Siloxyaluminum Alkyl Cations: Syntheses, Structures, and Reactions Related to Activation of Zirconocene Catalysts on Silica Gel Surfaces

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Binuclear siloxyaluminum methyl complexes of the type $Me_2Al(\mu\text{-}OSiR_3)_2AlMe_2$ react with protonated *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate, with release of CH_4, to form the dimethylaniline (DMA)-stabilized siloxyaluminum methyl cations $Me_2Al(\mu\text{-}OSiR_3)_2AlMe(NMe_2(C_6H_5))^+$. These cations abstract a Cl^- ligand from $(C_5H_5)_2ZrCl_2$, to give the dinuclear cation $\{(C_5H_5)_2ZrCl\}_2(\mu\text{-}Cl)^+$, and a CH_3^- ligand from $(C_5H_5)_2Zr(CH_3)_2$, to give by way of the DMA-stabilized cation $(C_5H_5)_2Zr(CH_3)NMe_2(C_6H_5)^+$ the CH-activation product $(C_5H_5)_2ZrCH_2NMe(C_6H_5)^+$; reaction with $Me_2Si(ind)_2ZrMe_2$ in toluene solution yields a moderately active catalyst for ethene polymerization. This reactivity of siloxyaluminum methyl cations is qualitatively similar to, although substantially lower than, that of a silica gel surface treated with trimethylaluminum and a cationizing agent.

Introduction

For practical applications, metallocene-based olefin-polymerization catalysts are in general adsorbed on a solid support, most frequently on a suitably modified silica gel.[1] Like their homogeneously dissolved analogues, these supported metallocene catalysts are generally activated by use of methylalumoxane. Several reports have dealt, however, also with their activation by boron-based cocatalysts.[2] In these cases, the silica gel support is usually treated first with an aluminum trialkyl compound and then with *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate (DMAB) and the metallocene dialkyl or dichloride complex.

The mechanisms by which the zirconocene complexes are activated for polymerization catalysis on silica gel support materials have remained largely unexplored. To identify intermediates and reaction steps which lead to the formation of the active catalyst species, we have sought to synthesize soluble, fully characterizable models for the alkylaluminum-treated silica surface. Silanol groups, the most reactive species on silica gel surfaces, are likely to react with an aluminum trialkyl reagent under release of alkane and formation of surface-bound

Si−O−Al units.[3] Simple silanols, R_3SiOH, react with the trialkylaluminum compounds AlR'_3 to form siloxyaluminum alkyl compounds (siloxalanes) of the type $[R_3\text{-}SiOAlR'_2]_2$, which have been shown to be dimeric in the solid state.[4]

To approach the question whether related surface-bound species might participate in the activation of supported metallocene catalysts, we have reacted the easily accessible siloxyaluminum alkyl compounds **1a−c** with cationizing reagents and assessed the reactivity of the resulting cations vis-à-vis zirconocene chloride and methyl complexes.

(1a)   (1b)   (1c)
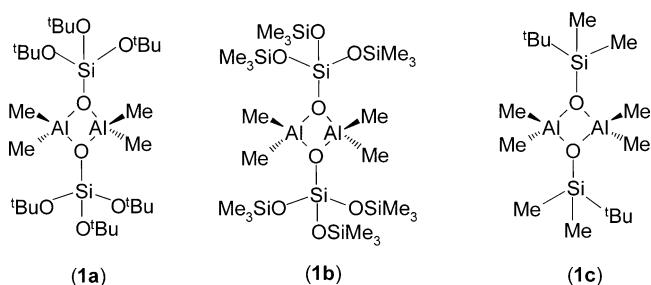
Results and Discussion

Synthesis and Cationization of Siloxyaluminum Alkyl Compounds 1a−c. As previously described for compound **1a** [4a] and for related representatives,[4b−g] the siloxalanes **1a−c** were prepared, in yields of 47−94%, by reaction of the appropriate silanol precursors with 1 equiv of trimethylaluminum in toluene solution at room

(1) (a) Soga, K.; Park, J. R.; Shiono, T. *Polym. Commun.* **1991**, *10*, 310. (b) Kaminaka, M.; Soga, K. *Makromol. Chem. Rapid Commun.* **1991,** *12*, 367. (c) Herrmann, H. F.; Bachmann, B.; Hierholzer, B.; Spaleck, W. Eur. Pat. Appl. 563917 A1, 1993. (d) Hungenberg, K. D.; Kerth, J.; Langhauser, F.; Marczinke, B.; Schlund, R. In *Ziegler Catalysts*; Mülhaupt, G., Fink, G., Brintzinger, H.-H., Eds.; Springer-Verlag: Berlin, 1995; Chapter 20. (e) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.
(2) (a) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci. A: Polym. Chem.* **1995**, *33*, 2093, (b) Hlatky, G. G.; Upton, D. J. *Macromolecules* **1996**, *29*, 8019, (c) Kristen, M. O. *Top. Catal.* **1999**, *7*, 89.

(3) (a) Nesterov, G. A.; Zakharov, V. A.; Fink, G.; Fenzl, W. *J. Mol. Catal.* **1991**, *69*, 129. (b) Bartram, M. E.; Michalske, T. A.; Rogers, J. W. *J. Phys. Chem.* **1991**, *95*, 4453. (c) Van Looveren, L. K.; Geysen, D. F.; Vercruysse, K. A.; Wouters, B. H.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 517. (d) Anwander, R.; Palm, C.; Groeger, O.; Engelhardt, G. *Organometallics* **1998**, *17*, 2027. (e) Uusitalo, A.-M.; Pakkanen, T. T.; Kröger-Laukkanen, M.; Niinistö, L.; Hakala, K.; Paavola, S.; Löfgren, B. *J. Mol. Catal. A: Chem.* **2000**, *160*, 343.

temperature. The products were obtained in the form of colorless powders or crystals, after removal of solvent (**1a**), crystallization (**1b**), or sublimation (**1c**), and characterized by their ^1H, ^{13}C, and ^{27}Al NMR spectra as well as by electron impact mass spectroscopy and elemental analysis (see the Experimental Section). They are thermally stable at room temperature and can be kept under a dry dinitrogen atmosphere for several months without noticeable decomposition.

