Reactivities of Silicas with Organometallic Methylating Agents

Ting Tao and Gary E. Maciel*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received June 10, 1999. Revised Manuscript Received December 1, 1999

Abstract: The surface of silica gel was modified by a variety of procedures aimed at the introduction of CH_3−Si moieties. The formation of these moieties by reactions of either $SOCl_2$-chlorinated silica or $SiCl_4$-modified silica with simple organometallic reagents (methyllithium, methylmagnesium bromide, dimethylzinc, or trimethylaluminum) was examined. Solid-state ^{29}Si and ^{13}C NMR techniques were used to characterize the resulting materials, especially to determine the extent of methylation of the silica surface. It was shown that, for a synthetic pathway that includes a chlorination step, methylmagnesium bromide was the best reagent for simply attaching a methyl group to a surface silicon atom. Methyllithium is very destructive to the silica framework, and trimethylaluminum forms a very small amount of Si−CH_3 moieties when allowed to react with silica itself, $SOCl_2$-chlorinated silica, or $SiCl_4$-treated silica. There was no obvious evidence that dimethylzinc reacted with dry silica or with either $SOCl_2$-modified or $SiCl_4$-modified silicas to form Si−CH_3 bonds.

Introduction

During the past 20 years, there has been an explosion of research based on "immobilizing" a potentially useful chemical moiety (e.g., a catalytic center, reaction center, or separation environment) on a silica surface.[1,2] For much of this type of work, the covalent, ionic, or van der Waals nature of attachment of the immobilized moiety is unknown. In some cases, there is an intentional strategy of making covalent linkages to the silica surface. The most common of these covalent strategies generates $\langle Si \rangle$−O−Si< linkages (where $\langle Si \rangle$ represents a silicon atom at the silica surface) via well-known silylation methods. However, the resulting $\langle Si \rangle$−O−Si< linkages may suffer the disadvantage of relatively easy solvolysis with polar solvents under certain conditions.
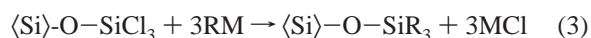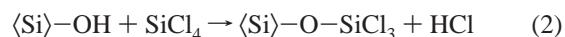
The direct attachment of alkyl or aryl groups to the silica surface via Si−C bonds has been of considerable interest in the development of highly specific surface modifications for catalysis and chemically bound stationary phases for chromatography.[1−7] Organosilica derivatives bound through $\langle Si \rangle$−C bonds appear to be much more stable to hydrolytic decomposition than those tethered through $\langle Si \rangle$−O bonds.[3−5,8] Surface-modified materials based on $\langle Si \rangle$−C linkages may be attractive from the point of view of generating new classes of highly stable modified silicas, where the pendent alkyl or aryl group may

contain some desired chemical functionality that one wishes to immobilize on a silica surface for use in, e.g., chromatography or catalysis.
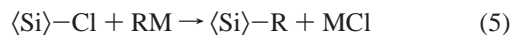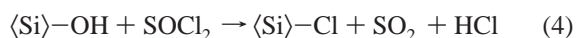
There are four rather different approaches that have been taken toward the preparation of organosilica derivatives with Si−C bonds. By far the most popular approach is the silica silylation procedure, involving reaction of $\langle Si \rangle$−OH groups with an organosilane reagent that has a reactive leaving group X (e.g., Cl, OR′, or NHSiMe_3) attached to silicon (eq 1).[3] A second

$$\langle Si \rangle\text{-OH} + X\text{−}SiR_3 \rightarrow \langle Si \rangle\text{−O−}SiR_3 + HX \qquad (1)$$
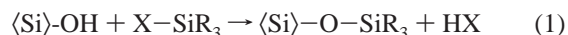
approach involves first the reaction of surface $\langle Si \rangle$−OH groups with $SiCl_4$ to form surface-bound $\langle Si \rangle$−O−$SiCl_3$ moieties, followed by a subsequent reaction with a suitable organometallic reagent (RM) to replace Si−Cl bonds with Si−C bonds (eqs 2 and 3).[6] A third approach includes first chlorinating surface

$$\langle Si \rangle\text{−OH} + SiCl_4 \rightarrow \langle Si \rangle\text{−O−}SiCl_3 + HCl \qquad (2)$$

$$\langle Si \rangle\text{-O−}SiCl_3 + 3RM \rightarrow \langle Si \rangle\text{−O−}SiR_3 + 3MCl \qquad (3)$$

silanols with thionyl chloride, $SOCl_2$, and then converting the chlorinated silica into a chemically modified Si−R type surface by reaction with organometallic compounds (eqs 4 and 5).[7,10−13]

$$\langle Si \rangle\text{−OH} + SOCl_2 \rightarrow \langle Si \rangle\text{−Cl} + SO_2 + HCl \qquad (4)$$

$$\langle Si \rangle\text{−Cl} + RM \rightarrow \langle Si \rangle\text{−R} + MCl \qquad (5)$$

Recently another approach has been introduced, based on the

---

* To whom correspondence should be addressed.

(1) Pesek, J. J.; Matyska, M. T.; Abuelafiya, R. R., Eds. *Chemically Modified Surfaces: Recent Developments*; Royal Society of Chemistry: Cambridge, 1996.

(2) Pesek, J. J.; Leigh, I. E., Eds. *Chemically Modified Surfaces*; Royal Society of Chemistry: Cambridge, 1994.

(3) Tertykh, V. A.; Belyakova, L. A. *Stud. Surf. Sci. Catal.* **1996**, *99*, 147.

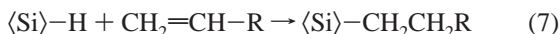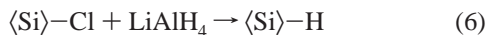(4) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* **1991**, *63*, 2634.

(5) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* **1989**, *61*, 2067.

(6) Locke, D. C.; Schmermund, J. T.; Banner, B. *Anal. Chem.* **1972**, *44*, 90.

(7) Saunders, D. H.; Barford, R. A.; Magidman, P.; Olszewski, L. T.; Rothbart, H. L. *Anal. Chem.* **1974**, *46*, 834.

(8) Spencer, W. F.; Gieseking, J. E. *J. Phys. Chem.* **1952**, *56*, 751.

(9) Deuel, H.; Wartmann, J.; Hutschneker, K.; Schobinger, U.; Güdel, C. *Helv. Chim. Acta* **1959**, *42*, 1160.

(10) Unger, K.; Thomas, W.; Adrian, P. *Kolloid - Z. Z. Polym.* **1973**, *251*, 45.

(11) Kumar K. R.; Choudary, B. M.; Jamil, Z.; Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 130.

(12) Choudary, B. M.; Bharathi, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1505.

(13) Kamitori, Y.; Hojo, M.; Masuda, R.; Kimura, T.; Yoshida, T. *J. Org. Chem.* **1986**, *51*, 1427.

conversion of chlorinated silica to silica with ⟨Si⟩−H bonds, followed by hydrosilation (eqs 6 and 7).[3,14]

$$\langle Si \rangle - Cl + LiAlH_4 \rightarrow \langle Si \rangle - H \qquad (6)$$

$$\langle Si \rangle - H + CH_2 = CH - R \rightarrow \langle Si \rangle - CH_2CH_2R \qquad (7)$$

It is obvious that the second approach ($SiCl_4$ pathway) adds an additional layer of silicon atoms on the silica surface, and if the reaction shown in eq 3 is complete, the net consequence of this sequence is quite similar to that of the silylation of silica gel with, e.g., trimethylchlorosilane or hexamethyldisilazane (eq 1), but with an additional layer of silicon-containing structures on the surface. In contrast, the third approach ($SOCl_2$ pathway) does a "more direct" modification of the silica surface, in which the surface hydroxyl groups are replaced by organic groups. The primary focus of the present work is to compare, by NMR spectroscopic evidence, the formation of methyl-terminated silicas via three of the routes indicated above. This work also provides baseline information on the reactivities of silica and modified silicas with organometallic methylating agents, information that should aid in finding the best synthetic procedures for new materials.

Although the immobilizations of phenyl and benzyl functionalities on silica surfaces by the formation of ⟨Si⟩−C bonds have been published,[6,7] the analogous preparation of methyl-terminated silicas of this type has not been reported previously. The main reasons we chose the methyl functionality for this study are the following: (1) Since the methyl group is the smallest hydrocarbon functionality, one might expect from steric considerations for it to produce the highest coverage of a hydrocarbon-capped hydrophobic surface. (2) The single resonance and small chemical shift anisotropy of a methyl group will simplify ^{13}C NMR issues. (3) Organometallic methylating agents are among the most common organometallic agents used in synthetic chemistry.

