $[\text{M-2Me}]^+$, 223 $[\text{M-(Me}_3\text{Si)}_2\text{MeC}]^+$ and 73 $[\text{Me}_3\text{Si}]^+$. (Found: C, 57.57; H, 10.10. $\text{C}_{19}\text{H}_{40}\text{OSi}_4$ calculated: C, 57.31; H, 10.2%).

Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}$ with ICl

A solution of ICl (0.2 g, 0.75 mmol) in CCl_4 (25 ml) was added to $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}$ (0.25 g, 0.5 mmol) in CCl_4 (15 ml) and the mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to leave a solid, which was recrystallized from EtOH to give $(\text{MeSi})_2\text{C}(\text{SiMe}_2\text{Cl})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (71%); m.p. 186°C ; with properties identical with that reported before.

Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeH}$ with IBr

A solution of IBr (0.21 g, 1 mmol) in CCl_4 (20 ml) was added to $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeH}$ (0.18 g, 0.5 mmol) in CCl_4 (10 ml) and the mixture was stirred at room temperature for 6 h. The solvent was removed under reduced pressure to leave a solid, which was recrystallized from EtOH to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (42%); $^1\text{HNMR}$ (CDCl_3) 0.2 (s, 18H, SiMe_3), 0.55 (s, 6H, SiMeBr), 1.1 (s, 6H, SiMe_2Aryl), 2.3 (s, 3H, Me-aryl) and 6.7–7.8 ppm (m, 4H, Aryl); m/z 430 $[\text{M-Me}]^+$, 351, 291, 275 and 73. (Found: C, 49.18; H, 9.05. $\text{C}_{18}\text{H}_{37}\text{BrSi}_4$ calculated: C, 48.51; H, 8.37%).

This rearranged bromide has already been made by a different way.¹²

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with Ag_2SO_4

A mixture of the bromide (0.22 g, 0.5 mmol) with Ag_2SO_4 (0.78 g, 2.5 mmol) in glacial CH_3COOH (15 mmol) was refluxed for 5 h. The solution was decanted from AgBr , then water and diethylether was added. The Et_2O layer was dried (MgSO_4) and then evaporated. The viscous residue was then purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give the product species $(\text{MeSi})_2\text{C}(\text{SiMe}_2\text{OOCCH}_3)\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (65%); $^1\text{HNMR}$ (CDCl_3) 0.1 s, 18H, SiMe_3), 0.2 (s, 6H, SiMe_2aryl), 0.45 (s, 6H, SiMe_2OAc), 2.1 (s, 3H, Me-aryl), 2.2 (s, 3H, OAc) and 7–8 ppm (m, 4H, aryl); m/z 424 $[\text{M}]^+$, 409 $[\text{M-Me}]^+$, 365 $[\text{M-OAc}]^+$ and 333 $[\text{M-(C}_6\text{H}_4\text{-Me-}p)]^+$ with properties identical to those described before.

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with HgSO_4

A mixture of the bromide (0.22 g, 0.5 mmol) and HgSO_4 (0.74 g, 2.5 mmol) in glacial CH_3COOH (20 ml) was refluxed for 18 h and the mixture worked-up as described in the section on the Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with Ag_2SO_4 . The viscous residue was then purified by preparative TLC (Silicagel 3:1 dichloromethane-cyclohexane as eluent) to give the product $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OOCCH}_3)\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (60%) with properties identical to those described before.

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with AgOOCCH_3

A mixture of the bromide (0.22 g, 0.5 mmol) with AgOOCCH_3 (0.25 g, 1.5 mmol) in glacial CH_3COOH (20 ml) was refluxed for 3 h. The mixture

was worked-up as described in the section on the Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with Ag_2SO_4 . The viscous residue was then purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OOCH}_3)\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with properties identical to those described before.

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with $\text{Hg}(\text{OOCCH}_3)_2$

A mixture of the bromide (0.22 g, 0.5 mmol) and $\text{Hg}(\text{OOCCH}_3)_2$ (0.8 g, 2.5 mmol) in glacial CH_3COOH (20 ml) was refluxed for 10 h. The mixture was worked up as described in the section on the Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with Ag_2SO_4 . The viscous residue was then purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give the product $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OOCH}_3)\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (71%) with properties identical to those described before.

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with AgBF_4 in MeOH

A mixture of the bromide (0.22 g, 0.5 mmol) and AgBF_4 (0.5 g, 2.5 mmol) in dried MeOH (20 ml) was stirred under reflux for 4.5 h. The solution was decanted from AgBr, then water and Et_2O was added. The Et_2O layer was shaken several times with water. The residue was recrystallized from MeOH and then purified further with sublimation at $100^\circ\text{C}/5$ mmHg to give pure rearranged methoxide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (64%); $^1\text{H NMR}$ (CDCl_3) 0.1 (s, 6H, SiMe_2 aryl), 0.2 (s, 18H, SiMe_3), 0.51 (s, 6H, SiMe_2OMe), 2.4 (s, 3H, Me aryl), 3.4 (s, 3H, OMe) and 7–8 ppm (m, 4H, Aryl); m/z 397 $[\text{M}^+]$, 382 $[\text{M-Me}]^+$, 306 $[\text{M}-(\text{C}_6\text{H}_4\text{Me-}p)]^+$ and 73 $(\text{Me}_3\text{Si})^+$. (Found: C, 57.4; H, 10.0. $\text{C}_{19}\text{H}_{40}\text{OSi}_4$ calculated: C, 57.5; H, 10.1%).

Reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{Br})\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ with AgBF_4 in Pr^iOH

A mixture of the bromide (0.22 g, 0.5 mmol) with AgBF_4 (0.5 g, 2.5 mmol) in dried Pr^iOH (50 ml) was stirred under reflux for 6 h. The solution was decanted from AgBr, then water and Et_2O was added. The Et_2O layer was shaken several times with water and evaporated. The viscous residue was purified by preparative TLC (Silicagel 1:1 dichloromethane-cyclohexane as eluent) to give the product $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OPr}^i)\text{SiMe}_2(\text{C}_6\text{H}_4\text{Me-}p)$ (40%); $^1\text{H NMR}$ (CDCl_3) 0.3 (s, 18H, SiMe_3), 0.5 (s, 6H, $\text{SiMe}_2\text{OPr}^i$), 0.65 (s, 6H, SiMe_2 -aryl), 1.1–1.4 (d, 6H, $\text{Me}_2\text{CH-}$), 2.4 (s, 3H, Me- aryl), 3.9–4.1 (m, 1H, Me_2CH),

6.7–7.8 ppm (m, 4H, Aryl); m/z 424 $[M]^+$, 409 $[M-Me]^+$, 318 $[M-Me(C_6H_4Me-p)]^+$, 146 $[SiMe_2(C_6H_4Me-p)]^+$, 73 $[Me_3Si]^+$.

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