Reactions of compounds **1a**−**c** with 1 equiv of the proton donor $[Me_2NHPh]^+[B(C_6F_5)_4]^-$ in toluene solutions led to the appearance of the ^1H NMR signal of methane in all three cases. Depending on the substituents at the Si centers, different products were obtained, however. With the *tert*-butoxy-substituted siloxalane **1a**, methane evolution was observed immediately at room temperature. After 1 h, all Al−Me ^1H NMR signals had completely disappeared, even though only 1 equiv of the anilinium salt had been used. Concomitantly, changes were observed in the ^1H NMR regions at 0.9 and 1.6 ppm, typical for Si-bound alkyl groups, and a new, unassigned signal appeared at 4.7 ppm. While we were unable to isolate any products from the reaction mixture, we conclude from these observations that a cationic product, initially formed with release of methane, might have undergone an exchange of methyl and *tert*-butoxy substituents between Si and Al centers. Transfer of an O*t*Bu group from Si to Al might form a silylium cation; subsequent transfer of Me from Al to Si would be consistent with the observed spectral changes.

The siloxalanes **1b**,**c**, on the other hand, required elevated temperatures of ca. 75 °C to react with DMAB. In both cases, evolution of methane and formation of a new aluminum methyl species with three distinct Al−Me signals were observed (Scheme 1). For the siloxy-substituted siloxalane **1b**, the reaction is complete after ca. 20 h, while complete conversion of the alkyl-substituted siloxalane **1c** takes ca. 75 h. The reaction products are isolated in yields of 28% (**2b**) and 88% (**2c**) as colorless solids. The low yield of **2b** is due to slow decomposition of the neutral siloxalane precursor **1b** at the reaction temperature. Both compounds were characterized as binuclear aluminum alkyl species with one neutral and one cationic aluminum center by their NMR spectra, by elemental analysis (see Experimental Section), and by a crystal structure determination.

Crystal Structures of Cationic Siloxyaluminum Alkyl Complexes 2b,c. Crystal structures of aniline-stabilized cationic aluminum alkyl complexes or of cationic siloxalanes have not been reported so far.[5] The structures of complexes **2b**,**c** (Table 1 and Figure 1)

(4) (a) Terry, K. W., Ganzel, P. K., Tilley, T. D. *Chem. Mater.* **1992**, *4*, 1290. (b) Schmidbaur, H. *J. Organomet. Chem.* **1963**, *1*, 28. (c) Mühlhaupt, R.; Calabrese, J.; Ittel, S. D. *Organometallics* **1991**, *10*, 0, 3403. (d) Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137. (e) Rennekamp, C.; Wessel, H.; Roesky, H. W.; Müller, P.; Schmidt, H.-G.; Noltemeyer, M.; Uson, I.; Barron, A. R. *Inorg. Chem.* **1999**, *38*, 5235. (f) McMahon, C. N.; Bott, S. G.; Alemany, L. B.; Roesky, H. W.; Barron, A. R. *Organometallics* **1999**, *18*, 5395. (g) Similar products have been obtained from a reaction of trimethylaluminum with a silsesquioxane containing a monosilanol functionality: Skowronska-Ptasinska, M. D.; Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2001**, *20*, 3519.

(5) Crystal structures of cationic aluminum alkyl complexes with boron-based counteranions: (a) Cosledan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705. (b) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (c) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

Scheme 1
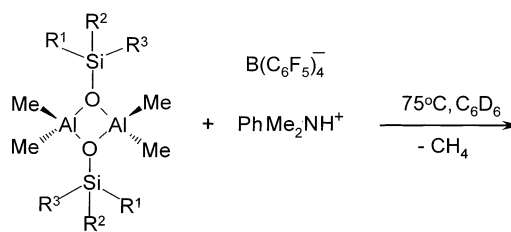
1b, 1c
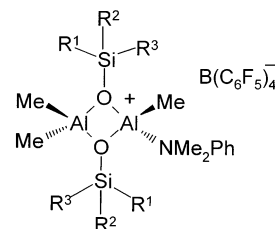
2b, **2c**

b) R[1], R[2], R[3] = $OSiMe_3$
c) R[1], R[2] = Me, R[3] = *t*Bu

Table 1. Selected Bond Distances (pm) and Angles (deg) for Complexes 2b,c

	2b	**2c**
Al1−N1	199.4(5)	201.5(3)
Al1−C1	194.0(6)	193.9(4)
Al2−C2	196.9(7)	195.3(4)
Al2−C3	195.3(7)	196.5(4)
Al1−O1	181.6(4)	180.1(3)
Al1−O2	183.0(4)	183.0(3)
O1−Al2	192.9(4)	
Al2−O1		191.4(3)
Al2−O2	191.9(4)	191.4(3)
Si1−O1	168.1(4)	
O1−Si1		172.5(3)
O2−Si5	167.9(4)	
O2−Si2		171.4(3)
Al1−Al2	277.7(4)	275.3(2)
O1−Al1−O2	86.0(2)	87.7(1)
O2−Al2−O1	80.5(2)	
O1−Al2−O2		82.1(1)
C1−Al1−N1	114.7(2)	112.7(2)
C3−Al2−C2	126.5(3)	
C2−Al2−C3		120.7(2)

show that the planarity of the Al−O−Al−O ring, previously found in neutral siloxalanes,[4] is not disturbed by conversion of a neutral to a cationic Al center in these complexes. Bond distances and angles of one of the Al centers are affected by this cationization in the following manner (Table 1).