In addition to being motivated by intrinsic interest in fundamental silica chemistry, we are also motivated for this study by our desire to further the use of spectroscopic methods for achieving a better understanding of surface modifications of silica. IR spectroscopy is one of the most common tools for studying surface-modified silicas.[15,16] Infrared absorptions at 2980, 1410, 1270, and 780 cm^{-1} are assigned to Si−R (R = alkyl or aryl) terminations of the surface.[17,18] Unfortunately, IR spectroscopy has not been able to tell the difference between a silicon atom bearing one methyl group and a silicon atom having two methyl groups, and quantitative measurement of surface coverage by IR spectroscopy can also be difficult. Solid-state NMR with cross polarization (CP)[19] and magic-angle spinning (MAS)[20] is another excellent spectroscopic tool[21,22] for studying molecular structure at the organic-moiety/silica interface. Pioneering research work in our laboratory,[23-29] and elsewhere,[30-33] has yielded valuable information regarding the nature of surface silanols and the nature of primary and secondary products of silica silylation reactions. In this paper we present results

obtained using solid-state ^{29}Si and ^{13}C NMR to probe the reactivity of unadulterated and modified silica surfaces with simple organometallic methylating reagents, and in the structural characterization of the resulting methyl-terminated silicas.

Experimental Section

Materials. Silica gel (Davisil), with a particle diameter range of 60−200 mesh and a surface area of 300 m^2/g, was obtained from Adrich. Benzene (from J. T. Baker) was first dried over 4 Å molecular sieves for 24 h and then refluxed over calcium hydride for another 24 h. Methyllithium, methylmagnesium bromide, and dimethylzinc were obtained from Aldrich (**CAUTION**: dimethylzinc is a pyrophoric and moisture-sensitive material),[34] and trimethylaluminum was purchased from Strem (**CAUTION**: trimethylaluminum is a pyrophoric and moisture-sensitive material).[35] Thionyl chloride (from Fisher Scientific Co.) was used immediately after distillation. Purities of the organometallic methylating agents were checked by solution-state ^{1}H and ^{13}C NMR and were found to be satisfactory (>95%).

NMR Spectroscopy. All solid-state ^{13}C MAS NMR spectra were obtained at room temperature at 22.6 MHz on a Chemagnetics M-90s spectrometer. Chemagnetics 14 mm PENCIL rotors were used at a spinning speed of about 3 kHz. Conditions for cross-polarization (CP)[19] experiments: [1]H decoupling, 45 kHz; CP contact time, 10 ms; repetition delay, 2 s. Conditions for direct-polarization (DP, no CP) experiments: a 90° pulse length of 6.5 μs, with 45 kHz ^{1}H decoupling; repetition delay, 10 s. [13]C spectra were externally referenced to liquid tetramethylsilane (TMS) based on substitution of the secondary reference, solid hexamethylbenzene (peaks at 16.9 and 132.3 ppm relative to TMS). Solid-state ^{29}Si CP-MAS NMR spectra were obtained at 39.7 MHz at room temperature on a Chemagnetics CMX-200 spectrometer: [1]H decoupling, 43 kHz; CP contact time, 10 ms; repetition delay, 1 s; Chemagnetics 9 mm PENCIL™ rotors were used at a spinning speed of about 3.5 kHz. [29]Si spectra were externally referenced to liquid TMS based on substitution of the secondary reference, solid tetrakis(trimethylsilyl)silane (TTMSS, peaks at −8.1 and −134.3 ppm relative to TMS). The carbon contents of methyl-terminated silica gels were analyzed by Huffman Laboratory, Golden, CO (Table 1).

(20) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, 1.
(21) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(22) Maciel, G. E. *Science* **1984**, *226*, 282.
(23) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.
(24) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4263.
(25) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Chromatogr.* **1981**, *205*, 438.
(26) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.
(27) Miller, M. L.; Linton, R. W.; Maciel, G. E.; Hawkins, B. L. *J. Chromatogr.* **1985**, *319*, 9.
(28) Chuang, I.-S.; Kinney, D. R.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 8695.
(29) Chuang, I.-S.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 401.
(30) Engelhardt, G.; Jancke, H.; Lippmaa, E.; Samoson, A. *J. Organomet. Chem.* **1981**, *210*, 295.
(31) Albert, K.; Pfleiderer, B.; Bayer, E. In *Chemically Modified Surfaces in Science and Industry*; Leyden, D. E., Collins, W. T., Eds.; Gordon and Breach Science Publishers: New York, 1988; p 287.
(32) Koehler, J.; Chase, D. B.; Farlee, R. D.; Vega, A. J.; Kirkland, J. J. *J. Chromatogr.* **1986**, *352*, 275.
(33) Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.
(34) Dimethylzinc bursts into flames upon exposure to air and reacts with explosive violence with water. Therefore, it must be handled in an inert atmosphere. See discussion in: Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*; Pergamon Press: New York, 1982; Vol. 2, p 827. Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie Academic & Professional: London, 1997; p 110.
(35) The spontaneous flammability of trimethylaluminum in air demands special precautions. All transfers, storage, and reactions must be done under an anhydrous atmosphere of pure nitrogen or argon. See the detailed discussion in: Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*: Pergamon Press:New York, 1982; Vol. 1, p 579;

(14) Chu, C.-H.; Jonsson, E.; Auvinen, M.; Pesek, J. J.; Sandoval, J. E. *Anal. Chem.* **1993**, *65*, 808.
(15) Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Dekker: New York, 1967.
(16) Miller, J. D.; Ishida, H. In *Silanes, Surfaces and Interfaces*; Leyden, D. E., Ed.; Gordon and Breach: New York, 1986; p 525.
(17) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.
(18) Zhang, Z.; Tanigami, Y.; Terai, R. *J. Non-Cryst. Solids* **1995**, *191*, 304.
(19) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

3120 *J. Am. Chem. Soc., Vol. 122, No. 13, 2000*

Tao and Maciel

Table 1. Analytical Data on Silica-Based Samples

sample I.D.[a]	C contents (mmol/g)		major functionality distribution (mmol/g)[d,e]						
	classical[b]	NMR[c]	$\geqslant$SiOSiMe$_3$	($\geqslant$SiO)$_2$SiMe$_2$	($\geqslant$SiO)$_2$Si(OH)Me	($\geqslant$SiO)$_3$SiMe	($\geqslant$SiO)$_2$Si(OH)$_2$	($\geqslant$SiO)$_3$SiOH	($\geqslant$SiO)$_4$Si
A	1.18	1.24	0.035 (0.041)	0.18 (0.21)	0.31 (0.69)[f]	0.38	0.021	2.39	(19.2)[g]
B	1.87	1.80	0.051 (0.065)	0.28 (0.42)	0.27 (0.71)[f]	0.47	0.12	1.66	(17.2)[g]
C	3.10	3.22	1.22 (1.07)					1.54	

[a] A, methyl-terminated silica represented in Figure 2C; B, methyl-terminated silica prepared by the SOCl$_2$−CH$_3$MgBr re-treatment of the sample of Figure 2C; C, trimethylsilylated silica represented in Figure 4A. [b] Obtained by elemental analysis, performed by Huffman Laboratories, Inc., Golden, CO. Estimated uncertainty ±2%. [c] Obtained by ^{13}C DP-MAS spin counting analysis. Estimated uncertainty ±10%. [d] Obtained by combining [29]Si CP-MAS and [29]Si DP-MAS spin counting analyses. Estimated uncertainty ±20%. [e] Values in parentheses were obtained by ^{13}C DP-MAS spin counting analysis. Estimated uncertainty ±10%. [f] Populations from both ($\geqslant$SiO)$_2$**Si**(OH)(CH$_3$) and ($\geqslant$SiO)$_3$**Si**CH$_3$. Estimated uncertainty ±10%. [g] Estimated uncertainty ±20%

Trichlorosilyloxy-silica. Dried silica gel (3.01 g) was suspended in a solution consisting of 10 mL of dried benzene and 10 mL of silicon tetrachloride. The mixture was stirred under dry N$_2$(g) protection at room temperature for 20 h, and then refluxed under N$_2$(g) in a 80 °C oil bath for another 4 h. The resulting mixture was distilled to remove excess benzene and silicon tetrachloride, and the remaining solid was dried under vacuum ($\leq$10^{-2} Torr) at room temperature for 4 h, yielding 3.19 g of white, trichlorosilyloxy-silica (elemental analysis: 5.40% Cl, corresponding to 0.51 mmol of Cl/g of SiO$_2$).