In the cations **2b**,**c**, Al−C bond lengths for the cationic Al centers (193 and 194 pm) are close to those for the neutral Al centers (195−197 pm).[6] Similarly, Si−O(Al) bond distances in the cationic siloxalanes **2b**,**c** (168−172 pm) are close to those in neutral siloxalanes (167−168 pm).[4b,c] Al−O bond distances and O−Al−O angles adjacent to neutral and cationic Al centers, however, differ significantly from each other: Al−O bond distances to cationic Al atoms are 8−11 pm shorter and O−Al−O bond angles are 5−6° larger than those at neutral Al centers. Al−N bond lengths in the cationic

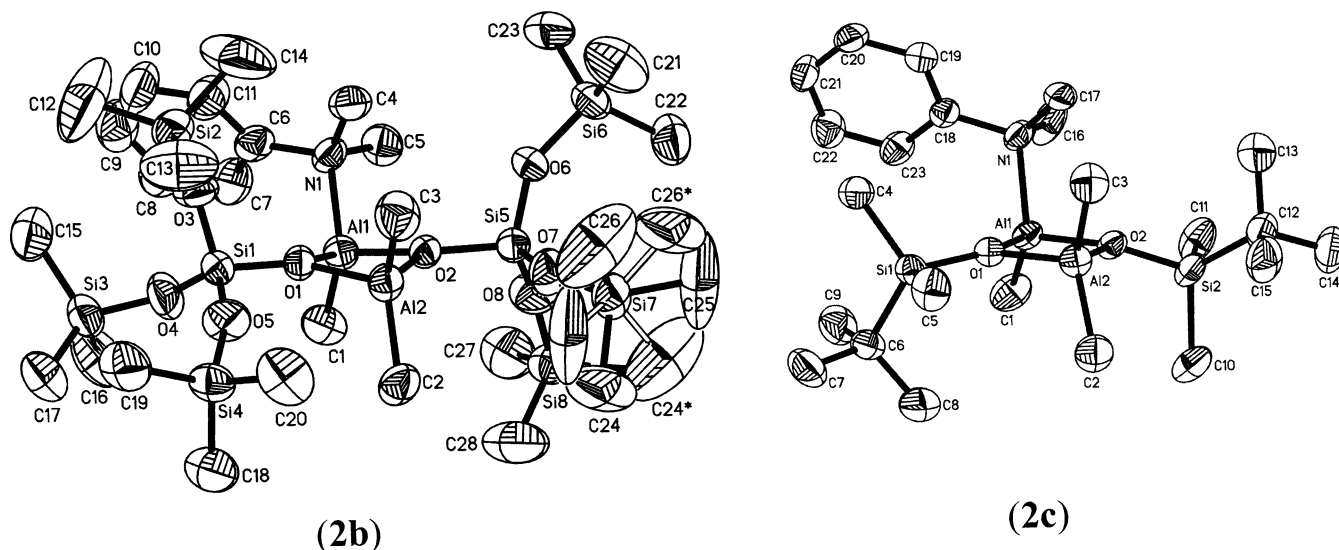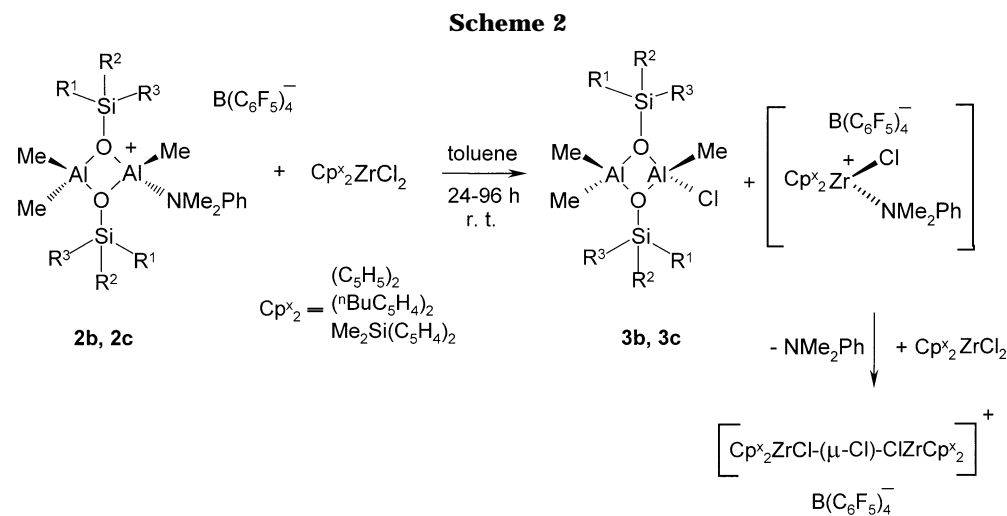(6) These bond lengths are comparable to values found in neutral siloxalanes (193−196 pm).[4]

(2b)   **(2c)**

Figure 1. Structure of complexes **2b,c** (B(C$_6$F$_5$)$_4^-$ anions omitted for clarity).

Scheme 2

complexes **2b,c** are shorter by 5−20 pm than those found for the coordination of a trialkylamine to neutral siloxalane complexes (206−225 pm).[7]

Reactions of the Siloxalane Cations 2b,c with Zirconocene Complexes. To explore possible reaction pathways toward catalytically active zirconocene alkyl cations, we have studied reactions of the aluminum alkyl cations **2b,c** with different zirconocene species, in particular with the dichloride and dimethyl derivatives of (C$_5$H$_5$)$_2$Zr, Me$_2$Si(C$_5$H$_4$)$_2$Zr, (MeC$_5$H$_4$)$_2$Zr, and (^{n}BuC$_5$H$_4$)$_2$Zr as model complexes.

In reactions of the aluminum alkyl cations **2b,c** with dicyclopentadienylzirconium dichloride derivatives, each binuclear Al cation was found to consume 2 equiv of the respective zirconocene complex. A neutral siloxalane species with three methyl groups and one chloride substituent is formed in these reactions. The isolated siloxalane complexes are characterized by ^{1}H, ^{13}C, and ^{27}Al NMR, by mass spectrometry, and by elemental analysis as **3b,c**. The stoichiometry of this reaction
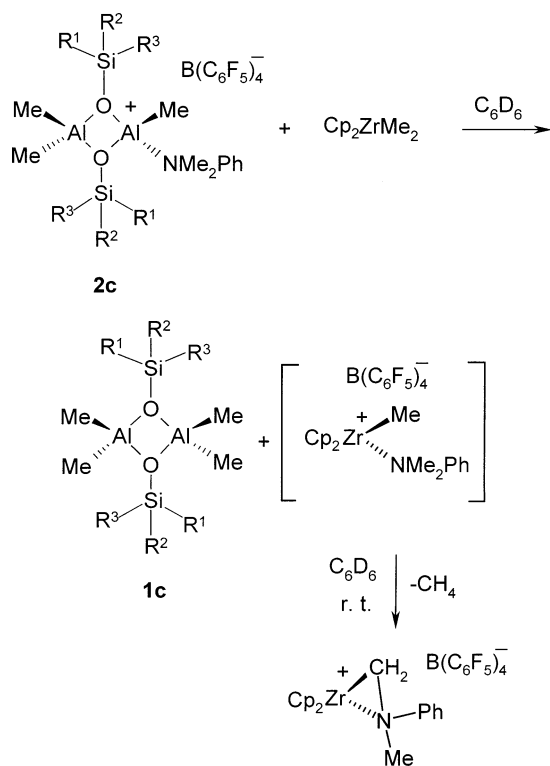
indicates that binuclear zirconocene chloride cations[8] arise from this reaction, as indicated in Scheme 2. Use of more than 1 equiv of the siloxalane cations, **2b,c**, per 2 equiv of the respective zirconocene dichloride complex does not result in further halide abstraction from the binuclear zirconocene cations. This is indicated by the presence of equal amounts of the neutral siloxalane product **3c** and of the cation **2c** after reaction of **2c** with 1 equiv of (C$_5$H$_5$)$_2$ZrCl$_2$ or Me$_2$Si(C$_5$H$_4$)$_2$ZrCl$_2$.

When the aluminum alkyl cations **2b,c** are reacted with a zirconocene dimethyl complex, abstraction of a CH$_3$ ligand from the zirconium center takes place with formation of the neutral tetramethylsiloxalane species **1b,c** (Scheme 3).[9] ^{1}H NMR signals of the expected DMA-stabilized zirconocene methyl cation cannot be detected in these reaction mixtures, however. Instead, we observe signals assignable to the respective C−H activation product.[10] Similar C−H activation products were observed by Jordan and co-workers when THF-stabilized

(7) (a) Hecht, E.; Gelbrich, T.; Thiele, K.-H.; Sieler, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 180. (b) Robson, D. A.; Rees, L. H.; Mountford, P.; Schroder, M. *Chem. Commun.* **2000**, 1269. (c) Thiele, K.-H.; Hecht, E.; Gelbrich, T.; Dumichen, U. *J. Organomet. Chem.* **1997**, *540*, 89. (d) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398.

(8) Such binuclear complexes have been studied before by means of low-temperature NMR spectroscopy ((a) Haselwander, T. Diplomarbeit, Universität Konstanz, 1993. (b) Haselwander, T.; Beck, S.; Brintzinger, H.-H. In *Ziegler Catalysts*; Mülhaupt, G., Fink, G., Brintzinger, H.-H., Eds.; Springer-Verlag: Berlin, 1995; p 181.) but have not been characterized by crystallography so far. Attempts to crystallize several of the chloride-bridged cationic species yielded the neutral zirconocene dichloride complexes in all cases.

Scheme 3

2c

1c

zirconocene methyl cations were treated with 2,6-lutidine.[11] This supports the notion that dimethyl-aniline-stabilized methyl cations are formed in a first reaction step.

When a toluene solution of $Me_2Si(ind)_2ZrMe_2$, saturated with 2 bar of ethene, is treated with the siloxalane cation **2c**, polyethene is indeed formed with moderate activity (see Experimental Section). An analogous reaction of a zirconocene dimethyl complex with a siloxalane cation formed on a silica surface by treatment with an aluminum alkyl compound and a cationizing reagent might thus similarly generate catalytically active zirconocene species.

Comparison between Model and Silica-Surface Reactions. To compare the reactivity of homogeneously dissolved aluminum alkyl siloxalanes with that of alkyl-aluminum treated silica surfaces, we have studied their respective reactions with zirconocene dichloride complexes and with the cation-generating activator DMAB.

Reactions of a trimethylaluminum-treated silica gel (see the Experimental Section) with a benzene solution

of a zirconocene dichloride complex such as ($^nBuC_5H_4)_2$-$ZrCl_2$ or $Me_2Si(C_5H_4)_2ZrCl_2$ led, within 24 h at 75 °C, to a methyl−chloride exchange similar to that observed before with Al_2Me_6 in C_6D_6 solution.[12] When 5 μmol of ($^nBuC_5H_4)_2ZrCl_2$ was reacted with 4.2 mg of the TMA-treated silica gel in 500 μL of C_6D_6, ($^nBuC_5H_4)_2Zr(Me)$-Cl was formed in the ratio $Zr(Me)Cl:ZrCl_2 = 1:12$; when 21 mg of the silica gel was used, the ratio $Zr(Me)Cl:ZrCl_2 = 1:5.5$ was observed. Reactions under the same conditions with $Me_2Si(C_5H_4)_2ZrCl_2$ result in the ratios $Zr(Me)Cl:ZrCl_2 = 1:6.2$ (4.2 mg of silica gel) and 1:3.1 (21 mg of silica gel), respectively. These reactions of zirconocene dichlorides with the trimethylaluminum-treated silica gel are comparable to the reactions with trimethylaluminum solutions, which likewise lead to partial formation of the zirconocene methyl chlorides. As was found for Al_2Me_6 in homogeneous solutions, the silica gel supported trimethylaluminum induces a higher degree of methylation with a Me_2Si-bridged complex than with an unbridged, alkyl-substituted zirconocene reaction system.[12] Analogous reactions are not observed, however, when the neutral tetramethylsiloxalanes **1b,c** are treated in C_6D_6 with one of the zirconocene dichlorides in ratios from 1:5 to 5:1. Apparently, the tendency of the alkylaluminum species to exchange one of its CH_3 groups with a chloride ligand of a zirconocene dichloride is strongly reduced when both μ-CH_3 groups of $Al_2(CH_3)_6$ are replaced by O−SiR_3 in **1b,c**.