Chlorinated Silica.[6] Davisil silica gel (20.83 g) was heated at 150 °C in a 100 mL flask for 24 h under vacuum at 10^{-3} Torr to a dry weight of 19.79 g. To 18.23 g of this dry silica gel in a 150 mL flask were added 20 mL of thionyl chloride and 40 mL of dry benzene. The resulting suspension was stirred under dry N$_2$(g) protection with the flask in a 85 °C oil bath for 48 h. The resulting product was filtered under an atmosphere of dry N$_2$(g), and the remaining thionyl chloride and benzene were then removed by vacuum ($\leq$10^{-2} Torr) at room temperature. Light brown chlorinated silica powder (18.45 g) was obtained (elemental analysis: 4.22% Cl, corresponding to 1.2 mmol of Cl/g of SiO$_2$).

Trimethylsilyl-Capped Silica. Dried silica gel (4.13 g) was refluxed (~80 °C) with 2.0 mL of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and 10 mL of dried benzene under dry N$_2$(g) protection for 12 h. The reaction mixture was filtered and washed with 50 mL of benzene, 50 mL of acetone, and 50 mL of methanol. The resulting material was dried at 100 °C under reduced pressure ($\leq$10^{-2} Torr) for 4 h, yielding 4.56 g of white powder.

Reactions of Trichlorosilyloxy-silica with Organometallic Reagents. (a) Methyl Grignard. To a 25 mL flask containing 0.97 g of trichlorosilyloxy-silica and 3.0 mL of dry benzene was added 3.0 mL of 3.0 M methylmagnesium bromide in diethyl ether over a 5-min period under dry N$_2$(g) in a flask cooled by an ice−water bath. The mixture was stirred for 24 h at room temperature and then for another 4 h in a 50 °C oil bath. The reaction mixture was then cooled in a dry ice/acetone bath and a 5 mL portion of 1.0 M HCl(aq) was added to decompose excess Grignard reagent. The resulting suspension was acidified to pH 4 by addition of 1.0 M HCl(aq). The resulting mixture was filtered and washed with successive portions of deionized water (3 × 50 mL), acetone (3 × 50 mL), and methanol (3 × 50 mL) and was finally dried under vacuum ($\leq$10^{-2} Torr) at 150 °C for 5 h, yielding 0.79 g of the resulting dry, white, methyl-terminated silica powder.

(b) Methyllithium. Trichlorosilyloxy-silica (2.12 g) was suspended in a stirred mixture of 5.0 mL of dry benzene and 5.0 mL of 1.4 M methyllithium in diethyl ether. The mixture was stirred for 24 h at room temperature under dry N$_2$(g) protection, and then for another 4 h with mild heating, using a 50 °C oil bath. The resulting reaction mixture was then cooled in a dry ice/acetone bath and a 5 mL portion of 1.0 M HCl(aq) was added to decompose excess lithium reagent. The resulting suspension was acidified to pH 4. The postreaction treatments described above for (a) were used to give 1.67 g of white powder.

(c) Dimethylzinc. Trichlorosilyloxy-silica (1.02 g) was suspended in a solution prepared by mixing 3.0 mL of dry benzene and 3.0 mL of 2.0 M dimethylzinc in toluene with a magnetic stirrer. Dry N$_2$(g) was used to protect the reaction from oxygen and moisture in air. The

mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the residual reaction mixture was cooled in a dry ice/acetone bath and 3 mL of 1-propanol was added to decompose excess dimethylzinc. The suspension was filtered and washed with three successive 20 mL portions of deionized water. The resulting modified silica was suspended in 20 mL of water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 0.92 g of dry white solid.

(d) Trimethylaluminum. To a 25 mL flask containing 0.98 g of trichlorosilyloxy-silica and 3.0 mL dry benzene was added 1.0 mL of trimethylaluminum by syringe under dry Ar(g) protection. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the residual reaction mixture was cooled in a dry ice/acetone bath and 3 mL of 1-propanol was added to decompose excess trimethylaluminum. The suspension was filtered and washed with three successive 20 mL portions of deionized water. The resulting modified silica was suspended in 20 mL of water and acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 0.90 g of white powder.

**Reactions of Chlorinated Silica with Organometallic Reagents. (a) Methyl Grignard.** To a 25 mL flask containing 4.20 g of chlorinated silica (prepared according to eq 4) and 20 mL of dry benzene was added 12 mL of 3.0 M methylmagnesium bromide in diethyl ether over a 5-min period under dry N$_2$(g) in a flask cooled by an ice−water bath. The mixture was stirred for 24 h at room temperature and then for another 4 h in a 50 °C oil bath. The reaction mixture was then cooled in a dry ice/acetone bath and a 25 mL portion of 1.0 M HCl-(aq) was added to decompose excess Grignard reagent. The resulting suspension was acidified to pH 4 by addition of 1.0 M HCl(aq). The resulting mixture was filtered and washed with successive portions of deionized water (3 × 50 mL), acetone (3 × 50 mL), and methanol (3 × 50 mL) and was finally dried under vacuum ($\leq$10^{-2} Torr) at 150 °C for 5 h. The weight of the resulting dry, white, methyl-terminated silica powder was 3.13 g.

(b) Methyllithium. Chlorinated silica (2.02 g) was suspended in a stirred mixture of 5.0 mL of dry benzene and 5.0 mL of 1.4 M methyllithium in diethyl ether. The mixture was stirred for 24 h at room temperature under dry N$_2$(g) protection, and then for another 4 h with mild heating, using a 50 °C oil bath. The resulting reaction mixture was then cooled in a dry ice/acetone bath and a 5 mL portion of 1.0 M HCl(aq) was added to decompose excess lithium reagent. The resulting suspension was acidified to pH 4. The postreaction treatments described above for (a) were used to give 1.67 g of white powder.

(c) Dimethylzinc. Chlorinated silica (3.98 g) was suspended in a solution prepared by mixing 15 mL of dry benzene and 9.0 mL of 2.0 M dimethylzinc in toluene with a magnetic stirrer. Dry N$_2$(g) was used to protect the reaction from oxygen and moisture in air. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the reaction mixture was cooled in a dry ice/acetone bath and 10 mL of 1-propanol was added to decompose excess dimethylzinc. The suspension was filtered and washed with three successive 50 mL portions of

deionized water. The resulting modified silica was suspended in 30 mL water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 3.78 g of dry, white solid.

(d) Trimethylaluminum. To a 25 mL flask containing 1.38 g of chlorinated silica and 6.0 mL of dry benzene was added 1.0 mL of trimethylaluminum by syringe under dry Ar(g) protection. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. The reaction mixture was then cooled in a dry ice/acetone bath and 5 mL of 1-propanol was added to decompose excess trimethylaluminum. The suspension was filtered and washed with three successive 50 mL portions of deionized water. The resulting modified silica was suspended in 20 mL of water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 1.05 g of white powder.

Reactions of Dried Silica Gel with Organometallic Reagents. (a) Methyl Grignard. To a 25 mL flask containing 1.97 g of dry silica gel and 6.0 mL of dry benzene was added 6.0 mL of 3.0 M methylmagnesium bromide in diethyl ether dropwise under dry N_2(g) protection in a flask cooled by an ice−water bath. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. The reaction mixture was then cooled using a dry ice/acetone bath and 10 mL of 1.0 M HCl(aq) was added to decompose excess Grignard reagent. The suspension was acidified to pH 4 by addition of 1.0 M HCl(aq). The resulting mixture was filtered and washed with successive portions of deionized water (3 × 50 mL), acetone (3 × 50 mL), and methanol (3 × 50 mL) and was finally dried under vacuum ($\leq 10^{-2}$ Torr) at 150 °C for 5 h, resulting in 1.86 g of dry, modified silica powder.

(b) Methyllithium. Dry silica gel (2.07 g) was suspended in a solution prepared by mixing 5.0 mL of dry benzene and 5.0 mL of 1.4 M methyllithium in diethyl ether with a magnetic stirrer. The mixture was stirred for 24 h at room temperature under dry N_2(g) protection, and then for another 4 h using a 50 °C oil bath. The resulting reaction mixture was then cooled in a dry ice/acetone bath and a 5 mL portion of 1.0 M HCl(aq) was added to decompose excess lithium reagent. The resulting suspension was acidified to pH 4. The postreaction treatments described above for (a) were used to give 1.45 g of white powder.

(c) Dimethylzinc. Dry silica gel (2.32 g) was suspended in a solution prepared by mixing 5.0 mL of dry benzene and 6.0 mL of 2.0 M dimethylzinc in toluene with a magnetic stirrer. Dry N_2(g) was used to protect the reaction from oxygen and moisture in air. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the reaction mixture was cooled in a dry ice/acetone bath and 6 mL of 1-propanol was added to decompose excess dimethylzinc. The suspension was filtered and washed with three successive 20 mL portions of deionized water. The resulting modified silica was suspended in 20 mL water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 2.23 g of dry, white solid product.