Another comparison between model and silica-surface reactions concerns their respective reactivities toward the cationization reagent DMAB. These reactions were followed by monitoring the evolution of methane. Methane evolution was observed instantaneously by the ^1H NMR signal at 0.15 ppm when the TMA-treated silica gel was reacted with DMAB in a benzene suspension at room temperature. Siloxalanes **2b,c**, on the other hand, needed several hours at 75 °C before methane could be detected in the reaction mixture.

With regard to the generation of catalytically active methyl−zirconocene cations, the siloxalane cations **2b,c** do not reach the reactivity of a TMA-treated, cationized silica gel surface. While the latter produces active catalyst species from $Cp^x_2ZrCl_2$,[2c] the siloxalane cations **2b,c** require $Cp^x_2ZrMe_2$ as a precursor for the generation of alkyl zirconocene cations.

The lower reactivity of the siloxalanes as compared to the TMA-treated silica gel surfaces is likely to be due to the presence of two bridging oxygen ligands between the Al centers of the binuclear siloxalane species. One might thus speculate that isolated SiOH functionalities on the silica gel surface might lead to Al complexes with only one oxygen ligand and, hence, higher reactivities. Efforts to model more reactive species of this type are underway in our laboratory.

Experimental Section

All reactions were performed under argon with Schlenk-line techniques or under nitrogen in a glovebox. Solvents were dried prior to use by reflux over and distillation from sodium or calcium hydride. Deuterated solvents were dried over 4 Å molecular sieves and used without further purification. Zirconocene dichloride, dimethyl and methyl chloride complexes

(9) Reaction of a zirconocene methyl chloride complex with **2c** in ratios of 1:5 to 5:1 leads to the abstraction of either a chloride or a methyl ligand from the zirconocene complex. Both reaction modes are indicated by the observation of the siloxalane products **1c** and **3c**. In reaction mixtures containing **2c** and excess of $(C_5H_5)_2Zr(Me)Cl$ or $(MeC_5H_4)_2Zr(Me)Cl$, the signal intensity for the chlorotrimethylsiloxalane **3c** goes through a maximum after ca. 3 h and then declines to zero, while that of the tetramethylsiloxalane **1c** increases steadily until the reaction is complete. The initially formed chlorotrimethylsiloxalane **3c** thus appears to undergo a chloro−methyl exchange with zirconocene methyl species present. Zirconocene dimethyl complexes such as $(C_5H_5)_2ZrMe_2$ and $(MeC_5H_4)_2ZrMe_2$ do indeed react with the neutral chlorotrimethylsiloxalane **3c** in C_6D_6 in a clean and complete 1:1 reaction within 10 days to form the respective zirconocene methyl chloride complexes and the tetramethylsiloxalane **1c**.

(10) This species was first observed by Horton (private communication).

(11) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833.

(12) Beck, S.; Brintzinger, H.-H. *Inorg. Chim. Acta* **1998**, *270*(1,2), 376.

were synthesized according to literature reports.[13,14] Other chemicals were purchased from commercial suppliers and used without further purification. Samples of [Me$_2$NHPh]$^+$-[B(C$_6$F$_5$)$_4$]$^-$, (^{n}BuC$_5$H$_4$)$_2$ZrCl$_2$, and alkylaluminum-treated silicas[15] were obtained as gifts from Targor GmbH.

[(^{t}BuO)$_3$SiOAlMe$_2$]$_2$ (1a). To a solution of 1.96 g (7.4 mmol) of (^{t}BuO)$_3$SiOH in 30 mL of toluene at −6 °C was added dropwise a solution of 0.54 g (7.5 mmol) of AlMe$_3$ in 20 mL of toluene with stirring over a period of 1 h. After the evolution of methane had ceased, the solution was stirred for 1 h at −6 °C before it was warmed to room temperature. After the mixture was stirred for another 12 h and the solvent removed in vacuo, 2.24 g (3.5 mmol, yield 94%) of **1a** was obtained as a colorless powder. ^{1}H NMR (250 MHz, C$_6$D$_6$, 7.15 ppm, 300 K, cf. ref 4a): δ 1.40 (s, 54H, ^{t}Bu), −0.12 (s, 12H, Al−Me$_2$). EI-MS: *m/z m/z* 625 (M$^+$ − Me), 569 (M$^+$ − Me, ^{t}Bu), 553 (M$^+$ − 2Me, ^{t}Bu), 513 (M$^+$ − Me, 2 ^{t}Bu), 457 (M$^+$ − Me, 3 ^{t}Bu), 401 (M$^+$ − Me, 4 ^{t}Bu), 385 (M$^+$ − 2 Me, 4 ^{t}Bu), 369 (M$^+$ − 3 Me, 4 ^{t}Bu), 345, 329, 313, 289, 255, 237, 193, 135, 57.

[(Me$_3$SiO)$_3$SiOAlMe$_2$]$_2$ (1b). The synthesis was performed in the same way as that of **1a** with 3.36 g (10.7 mmol) of (Me$_3$-SiO)$_3$SiOH and 0.80 g (11.1 mmol) of AlMe$_3$ in 100 mL of toluene. After removal of the solvent in vacuo and crystallization from a pentane solution at −60 °C, 2.30 g (3.12 mmol, 58% yield) of **1b** was isolated in form of colorless cubic crystals. ^{1}H NMR (250 MHz, C$_6$D$_6$, 7.15 ppm, 300 K): δ 0.22 (s, 54H, Si−Me), −0.25 (s, 12H, Al−Me$_2$). ^{13}C NMR (250 MHz, C$_6$D$_6$, 128 ppm, 300 K): δ 1.8 (Si−Me), −8.3 (Al-Me$_2$). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): δ 158.2, $w_{1/2}$ = ca. 5400 Hz. EI-MS: *m/z* 721 (M$^+$ − Me), 353 (M/2$^+$ − Me), 281 (M/2$^+$ − Me, Me$_3$Si), 191, 147, 73. Anal. Calcd for C$_{22}$H$_{66}$Al$_2$O$_8$Si$_8$: C, 35.83; H, 9.02. Found: C, 35.77; H, 9.43.