(d) Trimethylaluminum. To a 25 mL flask containing 2.10 g of dry silica gel and 8.0 mL of dry benzene was added 2.0 mL of trimethylaluminum by syringe under dry Ar(g) protection. The mixture was stirred for 24 h at room temperature, and then for another 4 h using a 50 °C oil bath. The reaction mixture was then cooled in a dry ice/acetone bath and 7 mL of 1-propanol was added to decompose excess trimethylaluminum. The suspension was filtered and washed with three successive 50 mL portions of deionized water. The resulting material was suspended in 20 mL of water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to yield 1.98 g of white, modified silica solid.

Reactions of Trimethylsilylated Silica with Organometallic Reagents. (a) Methyl Grignard. To a 25 mL flask containing 0.95 g of trimethylsilylated silica and 3.0 mL of dry benzene was added 3.0 mL of 3.0 M methylmagnesium bromide in diethyl ether dropwise under dry N_2(g) protection, using an ice−water cooling bath. The mixture was stirred for 24 h at room temperature, and then for another 4 h using a 50 °C oil bath. The reaction mixture was then cooled in a dry ice/acetone bath and 5 mL of 1.0 M HCl(aq) was added to decompose
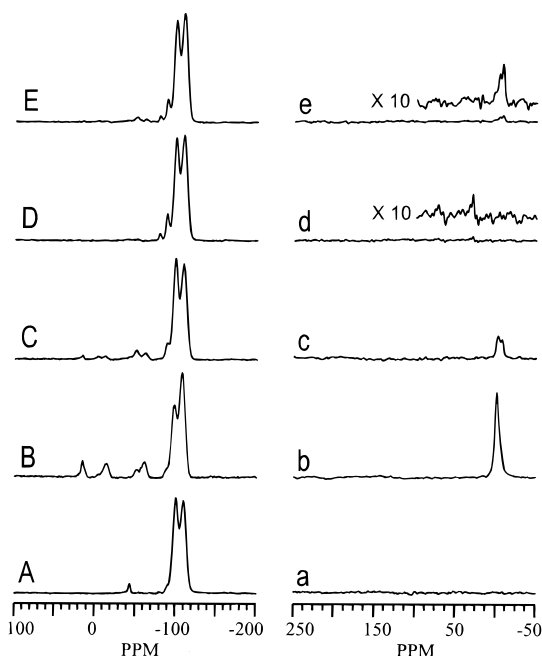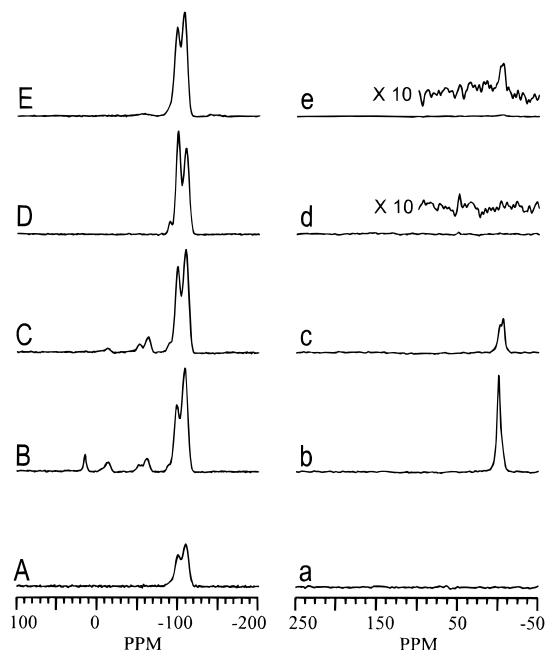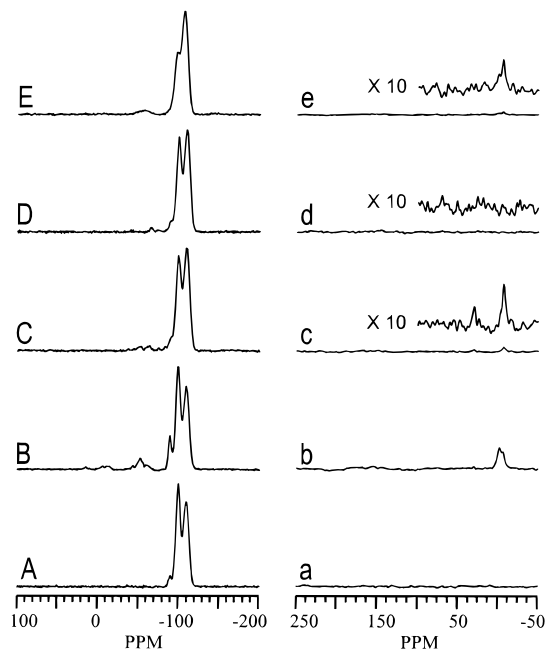

Figure 1. Solid-state ^{29}Si (left column) and ^{13}C (right column) CP-MAS NMR spectra of the reaction products of SiCl$_4$-treated silica gel (A and a) with methyllithium (B and b), methylmagnesium bromide (C and c), dimethylzinc (D and d), and trimethylaluminum (E and e). Each ^{29}Si spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 10 ms; ^{1}H decoupling, 43 kHz; 1 s repetition delay; and 7200 scans. Each ^{13}C spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 5 ms; ^{1}H decoupling, 43 kHz; 2 s repetition delay; and 7200 scans.

excess Grignard reagent. The resulting suspension was acidified to pH 4 by 1.0 M HCl(aq). The resulting mixture was filtered and washed with successive portions of deionized water (3 × 25 mL), acetone (3 × 25 mL), and methanol (3 × 25 mL), and was finally dried under vacuum ($\leq 10^{-2}$ Torr) at 150 °C for 5 h, yielding 0.94 g of the dry modified silica solid.

(b) Methyllithium. Trimethylsilylated silica (0.99 g) was suspended in a solution prepared by mixing 3.0 mL of dry benzene and 3.0 mL of 1.4 M methyllithium in diethyl ether with a magnetic stirrer. The mixture was stirred for 24 h at room temperature under dry N_2(g) protection, and then for another 4 h using a 50 °C oil bath. The resulting reaction mixture was then cooled in a dry ice/acetone bath and a 3 mL portion of 1.0 M HCl(aq) was added to decompose excess lithium reagent. The resulting suspension was acidified to pH 4. The postreaction treatments described above for (a) were used to give 0.45 g of white powder.

(c) Dimethylzinc. Trimethylsilylated silica (0.75 g) was suspended in a solution prepared by mixing 3.0 mL of dry benzene and 3.0 mL of 2.0 M dimethylzinc in toluene with a magnetic stirrer. Dry N_2(g) was used to protect the reaction from oxygen and moisture in air. The mixture was stirred for 24 h at room temperature and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the reaction mixture was cooled in a dry ice/acetone bath and 3 mL of 1-propanol was added to decompose excess dimethylzinc. The suspension was filtered and washed with three successive 20 mL portions of deionized water. The resulting modified silica was suspended in 20 mL of water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to give 0.74 g of dry product.

(d) Trimethylaluminum. To a 25 mL flask containing 1.56 g of trimethylsilylated silica and 5.0 mL dry benzene was added 1.5 mL of trimethylaluminum by syringe under dry Ar(g) protection. The mixture was stirred for 24 h at room temperature, and then for another 4 h using a 50 °C oil bath. After removal of the solution layer by a syringe, the reaction mixture was cooled in a dry ice/acetone bath and 5 mL of 1-propanol was added to decompose excess trimethylaluminum. The

Figure 2. Solid-state ^{29}Si (left column) and ^{13}C (right column) CP-MAS NMR spectra of the reaction products of SOCl$_2$-chlorinated silica (A and a) with methyllithium (B and b), methylmagnesium bromide (C and c), dimethylzinc (D and d), and trimethylaluminum (E and e). Each ^{29}Si spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 10 ms; ^{1}H decoupling, 43 kHz; 1 s repetition delay; and 7200 scans. Each ^{13}C spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 5 ms; ^{1}H decoupling, 43 kHz; 2 s repetition delay; and 7200 scans.

Figure 3. Solid-state ^{29}Si (left column) and ^{13}C (right column) CP-MAS NMR spectra of the reaction products of dry silica gel (A and a) with methyllithium (B and b), methylmagnesium bromide (C and c), dimethylaluminum (D and d), and trimethylaluminum (E and e). Each ^{29}Si spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 10 ms; ^{1}H decoupling, 43 kHz; 1 s repetition delay; and 7200 scans. Each ^{13}C spectrum was obtained with the following conditions: ^{1}H 90° pulse, 6.0 μs; CP contact time, 5 ms; ^{1}H decoupling, 43 kHz; 2 s repetition delay; and 7200 scans.

suspension was filtered and washed with three successive 50 mL portions of deionized water. The resulting gel was suspended in 20 mL of water and was acidified to pH 4 by addition of 1.0 M HCl(aq). The postreaction treatments described above for (a) were used to yield 1.25 g of white powder.

Results and Discussion

As with any NMR technique, quantitative interpretation of peak intensities can be made in CP-MAS spectra only if the relevant spin dynamics have been characterized and taken into account. Until a discussion of quantitation below, our interpretation of the CP-MAS spectra will be entirely qualitative. At a qualitative level, we know from earlier work in this group, and elsewhere, that the CP-MAS approach emphasizes ^{29}Si nuclei at the surface, relative to ^{29}Si nuclei in particle interiors.

Figures 1A, 2A, 3A, and 4A show solid-state ^{29}Si CP-MAS spectra obtained (with ^{1}H → ^{29}Si cross polarization)[23] from SiCl$_4$-modified silica, SOCl$_2$-chlorinated silica, dry silica gel, and a trimethylsilylated silica. The spectrum in Figure 3A represents well-known structural units of the silica surface: (≥SiO)$_2$**Si**(OH)$_2$ (Q$_2$), (≥SiO)$_3$**Si**OH (Q$_3$), and (≥SiO)$_4$**Si** (Q$_4$), where the symbol (≥SiO)**Si** stands for a siloxane bridge to another silicon atom. These types of surface moieties are typically present in commercial silicas.[23–29] Reaction of silica with SiCl$_4$ (eq 2) at room temperature creates a small amount of ⟨Si⟩−O−**Si**Cl$_3$ moieties, as evidenced by a small peak at −43 ppm in Figure 1A. Although the ^{29}Si NMR chemical shift and line shape of surface attached ⟨Si⟩−O−**Si**Cl$_3$ moieties have been reported in the literature,[36] the assignment of a *single* peak at −43 ppm for ⟨Si⟩−O−**Si**Cl$_3$ may be questioned, because the three quadrupolar Cl nuclei directly bound to **Si** might be

expected to produce a complex multiplet in the ^{29}Si resonance. To clarify this assignment, two model compounds, *N*-acetyl-*p*-aminophenoxytrichlorosilane and 9-phenanthroxytrichlorosilane, were synthesized by the reactions of silicon tetrachloride with *N*-acetyl-*p*-aminophenol and 9-phenanthrol, respectively. Both *N*-acetyl-*p*-aminophenoxytrichlorosilane and 9-phenanthrox-ytrichlorosilane show single peaks in their solid-state ^{29}Si CP-MAS spectra (not shown here), at −39 and −43 ppm, respectively. The fact that a single, sharp peak, rather than a complex multiplet, is observed for ⟨Si⟩−O−**Si**Cl$_3$ is presumably due to self-decoupling of the ^{35}Cl and ^{37}Cl nuclei.[37]

The ^{29}Si CP-MAS spectrum (Figure 2A) of the chlorinated silica prepared by the SOCl$_2$ approach (eq 4) shows a decrease of the Q$_3$/Q$_4$ intensity ratio due to the replacement of ⟨Si⟩−OH by ⟨Si⟩−Cl on the silica surface. One can see that both Q$_3$ and Q$_4$ intensities in Figure 2A are not only smaller than those in Figure 3A (silica gel), but are also smaller than those in Figure 1A. This reflects the fact that the replacement of ⟨Si⟩−OH by ⟨Si⟩−Cl is more efficient in the SOCl$_2$ approach, and hence fewer protons in the sample of Figure 2A are available to contribute to ^{1}H−^{29}Si cross polarization. Figure 4A shows the ^{29}Si CP-MAS spectrum of the trimethylsilylated-silica, which was prepared by the well-known methodology represented in eq 1, employing 1,1,1,3,3,3-hexamethyldisilazane, [(CH$_3$)$_3$-Si]$_2$NH, as the silylating agent.[38] In this spectrum, the intense peak at 13 ppm corresponds to surface-attached (CH$_3$)$_3$**Si**−O−⟨Si⟩ groups.

On the basis of the chemistry represented by eqs 2−5, methyl-terminated silica gels were synthesized via both SiCl$_4$ and SOCl$_2$

(36) Martens, J. A.; Geerts, H.; Grobet, P. J.; Jacobs, P. A. *J. Chem. Soc., Chem. Commun.* **1990**, 1418.

(37) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*; Pitman: London, 1983; p 140.

(38) Shimada, T.; Hirose, R.; Morihara, K. *Bull. Chem. Soc. Jpn.* **1994**, 67, 227.
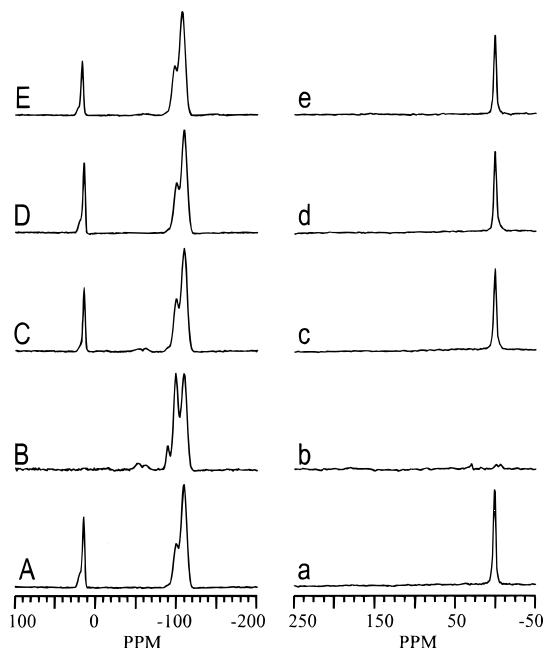
Figure 4. Solid-state ^{29}Si (left column) and ^{13}C (right column) CP-MAS NMR spectra of the reaction products of trimethylsilylated silica gel (A and a) with methyllithium (B and b), methylmagnesium bromide (C and c), dimethylzinc (D and d), and trimethylaluminum (E and e). Each ^{29}Si spectrum was obtained with the following conditions: ^1H 90° pulse, 6.0 μs; CP contact time, 10 ms; ^1H decoupling, 43 kHz; 1 s repetition delay; and 7200 scans. Each ^{13}C spectrum was obtained with the following conditions: ^1H 90° pulse, 6.0 μs; CP contact time, 5 ms; ^1H decoupling, 43 kHz; 2 s repetition delay; and 7200 scans.

pathways, using simple methylmetallic species (MeLi, MeMgBr, Me_2Zn, or Me_3Al) as the organometallic agent (RM). Solid-state CP-MAS ^{29}Si NMR spectra of the derivatized silicas prepared by the two-step methods represented by eqs 2 and 3 and by eq 4 and 5 with RMs are shown in Figures 1B–E and 2B–E, respectively.

It should be noted that ^{29}Si NMR chemical shifts (δ_{si}) are extremely sensitive to the type, position, and bonding characteristics of silicon's neighboring atoms.[39,40] In a polysiloxane structural unit, $(\geqslant SiO)_n Si(OH)_{4-n}$, where n = 1–4, a ^{29}Si chemical shift difference of approximately 10 ppm is generally observed for each additional siloxane bridge, Si–O–Si (relative to the corresponding SiOH moiety), i.e., $\delta_{si}(Q_1)$ = −80 ppm, $\delta_{si}(Q_2)$ = −90 ppm, $\delta_{si}(Q_3)$ = −100 ppm, and $\delta_{si}(Q_4)$ = −110 ppm. The replacement of R (R = alkyl or aryl) for oxygen in the formula $(\geqslant SiO)_n Si(OH)_{4-n}$ leads to a large low-shielding shift (decreased shielding). In a given $R_m(\geqslant SiO)_n Si(-O)_{4-m-n}$ system (where $m + n \leq 4$), each replacement of $(\geqslant SiO)$ or (OH) with R induces a ^{29}Si chemical shift change of about 30–40 ppm to lower shielding, e.g., from $(\geqslant SiO)_3 SiOH$ at −100 ppm to $(\geqslant SiO)_3 SiCH_3$ at −62 ppm. These peak assignments can be made on the basis of the usual kinds of empirical correlations of chemical shift with structure from liquid sample data.[39] In addition, in solid-state CP-MAS ^{29}Si NMR, the dynamics of the $^1H-^{29}Si$ CP process has also been used to assist in making assignments.[41]

(39) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 235.
(40) Engelhardt, G. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Becker, E. D., Eds.; John Wiley & Sons, Ltd.: Sussex, 1996; Vol. 7, p 4398.
(41) Maciel, G. E. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Becker, E. D., Eds.; John Wiley & Sons, Ltd.: Sussex, 1996; Vol. 7, p 4370.
(42) Mann, B. E.; Taylor, B. F. *13C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 62.