[^{t}BuMe$_2$SiOAlMe$_2$]$_2$ (1c). The synthesis was performed in the same way as that of **1a** with 10.0 g (75.7 mmol) of ^{t}BuMe$_2$-SiOH and 5.50 g (76.3 mmol) of AlMe$_3$ in 200 mL of toluene. The solvent was removed in vacuo, and the glassy residue was purified by two successive sublimations in vacuo at 60 °C to afford 6.71 g (17.8 mmol, 47% yield) of pure **1c** in form of a white powder. ^{1}H NMR (250 MHz, C$_6$D$_6$, 7.15 ppm, 300 K): δ 0.88 (s, 18H, ^{t}Bu), 0.14 (s, 12H, Si−Me$_2$), −0.34 (s, 12H, Al−Me$_2$). ^{13}C NMR (250 MHz, C$_6$D$_6$, 128 ppm, 300 K): δ 25.8 (C(CH$_3$)$_3$), 18.4 (C(CH$_3$)$_3$), −2.6 (Si−Me$_2$), −6.3 (Al−Me$_2$). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): δ 156.4; $w_{1/2}$ = ca. 1800 Hz. EI-MS: *m/z* 361 (M$^+$ − Me), 319 (M$^+$ − ^{t}Bu), 247 (M$^+$ − Me, 2 ^{t}Bu), 205 (M$^+$ − AlMe$_2$, ^{t}BuMe$_2$Si), 189 (M/2$^+$), 173 (M/2$^+$ − Me), 131, 73. Anal. Calcd for C$_{16}$H$_{42}$Al$_2$O$_2$Si$_2$: C, 51.02; H, 11.24. Found: C, 51.0; H, 11.13.

[((Me$_3$SiO)$_3$SiO)$_2$Al$_2$Me$_3$NMe$_2$Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (2b). A 1.94 g portion (2.63 mmol) of **1b** and 1.18 g (1.47 mmol, 0.56 equiv) of [Me$_2$NHPh]$^+$[B(C$_6$F$_5$)$_4$]$^-$ were dissolved in 70 mL of toluene and heated to 65 °C for 20 h. Toluene was removed in vacuo, and the remaining dark blue oil was washed twice with pentane and then purified by redissolving in chlorobenzene and precipitating a byproduct by addition of a small amount of pentane. The supernatant liquid was evaporated to dryness. The resulting colorless foam was washed once with pentane and dried in vacuo to afford 0.64 g (0.42 mmol, 28% yield) of **2b** in the form of a colorless powder. Crystals suitable for an

X-ray structure determination were isolated from a concentrated solution of **2b** in chlorobenzene into which pentane was slowly allowed to diffuse at room temperature. ^{1}H NMR (250 MHz, CDCl$_3$, 7.24 ppm, 300 K): δ 7.5−7.4 (m, Ph) 7.4−7.3 (m, Ph), 3.14 (s, 6H, N−Me$_2$), 0.18 (s, 54H, ^{t}Bu), −0.47 (s, 3H, Al−Me), −0.61 (s, 3H, Al−Me), −0.97 (s, 3H, Al−Me). ^{13}C NMR (250 MHz, CDCl$_3$, 77.0 ppm, 300 K): δ 146.2 (B(C$_6$F$_5$)$_4$), 138.2 (B(C$_6$F$_5$)$_4$), 134.3 (B(C$_6$F$_5$)$_4$), 130.8 (arom), 129.6 (arom), 120.6 (arom), 46.6 (N−Me), 1.8 (Si−Me), −7.0 (Al−Me), −9.7 (Al−Me), −13.8 (Al−Me). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): no resolved signals detectable. Anal. Calcd for C$_{53}$H$_{74}$Al$_2$BF$_{20}$NO$_8$-Si$_8$: C, 41.81; H, 4.90; N, 0.92. Found: C, 40.47; H, 4.94; N, 0.82.

[(^{t}BuMe$_2$SiO)$_2$Al$_2$Me$_3$NMe$_2$Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (2c). A 4.00 g portion (10.6 mmol) of **1c** and 4.25 g (5.30 mmol, 0.5 equiv) of [Me$_2$NHPh]$^+$[B(C$_6$F$_5$)$_4$]$^-$ were dissolved in 400 mL of toluene and heated to 65 °C for 90 h. Toluene was removed in vacuo from the resulting biphasic system, and the remaining dark green residue was washed several times with pentane under treatment with ultrasound to remove excess **1c**. A 5.43 g portion (4.67 mmol, 88% yield) of **2c** was obtained as a colorless powder. Crystals suitable for X-ray structure determination were isolated from a solution of **2c** in chlorobenzene into which pentane was slowly transferred by diffusion at room temperature. ^{1}H NMR (250 MHz, CDCl$_3$, 7.24 ppm, 300 K): δ 7.6−7.5 (m, Ph) 7.4−7.3 (m, Ph), 3.16 (s, 6H, N−Me$_2$), 0.94 (s, 18H, ^{t}Bu), 0.19 (s, 6H, Si−Me), −0.08 (s, 6H, Si−Me), −0.11 (s, 3H, Al−Me), −0.42 (s, 3H, Al−Me), −0.48 (s, 3H, Al−Me). ^{13}C NMR (250 MHz, CDCl$_3$, 77.0 ppm, 300 K): δ 146.2 (B(C$_6$F$_5$)$_4$), 138.2 (B(C$_6$F$_5$)$_4$), 134.3 (B(C$_6$F$_5$)$_4$), 131.3 (arom), 130.1 (arom), 120.9 (arom), 47.9 (N−Me), 25.8 (Si−C(CH$_3$)$_3$), 18.8 (Si−C(CH$_3$)$_3$), −1.8 (Si−Me), −2.2 (Si−Me), −2.8 (Al−Me), −4.3 (Al−Me), −5.1 (Al−Me). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): δ 165.2, $w_{1/2}$ = ca. 7900 Hz; 117.6, $w_{1/2}$ = ca. 3600 Hz. Anal. Calcd for C$_{47}$H$_{50}$Al$_2$BF$_{20}$NO$_2$Si$_2$: C, 48.55; H, 4.34; N, 1.21. Found: C, 49.55; H, 4.69; N, 0.98.