Figure 1B shows the ^{29}Si CP-MAS spectrum obtained on the sample prepared by reaction of $SiCl_4$-modified silica with methyllithium. In addition to the peaks between −80 and −115 ppm, which represent the basic structure of the original silica surface, one sees four additional peaks due to the formation of Si–CH_3 bonds, and assigned to $(\geqslant SiO)Si(CH_3)_3$ at 13 ppm, $(\geqslant SiO)_2 Si(CH_3)_2$ at −15 ppm, $(\geqslant SiO)_2(OH)SiCH_3$ at − 52 ppm and $(\geqslant SiO)_3 SiCH_3$ at − 60 ppm.[25,26,31] Figure 1b shows the ^{13}C CP-MAS spectrum obtained for the same sample; its ^{13}C intensity between 1 and −5 ppm also indicates the formation of Si–CH_3 bonds. The apparent amount of Si–CH_3 implied by these ^{29}Si and ^{13}C NMR intensities seems to overemphasize the formation of Si–CH_3 moieties, since Si–C bonds can presumably form only by the reaction of methyllithium with surface –$SiCl_3$ groups (represented by the small ^{29}Si intensity shown in Figure 1A). This issue, related to CP dynamics and intrinsic reaction mechanisms, is discussed below, when related data are presented from methyllithium treatments of other types of modified silica.

Figures 1C and 1c show ^{29}Si and ^{13}C CP-MAS spectra of the sample prepared by reaction of $SiCl_4$-modified silica with methylmagnesium bromide. One can see that the patterns of ^{29}Si and ^{13}C NMR signals shown in Figures 1C and 1c are very similar to those shown in Figures 1B and 1b, with peaks due to formation of Si–CH_3 moieties, but with much smaller intensities. These results demonstrate that not all surface $Cl_3SiO-\langle Si \rangle$ groups were converted into $(CH_3)_3 SiO-\langle Si \rangle$ groups by methylmagnesium bromide treatment. Most of the Si–CH_3 intensities shown in Figure 1C and 1c correspond to $(\geqslant SiO)_2(OH)SiCH_3$ and $(\geqslant SiO)_3 SiCH_3$.

The trichlorosilyloxy silica sample treated with dimethylzinc shows no evidence of formation of Si–CH_3 bonds, based on its ^{29}Si and ^{13}C NMR spectra (Figures 1D and 1d). A small $(\geqslant SiO)Si(OH)_3$ (Q_1) peak is seen in the ^{29}Si CP-MAS spectrum (Figure 1D) at −77 ppm due to hydrolysis of the $Cl_3SiOSi-$ group. Figures 1E and 1e show the ^{29}Si and ^{13}C NMR spectra obtained on a trichlorosilyloxy silica that was treated with trimethylaluminum; only very small intensities are seen for $(\geqslant SiO)_2(OH)SiCH_3$ and $(\geqslant SiO)_3 SiCH_3$ moieties.

The ^{13}C CP-MAS spectrum in Figure 1b shows a hint of a higher-shielding shoulder on the $(\geqslant SiO)Si(CH_3)_3$ peak (with a maximum intensity at about 2.1 ppm). Analogous higher-shielding features are more apparent in the less intense pattern of Figure 1c. These higher-shielding intensities are due to $(SiO)_2 Si(CH_3)_2$ methyls at −1.3 ppm and $(\geqslant SiO)_3 SiCH_3$ methyls at −5.2 ppm.[42] Apparently, a much higher fraction of the Si–C bonds are in the $(\geqslant SiO)_2 Si(CH_3)_2$ and $(\geqslant SiO)_3 SiCH_3$ forms in the sample prepared with CH_3MgBr than that prepared with CH_3Li.

The ^{29}Si and ^{13}C NMR spectra of the methyllithium-treated $SOCl_2$-chlorinated silica sample are shown in Figures 2B and 2b, which are quite similar to Figures 1B and 1b. In terms of eqs 2−5, one might expect the $SiCl_4$ pathway to produce more $(\geqslant SiO)Si(CH_3)_3$ moieties because of the reaction of the $(\geqslant SiO)-SiCl_3$ intermediate with CH_3Li, while the $SOCl_2$ pathway would be expected to generate more $(\geqslant SiO)_3 SiCH_3$ moieties by modification of the original single silanols (Q_3) on the silica surface. Hence, the similarity of the spectra shown in Figures 1B and 2B suggests that a more common intrinsic pattern of reactions, rather than simply the reaction schemes represented in eqs 2−5, is operative.

Upon examining Figure 2B, it is not straightforward to explain why high ^{29}Si NMR intensities of *both* $(\geqslant SiO)Si(CH_3)_3$ and $(\geqslant SiO)_2 Si(CH_3)_2$ species are seen, since there is little $(\geqslant SiO)-$

Si(OH)$_3$ on an unmodified silica surface (none seen in Figure 3A); it therefore seems unlikely that the SOCl$_2$ approach represented in eqs 4 and 5 could produce a substantial amount of (≻SiO)Si(Cl)$_3$, which ostensibly would subsequently react with methyllithium to form (≻SiO)**Si**(CH$_3$)$_3$. Therefore, it appears that methyllithium plays a much more complicated ("destructive") role, breaking down a portion of the silica framework, and ultimately creating a complex array of surface functionalities, including (≻SiO)**Si**(CH$_3$)$_3$ and (≻SiO)$_2$**Si**(CH$_3$)$_2$.

For further examination of the reactivities of the various organometallic reagents toward a SOCl$_2$-chlorinated silica, the ^{29}Si CP-MAS and ^{13}C CP-MAS spectra of samples resulting from reactions of the chlorinated silica with the other three CH$_3$M reagents are also given in Figures 2C−E and 2c−e, respectively. In the ^{29}Si CP-MAS spectrum of the sample resulting from reaction of chlorinated silica with methylmagnesium bromide (Figure 2C), one sees, in addition to peaks corresponding to the silica framework, additional major peaks corresponding to the functionalities (≻SiO)$_3$**Si**CH$_3$ (peak at −63 ppm) and (≻SiO)$_2$(HO)**Si**CH$_3$ (peak at −52 ppm), with a much weaker peak at −15 ppm, indicating the presence of (≻SiO)$_2$-**Si**(CH$_3$)$_2$ and almost no (≻SiO)**Si**(CH$_3$)$_3$ (13 ppm). The two stronger peaks at −63 and −52 ppm could be due to species generated from the conversion of the original silanol functionalities, ⟨**Si**⟩(OH)$_n$, on the silica surface ($n = 1$ or 2), as described in eqs 4 and 5, without requiring any "damage" of the silica framework. The (≻SiO)$_2$(HO)**Si**CH$_3$ peak at −52 ppm might result from the partial conversion of geminal silanols, (≻SiO)$_2$-⟨**Si**⟩(OH)$_2$, according to eqs 4 and 5, or from partial degradation of single silanol moieties, (≻SiO)$_3$⟨**Si**⟩OH.

The NMR results obtained in this work provide no obvious evidence that dimethylzinc reacts with the chlorinated silica *to form direct silicon−carbon bonds*. Figure 2D shows the ^{29}Si CP-MAS spectrum of a dimethylzinc-treated chlorinated-silica sample; this spectrum appears to be essentially identical with the spectrum of the original silica (Figure 3A) *before chlorination*. The fact that the spectrum in Figure 2D does not look like that of chlorinated silica in Figure 2A is due to the use of water to decompose excess dimethylzinc in the workup procedure used to prepare the sample of Figure 2D; in this procedure the ⟨Si⟩−Cl functionalities have been hydrolyzed to ⟨Si⟩−OH. The ^{29}Si CP-MAS spectrum of trimethylaluminum-treated chlorinated silica (Figure 2E) shows very little intensity of (≻SiO)$_3$**Si**CH$_3$ at −60 ppm. These "negative" results from the dimethylzinc treatment of chlorinated silica and the trimethylaluminum treatment of chlorinated silica, as well as the analogous results discussed above for SiCl$_4$-modified silica, in contrast to the cases of CH$_3$Li or CH$_3$MgBr reagents, are somewhat surprising in terms of the reactive natures typical of these CH$_3$M reagents. This reactivity pattern may be due in part to the formation of Lewis acid/base complexes of CH$_3$M species (e.g., with oxygen and/or chlorine sites on the chlorinated silica surface) that are either stable (in the Zn and Al cases) or undergo CH$_3$ transfer (in the Li and Mg cases) prior to subsequent workup of the reaction mixture with water. This rough hypothesis can be rationalized in terms of simple (and admittedly arbitrary) bond-energy considerations.