Reaction of 2b with Cp$_2$ZrCl$_2$. A 0.44 g portion (0.29 mmol) of **2b** and 0.25 g (0.86 mmol) of Cp$_2$ZrCl$_2$ were dissolved in 80 mL of toluene in a glovebox, and the solution was stirred at room temperature for 4 days. A light green crystalline residue of the cationic zirconocene complex precipitated from the reaction mixture, and was separated from the liquid phase by centrifugation. After removal of solvent, the resulting residue was extracted with two 30 mL portions of pentane, evaporation of which yielded 0.19 g (0.25 mmol, 87% yield) of a colorless powder of [(Me$_3$SiO)$_3$SiO]$_2$Al$_2$Me$_3$Cl (**3b**). ^{1}H NMR (250 MHz, C$_6$D$_6$, 7.15 ppm, 300 K): δ 0.23 (s, 54H, Si−Me), −0.10 (s, 3H, Al−Me), −0.20 (s, 3H, Al−Me), −0.27 (s, 3H, Al−Me). ^{13}C NMR (250 MHz, C$_6$D$_6$, 128.0 ppm, 300 K): δ 25.7 (Si−Me), −8.6 (Al−Me). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): δ 123.2, $w_{1/2}$ = ca. 2900 Hz (Al−(Me)Cl) and, overlapping with it, one broad signal at ca. 160 ppm, $w_{1/2}$ = ca. 17 000 Hz (Al−Me$_2$). EI-MS: *m/z* 741 (M$^+$ − Me), 297, 281, 73. Anal. Calcd for C$_{21}$H$_{63}$Al$_2$ClO$_8$Si$_8$: C, 33.28; H, 8.38. Found: C, 33.51; H, 7.75.

Reaction of 2c with Cp$_2$ZrCl$_2$. A 0.80 g portion (0.68 mmol) of **2c** and 0.51 g (1.73 mmol) of Cp$_2$ZrCl$_2$ were dissolved in 150 mL of toluene in a glovebox and stirred at room temperature for 24 h. A light green crystalline residue of the binuclear cationic zirconocene complex precipitated from the reaction mixture and was separated from the liquid phase by centrifugation. After removal of the solvent, the resulting colorless residue was extracted twice with 100 mL of pentane. Evaporation of pentane resulted in a light yellow powder of **2c**. The crude product thus obtained was purified by sublimation at 100 °C over 3 h in vacuo to afford 0.19 g (0.48 mmol, 70% yield) of pure (^{t}BuMe$_2$SiO)$_2$Al$_2$Me$_3$Cl (**3c**) in the form of a colorless powder. ^{1}H NMR (250 MHz, C$_6$D$_6$, 7.15 ppm, 300 K): δ 0.89 (s, 18H, ^{t}Bu), 0.21 (s, 6H, Si−Me), 0.15 (s, 6H, Si−Me), −0.23 (s, 3H, Al−Me), −0.31 (s, 3H, Al−Me), −0.39 (s, 3H, Al−Me). ^{13}C NMR (250 MHz, C$_6$D$_6$, 128.0 ppm, 300 K): δ 25.7

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(15) Alkylaluminum-treated silica gels were synthesized at Targor GmbH by slowly adding a 2 M trimethylaluminum solution to a suspension of silica gel in toluene, so that the temperature does not rise above 25 °C. The silica gel is collected by filtration under an atmosphere of dry nitrogen and washed several times with toluene to completely remove any residual trimethylaluminum.

(Si−C(CH_3)$_3$), 18.4 (Si−C(CH$_3$)$_3$), −2.7 (Al−Me), −2.8 (Al−Me), −6.7 (Al−Me). ^{27}Al NMR (400 MHz, C$_6$H$_5$F, 358 K): δ 122.7, $w_{1/2}$ = ca. 2600 Hz (Al−(Me)Cl); 158.6, $w_{1/2}$ = ca. 1200 Hz (Al−Me$_2$). EI-MS: m/z 381 (M$^+$ − Me), 339 (M$^+$ − ^{t}Bu), 205 (M$^+$ − ^{t}BuMe$_2$Si, AlMeCl), 189 (M$^+$ − Me$_2$^{t}BuSiO, AlMeCl), 131, 75. Anal. Calcd for C$_{15}$H$_{39}$Al$_2$ClO$_2$Si$_2$: C, 45.37; H, 9.90. Found: C, 43.84; H, 9.27.

Reactivity Studies on the NMR Scale. All reactivity studies were performed in C$_6$D$_6$, since all compounds were stable in that solvent. The reactions were followed by ^{1}H NMR spectroscopy at room temperature. The NMR tubes were dried prior to use at 200 °C in vacuo for 48 h. Stock solutions of the individual compounds were prepared in a glovebox and mixed at room temperature at various ratios of the reactants. The NMR tubes were sealed and kept at −80 °C until the first measurement. When higher temperatures were necessary to perform a reaction, the NMR tubes were heated in an oil bath and cooled to room temperature before measuring the spectra.