Solution-state ^{1}H NMR analyses (not shown here) performed on the decanted solutions present after treatments of chlorinated silica with (CH$_3$)$_2$Zn and (CH$_3$)$_3$Al for 24 h show that the majority of the dimethylzinc ($\delta_H = -0.7$ ppm) and trimethyl-aluminum ($\delta_H = -0.5$ ppm) introduced in excess at the beginning of the treatments remain unreacted. The amount of initially added (CH$_3$)$_2$Zn or (CH$_3$)$_3$Al that is not accounted for

in the supernatant liquids of the final reaction mixtures is about 1.8 mmol/g of SiO$_2$ or 2.0 mmol/g of SiO$_2$, respectively; these numbers can be compared with the 1.2 mmol of Cl/g of SiO$_2$ in the chlorinated silica starting material (by elemental analysis). Thus, it appears that substantial amounts of (CH$_3$)$_2$Zn and (CH$_3$)$_3$Al react, or at least strongly interact, with the chlorinated silica surface, but not to form Si−CH$_3$ bonds. More extensive studies are underway to determine the structures present at each major stage of these overall conversions.

The ^{13}C NMR signals between 1 and −5 ppm, which correspond to CH$_3$ groups attached to silicon, are seen in the ^{13}C CP-MAS spectra of CH$_3$Li-treated SOCl$_2$-chlorinated silica (Figures 2b) and of CH$_3$MgBr-treated SOCl$_2$-chlorinated silica (Figure 2c), while no ^{13}C signals were found in the CP-MAS spectrum of the (CH$_3$)$_2$Zn-treated SOCl$_2$-chlorinated silica sample (Figure 2d), and only a very small ^{13}C signal was found for SOCl$_2$-chlorinated silica that was treated with trimethyl-aluminum (Figure 2e). By analyzing the ^{13}C NMR line shapes, one can discern structural differences among the samples represented in Figures 1b, 2b, and 2c. The ^{13}C CP-MAS spectra in Figures 1b and 2b have a dominant peak at about 1 ppm, which corresponds to the resonance from the (≻SiO)Si(**CH$_3$**)$_3$ structural unit. Some intensity between −1 and −5 ppm in Figures 1b and 2b is due to ^{13}C resonances from (≻SiO)$_2$Si-(**CH$_3$**)$_2$ and (≻SiO)$_3$Si**CH$_3$** functionalities,[42] although they were not resolved as distinct peaks. The methyl-terminated sample in Figure 2c shows another type of surface modification, compared to the samples in Figures 1b and 2b. The highest peak in Figure 2c, at −5 ppm, indicates a high population of (≻SiO)$_3$Si**CH$_3$** species, while some intensity appears as a shoulder at −1 ppm, which is the contribution from (≻SiO)$_2$Si-(**CH$_3$**)$_2$ species. There is no distinct signal at 1 ppm in Figure 2c for (SiO)Si(**CH$_3$**)$_3$ species. The thrust of these ^{29}Si and ^{13}C CP-MAS spectra of Figure 2 is that methylmagnesium bromide is by far the most suitable of these four CH$_3$M reagents to synthesize methyl-modified silica from SOCl$_2$-chlorinated silica, while largely maintaining the integrity of the silica framework.

To better understand the nature of these systems and their reactions, a series of experiments was carried out in which the four CH$_3$M reagents were allowed to react with dried silica gel, with no prior treatment by SiCl$_4$ or SOCl$_2$. One expects, at minimum, that the CH$_3$M reagents will deprotonate silanol groups (eq 8). Any other chemical transformations that occur

$$CH_3Li + \langle Si \rangle - OH \rightarrow \langle Si \rangle - OLi + CH_4 \qquad (8)$$

will be of interest in determining the usefulness of these CH$_3$M reagents in synthetic procedures which involve silica.

The ^{29}Si and ^{13}C CP-MAS spectra of the materials resulting from treatment of dried silica gel with the CH$_3$M reagents are shown in Figure 3. The ^{29}Si spectrum indicates that the dried silica sample which had been treated with CH$_3$Li (Figure 3B) has a markedly changed chemical structural composition at the surface, in comparison to the surface of the dry silica gel (Figure 3A). In the spectrum of Figure 3B one can see substantial intensity at −60 ppm, and small intensities at −15 ppm and even 13 ppm, corresponding to formation of (≻SiO)$_3$**Si**CH$_3$, (≻SiO)$_2$**Si**(CH$_3$)$_2$, and (≻SiO)**Si**(CH$_3$)$_3$ functionalities, respectively. Comparison of the spectra of Figure 3A and Figure 3B also shows a major redistribution of intensities in the Q$_2$−Q$_3$−Q$_4$ region, especially a major increase in the relative intensity of the Q$_2$ peak (−89 ppm). If the action of CH$_3$Li had been limited to just deprotonation of ⟨Si⟩OH groups (eq 8), there would be little change in the peak positions. We have found little effect on peak position in the ^{29}Si CP-MAS spectra (not

shown here) of silica gel upon stirring the sample with aqueous solutions covering a wide range of pH (from 2 to 10). Relative ^{29}Si NMR intensities could be effected by changes in the relevant spin dynamics. Nevertheless, one can state that qualitative changes observed in the ^{29}Si NMR spectra indicate that some of the silica framework is damaged by the CH$_3$Li reagent, i.e., some siloxane linkages ($\langle$Si$\rangle$−O−$\langle$Si$\rangle$) have been cleaved, and CH$_3$−$\langle$Si$\rangle$ linkages have been formed. Thus, methyllithium apparently reacts directly with $\langle$Si$\rangle$−O bonds according to an overall scheme of the type,

$$CH_3Li + \langle Si \rangle - O - X \rightarrow \langle Si \rangle - CH_3 + LiOX \qquad (9)$$
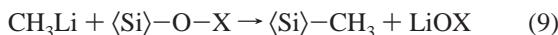
where X = Si$\leqslant$ or H. The other organometallic reagents examined, methylmagnesium bromide, dimethylzinc, and trimethylaluminum, apparently cause much less damage to the silica surface framework, as evidenced by the ^{29}Si CP-MAS spectra in Figures 3C−E; in these spectra only small intensities in the ($\geqslant$SiO)$_3$**Si**CH$_3$ region ($\sim$ −60 ppm) can be detected.

The ^{29}Si CP-MAS spectrum of trimethylaluminum-treated silica (Figure 3E) has a decreased Q$_3$ intensity, relative to that of the original silica, which might be due to aluminum incorporation into the silica surface, forming silica−alumina linkages of the type $\langle$Si$\rangle$-O−Al$\leqslant$. While the ^{29}Si chemical shifts of such moieties are in the range normally expected for the silica surface, the replacement of −OH by −O−Al$\leqslant$ would be expected to reduce the efficiency of ^{1}H−$\langle^{29}$Si$\rangle$ cross polarization. The ^{27}Al NMR spectrum (presented in Supporting Information) of the sample represented in Figure 3E is consistent with the formation of $\langle$Si$\rangle$−O−Al$\leqslant$ linkages from about 30% of the silanol groups on the silica surface. This spectrum shows intensities in the following order: 6-coordinate Al > 4-coordinate Al > 5-coordinate Al. ^{27}Al MAS spectra (presented in Supporting Information) of the three (CH$_3$)$_3$Al-treated samples represented in Figures 1E,e, 2E,e and 4E,e (after synthetic workup) show rather little ^{27}Al NMR intensity.

The ^{13}C CP-MAS spectra of the samples represented in Figure 3 also show that methyllithium is the most effective, among the organometallic reagents examined, in transforming Si−O−X linkages into Si−CH$_3$ linkages (Figure 3, right column). A substantial ^{13}C signal at about −1 and −5 ppm, due to ($\geqslant$SiO)$_2$**Si**(CH$_3$)$_2$ and ($\geqslant$SiO)$_3$**Si**CH$_3$ moieties, is clearly seen in the ^{13}C spectrum of the silica gel sample that had been reacted with methyllithium (Figure 3b). Small ^{13}C signals at about −5 ppm were found in the ^{13}C CP-MAS spectra of the CH$_3$MgBr-treated silica and (CH$_3$)$_3$Al-treated silica samples (Figures 3c and 3e), while no such signal was detected from the (CH$_3$)$_2$-Zn-treated silica sample (Figure 3d).

Additional experimental evidence was obtained from the reactions of the four CH$_3$M compounds with trimethylsilylated silica. When the trimethylsilylated silica sample represented in Figure 4A was treated with methyllithium, the (CH$_3$)$_3$**Si**-O-$\langle$Si$\rangle$ peak at 13 ppm disappeared in the ^{29}Si CP-MAS spectrum (Figure 4B) of the resulting product. This indicates again that methyllithium reacts with Si−O−Si linkages, in this case severing all (CH$_3$)$_3$**Si**−O−$\langle$Si$\rangle$ linkages at the surface. The spectrum also shows a dramatic increase in the Q$_3$/Q$_4$ intensity ratio and some small intensity in the ($\geqslant$SiO)$_3$**Si**CH$_3$ region (−50 to −65 ppm); both observations are consistent with cleavage of $\langle$Si$\rangle$−O−Si(CH$_3$)$_3$ linkages. In contrast, none of the other three CH$_3$M compounds, methylmagnesium bromide, dimethylzinc, or trimethylaluminum, causes a significant change in the trimethylsilylated silica, as attested by the spectra in Figures 4C, 4D, and 4E, which are nearly identical with the spectrum of the starting material (Figure 4A). Support for these interpreta-

tions is provided by the ^{13}C CP-MAS spectra (Figure 4, right column), obtained on the same set of samples. In Figure 4 one sees that no distinct ^{13}C signals were detected from the CH$_3$-Li-treated trimethylsilylated silica (Figure 4b), but the ^{13}C CP-MAS spectra (Figures 4c, 4d, and 4e) of CH$_3$MgBr-treated, (CH$_3$)$_2$Zn-treated, and trimethylaluminum-treated trimethylsilylated silica are very similar to that of the unreacted trimethylsilylated silica (Figure 4a).

Overall, the ^{29}Si and ^{13}C NMR results in Figures 1−4 indicate that, aside from deprotonation, reactivities of the organometallic reagents toward silica gel, SOCl$_2$-chlorinated silica, SiCl$_4$-modified silica, or trimethylsilylane-capped silica are in the following order of decreasing efficiencies: methyllithium > methylmagnesium bromide > trimethylaluminum $\geq$ dimethylzinc. Methyllithium is a very reactive nucleophile that can damage the silica framework by breaking Si−O−Si linkages. This severe damage to the silica framework calls for caution in the use of organolithium reagents in modifying silica surfaces. Experimental results (not shown here) demonstrate that both phenyllithium and *n*-butyllithium also react with silica surfaces to form R−Si and Ar−Si moieties. When one considers the utility of organometallic compounds for modifications of silica surfaces, it appears that Grignard reagents, while sufficiently reactive to attack $\langle$Si$\rangle$−Cl moieties, are apparently sufficiently mild to preserve the structural integrity of the silica framework. Dimethylzinc is the most inert reagent chosen in this study in terms of its chemical interaction with silica or surface-modified silica, transforming neither $\langle$Si$\rangle$−O−Si$\leqslant$ nor even $\langle$Si$\rangle$−Cl moieties into $\langle$Si$\rangle$−CH$_3$ groups, at least under the conditions of this study. The behavior of trimethylaluminum with silica is of special interest because of the involvement of alkylaluminum species in catalyst/cocatalyst systems for olefin polymerization.[43−45] On the basis of solid-state NMR results in this study, trimethylaluminum causes only very small damage to the silica framework.

To understand the surface coverage of methyl groups more quantitatively, we analyzed the sample represented in Figure 2C (i.e., SOCl$_2$-chlorinated silica that was treated with CH$_3$-MgBr) by ^{13}C NMR spin counting.[46] For this purpose, a ^{13}C DP-MAS experiment with a 10 s repetition delay was carried out on a mixture of the sample represented in Figure 2C (0.7426 g) and Delrin (0.0472 g). From the ratio of the peak intensities of the methyl-terminated silica sample to the intensity of the Delrin peak (after relaxation corrections based on measured T_1^C values), it was determined that the sample represented in Figure 2C has a carbon content of 1.24 mmol/g ($\pm$10% error). Elemental analysis of the same methyl-terminated silica shows a carbon content of 1.18 mmol/g, in reasonable agreement with ^{13}C spin counting. On the basis of literature reports for a wide variety of amorphous silicas, the average OH coverage on a fully hydroxylated surface is 4.9 OH/100 Å^2, a value that is apparently largely independent of the origin and detailed structural characteristics of the silica,[47,48] which corresponds to about 2.4 mmol of OH/g in a silica with a surface area of 300 m^2/g, as was used in this study. Therefore, the methyl-cap coverage based on the original surface OH content is estimated to be about 50%. This surface coverage can be increased by repeated treatment of the methyl-terminated sample with SOCl$_2$, then methylmagnesium bromide. ^{13}C spin counting performed

(43) Sinclair, K. B.; Wilson, R. B. *Chem. Ind. (London)* **1994**, 857.
(44) Kaminsky, W.; Duch, A. *Stud. Surf. Sci. Catal.* **1996**, *100*, 91.
(45) Kaminsky, W.; Winkelbath, H. *Top. Catal.* **1999**, *7*, 61.
(46) Zhang, M.; Maciel, G. E. *Anal. Chem.* **1989**, *61*, 2579.
(47) Zhuravlev, L. T. *Langmuir* **1987**, *3*, 316 and references therein.
(48) Chuang, I.-S.; Maciel, G. E. *J. Phys. Chem. B* **1997**, *101*, 3052.

on such a re-treated sample yields a carbon content of 1.80 mmol/g. Elemental analysis of the $SOCl_2/CH_3MgBr$ re-treated sample also indicates an increase in the carbon content, from 1.18 mmol/g to 1.87 mmol/g, corresponding to a methyl-cap coverage of ca. 79%.

Quantitation is generally not available from a single CP-MAS experiment, unless one knows independently the relevant spin-dynamics parameters. However, data from a series of experiments in which the CP "contact time" is varied can be analyzed to provide values of the $^1H \rightarrow X$ CP time constant (T_{H-X}), the rotating-frame ^1H spin−lattice relaxation time ($T^H_{1\rho}$), and a measure of the relevant spin population (M_i) of interest. Variable contact-time $^1H \rightarrow ^{29}Si$ CP-MAS experiments were carried out on the samples represented in Figures 2C and 4A and on the sample of Figure 2C after $SOCl_2/CH_3MgBr$ re-treatment; the results are given in Table 1. The spin population results constitute quantitative *relative* populations (ca. ±10% for the more intense peaks; ca. ±20% for less intense peaks) for all ^{29}Si peaks except that of Q_4 silicon. Many, if not most, of the Q_4 silicons are sufficiently far from the surface that they do not contribute substantially to ^{29}Si signals derived from $^1H \rightarrow ^{29}Si$ CP. In contrast to the CP case, direct-polarization (DP, no CP) MAS experiments can be carried out and interpreted quantitatively for the Q_3 and Q_4 signals of a silica system, if ^{29}Si spin−lattice relaxation is taken into account properly. However, other signals in the DP-MAS ^{29}Si spectra of the samples of this study are typically not sufficiently intense to support quantitation. Thus, the strategy imployed for quantitation of silicon content in the present study was to use DP-MAS experiments to derive absolute Q_4 and Q_3 amounts by using a known amount of tetrakis(trimethylsilyl)silane as an intensity reference, and then use CP-MAS experiments to relate ^{29}Si signals of other silicon moieties to the Q_3 signals. The spin populations derived in this manner are summarized in Table 1; they are in very good agreement with the results obtained from ^{13}C spin counting and elemental analysis. Furthermore, the high-resolution ^{29}Si NMR spectra were able to distinguish between ($\geqslant$SiO)$_3$**Si**CH$_3$ and ($\geqslant$SiO)$_2$(HO)**Si**CH$_3$ functionalities and to provide their populations individually.

Conclusions

Both ^{29}Si and ^{13}C CPMAS NMR methods give direct evidence that silicon−carbon bonds are formed by the $SOCl_2/CH_3M$ and $SiCl_4/CH_3M$ procedures for methylating a silica surface, when methyllithium or methyl Grignard are used as CH_3M. ^{29}Si NMR spectra are able to distinguish among ($\geqslant$SiO)$_3$**Si**CH$_3$, ($\geqslant$SiO)$_2$**Si**(CH$_3$)$_2$, and ($\geqslant$SiO)**Si**(CH$_3$)$_3$ moieties and to obtain quantitative information that might not be easy to obtain by other spectroscopic methods. The ^{29}Si and ^{13}C NMR results show that organolithium reagents, which represent one of the most widely used types of organometallic methylating reagents, have a strong potential risk of damage to the silica framework. Grignard reagents are more reliable for use in silica-containing materials without seriously damaging the silica framework. Both dimethylzinc and trimethylaluminum are essentially inactive toward silica gel, $SiCl_4$-treated silica, $SOCl_2$-chlorinated silica, and trimethylsilylated silica, *in terms of breaking siloxane linkages*, at least under the conditions examined in this work. Further work is underway to establish the nature of the initial interactions between CH_3M reagents and chlorinated or unchlorinated silica surfaces.

Supporting Information Available: ^{27}Al spectra of Davisil silica gel untreated and after workup with trimethylaluminum-treated silica gel, trimethlyaluminum-treated chlorinated silica, trimethylaluminum-treated trimethylsilylated silica, and tri-methylaluminum-treated $SiCl_4$-modified silica (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA991950R