Reactions of excess **2c** with zirconocene dichloride complexes at 300 K gave rise, besides signals of **3c** described above, to the following ^{1}H NMR signals: [{(C$_5$H$_5$)$_2$ZrCl}$_2$-μ-Cl]$^+$B-(C$_6$F$_5$)$_4$$^−$, 5.89 (s, 20 Cp H); [{Me$_2$Si(C$_5$H$_4$)$_2$ZrCl}$_2$-μ-Cl]$^+$B-(C$_6$F$_5$)$_4$$^−$, 5.71 (m, 8H, Cp H), 5.36 (m, 8H, Cp H), 0.16 (s, 12H, Me−Si); [{(^{n}BuC$_5$H$_4$)$_2$ZrCl}$_2$-μ-Cl]$^+$B(C$_6$F$_5$)$_4$$^−$, 5.98 (broad, 8H, Cp H), 5.90 (broad, 8H, Cp H), 2.33 (broad, 8H, CH_2CH$_2$CH$_2$-CH$_3$), ca. 1.27 (broad, 8H, CH$_2$$CH_2CH_2CH_3$), 1.20 (m, 8H, CH$_2$-CH$_2$$CH_2CH_3$), 0.85 (t, 12H, CH$_2CH_2CH_2$$CH_3$). Reactions with the zirconocene dimethyl complex (C$_5$H$_5$)$_2$ZrMe$_2$ at 300 K gave rise, besides the signals of **1c** described above, to the following ^{1}H NMR signals: (C$_5$H$_5$)$_2$ZrCH$_2$NMe(C$_6$H$_5$)$^+$B-(C$_6$F$_5$)$_4$$^−$,[10] 7.0−6.6 (m, 5H, C$_6$$H_5$), 5.41 (s, 5H, Cp H), 5.13 (s, 5H, Cp H), 2.79 (d, 1H, N−CH^1−Zr), 2.29 (s, 3H, N−Me), 2.01 (d, 1H, N−CH^2−Zr).

Reactions with Alkylaluminum-Treated Silica Gels. For these studies, samples of a spray-dried silica gel obtained from W. R. Grace & Co., Columbia, MA 21044, with particle size 70 μm, were used, which had been dried at 180 °C in vacuo for 8 h, subsequently treated with Al$_2$Me$_6$, and dried again in vacuo.[15] An elemental analysis yielded values of 4.3 g of Al and 38 g of Si per 100 g of silica gel. A defined quantity of the alkylaluminum-treated silica gel was weighed directly into an NMR tube, and a stock solution of the reactant in C$_6$D$_6$ was added. The reaction mixture was stored at the temperature indicated and shaken from time to time for a few minutes, before ^{1}H NMR spectra were taken.

Ethene Polymerization with 2c as Activator. Since addition of any alkylaluminum scavenger to the reaction system would lead to complicating alkyl exchange reactions, an excess of the dimethyl zirconocene complex was used to eliminate impurities. To a solution of 20 mg (48 μmol) of Me$_2$-Si(ind)$_2$ZrMe$_2$ in 100 mL of toluene, saturated in a 250 mL autoclave at 30 °C with 2 bar of ethene for 20 min, was added 5 mL of a toluene solution of 5.8 mg (5 μmol) of cation **2c** by way of a pressure-addition vessel. After 6 h, the reaction mixture was poured into 200 mL of a mixture of methanol and aqueous HCl. Collection and drying of the precipitate yielded 1.14 g of polyethene.

Crystal Structure Determinations. X-ray diffraction analysis was carried out on a Siemens P4 four-circle diffractometer using Mo Kα radiation (71.073 pm) and a graphite monochromator (Table 2). Crystal decay was monitored by measuring 3 standard reflections every 100 reflections. The structures were solved using direct methods.[16] Hydrogen atoms were refined on calculated positions with fixed isotropic U values, using riding model techniques.[16] Absorption corrections

Table 2. Crystallographic and Experimental Data^a for Complexes 2b,c

	2b	**2c**
formula	C$_{53}$H$_{74}$Al$_2$BF$_{20}$-NO$_8$Si$_8$	C$_{47}$H$_{50}$Al$_2$BF$_{20}$-NO$_2$Si$_2$
cryst color and form	colorless prism	colorless plate
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	14.206(21)	10.538(7)
b (Å)	16.071(19)	15.501(15)
c (Å)	18.036(25)	18.797(11)
α (deg)	83.88(7)	91.84(5)
β (deg)	81.39(11)	101.72(3)
γ (deg)	71.80(9)	94.03(5)
Z; V (Å^3)	2; 3860(9)	2; 2996(4)
crystal size (mm)	0.2 × 0.3 × 0.4	0.2 × 0.4 × 0.5
T (K); d_{calcd} (g/cm^3)	248; 1.310	248; 1.288
μ (mm^{-1}), F(000)	0.254; 1572	0.185; 1188
scan mode; θ range (deg)	ω; 1.1−26	ω; 1.1−26
no. of rflns collected	12 576	11 707
no. of indep rflns	10 987 (R_{int} = 3.67%)	11 207 (R_{int} = 2.94%)
no. of obsd rflns ($I > 2\sigma(I)$)	5518	6354
no. of params; GOF	848; 1.009	676; 0.982
$R(F)$, $R_w(F^2)^a$ (obsd data)	6.26, 11.0%	6.03, 14.4%
$R(F)$, $R_w(F^2)^a$ (all data)	15.4, 15.9%	11.3, 16.3%
largest diff peak (e/Å^3)	0.384	0.363

^{a} Weighting scheme: **2c**, $w^{-1} = \sigma^2(F_o^2) + (0.079P)^2$; **2b**: $w^{-1} = \sigma^2(F_o^2) + (0.036P)^2 + 3.36P$. $P = (F_o^2 + 2F_c^2)/3$.

were applied using ψ-scan data. One TMS group in **2b** was found to be disordered, with occupation factors refined to 0.7 and 0.3, respectively. Residual electron densities up to 3 e/Å^3 without bonding contacts to the molecule were found in the proximity of an inversion center in **2c**. A void of 459 Å^3 in the elemental cell and 149 electrons in this solvent area were reported by the SQUEEZE program,[17] which is reasonably close to the sum of 142 electrons expected for two pentane molecules and one chlorobenzene molecule in the unit cell. Since other attempts to fit the solvents used in the crystallization process to the very diffuse electron densities failed and geometrical parameters drastically improved by the application of SQUEEZE (e.g. the variation in the four chemically equivalent B−C distances was reduced from 30 to 4 pm), we corrected the residual electron density in the structural void with the SQUEEZE program as "diffuse solvent".[17] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 189032 and 189033. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

Supporting Information Available: Full listings of crystallographic data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for complexes **2b**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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