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Bulky Siloxyaluminum Alkyls as Models for Al_2Me_6-Treated Silica Gel Surfaces. Characterization of a Dimethylaniline-Stabilized Dimethylaluminum Cation

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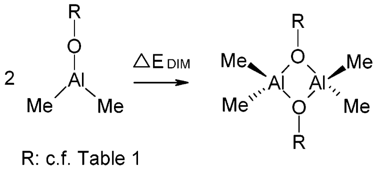
Reaction of a particularly bulky silanol, (2,4,6-$Me_3C_6H_2$)$_3$SiOH, with Al_2Me_6 gives, instead of the otherwise preferred unreactive binuclear siloxalanes with two siloxy bridges, a binuclear siloxalane with one siloxy and one methyl bridge, $Me_2Al(\mu$-OSi(2,4,6-$Me_3C_6H_2)_3$)(μ-Me)$AlMe_2$. This species reacts with zirconocene dichlorides under chloride/methyl exchange; with the cationizing reagent $PhMe_2NH^+B(C_6F_5)_4^-$ it forms the $B(C_6F_5)_4^-$ salt of the mononuclear cation $AlMe_2(NPhMe_2)_2^+$.

Introduction

Alkylaluminum-treated silica gels are frequently used as solid supports for practical applications of metallocene and other single-site organometallic polymerization catalysts,[1] yet the SiO-bound alkyl aluminum species thought to be present on their surfaces are still incompletely understood with respect to their structures and reactivities.[2] Insights in this regard can be expected from studies on soluble, structurally characterized compounds formed by reaction of trialkylaluminum compounds with silanols serving as models for surface SiOH groups.

We have recently shown that binuclear siloxalanes of the type $Me_2Al(\mu\text{-}OSiR_3)_2AlMe_2$, ubiquitously formed from trimethylaluminum and various silanols,[3] react with a cationization reagent such as dimethylanilinium perfluorotetraphenyl borate, $[PhMe_2NH]^+[B(C_6F_5)_4]^-$, to form dimethylaniline-stabilized binuclear cations of the type $Me_2Al(\mu\text{-}OSiR_3)_2AlMe(NPhMe_2)^+$.[4] These cations induce a slow conversion of dimethyl zirconocene to an unstable cationic product, presumably $Cp_2ZrMe(NPhMe_2)^+$, which catalyzes the polymerization of ethene, albeit with low activity.[4]

Scheme 1



Binuclear siloxalane cations thus show a reactivity qualitatively similar to that of silica gels treated first with Al_2Me_6 and then with the cationizing reagent $[PhMe_2NH]^+[B(C_6F_5)_4]^-$, which act as efficient activators of zirconocene compounds for the catalytic polymerization of ethene.[5] Compared to these silica gel surface systems, however, the hitherto described binuclear siloxalane cations are relatively unreactive,[4] probably due to their stabilization by two siloxy bridges. Following the hypothesis that isolated siloxy units, a predominant functionality on surfaces of calcinated silica gels,[6] might give rise to more reactive species with only one siloxy moiety, we have sought to generate models for such surface-bound siloxalanes by use of sterically particularly demanding silanols and to study their reactivity, e.g., vis-à-vis typical cationization reagents.[7]

Results and Discussion

1. Design and Synthesis of Siloxalanes with Spatially Demanding Siloxy Groups. To assess the steric requirements necessary to prevent dimerization of a siloxalane according to Scheme 1, we have calculated energy changes ΔE_{DIM} for these dimerization reactions by simple MNDO methods contained in the HYPERCHEM software package (see Experimental Section). For some siloxalanes and alkoxalanes, which

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Table 1. Energy Differences ΔE_{DIM} (in kcal/mol) Calculated for Siloxalane and Alkoxalane Dimerization Reactions According to Scheme 1

R	ΔE_{DIM}
$PhMe_2Si^a$	−25
$(2,4,6\text{-}^tBu_3Ph)CH_2{}^b$	−35
isoborneyl[c]	−13
Ph_3Si	−9
$(3,5\text{-}^tBu_2Ph)_3Si$	0
$(2,6\text{-}Me_2Ph)_3Si$	+64
$(2,6\text{-}^iPr_2Ph)_3Si$	+164
$(2,6\text{-}^tBu_2Ph)_3Si$	+217

[a−c] Known to be dimeric as solids and in solution (refs 3c, 3h, 3i, respectively).

are known to be dimeric in the solid state and in solution,[3] these calculations yield negative ΔE_{DIM} values between −35 and −13 kcal/mol (Table 1). For unsubstituted and 3,5-substituted tris(di-*tert*-butylphenyl)siloxy derivatives, rather low ΔE_{DIM} values of −9 and 0 kcal/mol were obtained, indicating that compounds of this type would likewise tend to form dimers. Substantially less favorable dimerization energies of +64, +164, and +217 kcal/mol, however, are calculated for the yet unknown siloxalanes with three 2,6-dimethyl-, 2,6-diisopropyl-, and 2,6-di-*tert*-butyl-substituted phenyl rings, respectively. Silanols with three 2,6-dialkyl-substituted phenyl rings thus appeared suitable to stabilize monomeric siloxalanes.

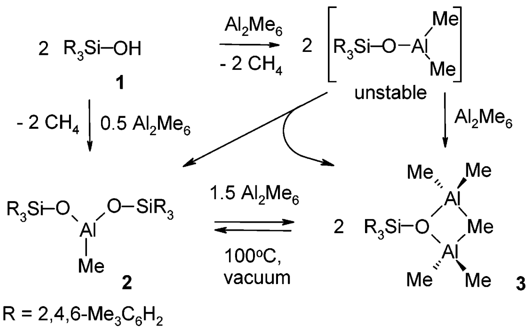
To hydrolyze the Si−Cl bond in sterically crowded triaryl silyl chlorides, rather drastic reaction conditions, such as refluxing $EtOH/KOH/H_2O$ mixtures, are required.[8] Applied to tris(2,4,6-trimethylphenyl)silyl chloride,[9] such a reaction gave, within 12 h, a 86% yield of tris(2,4,6-trimethylphenyl)silanol **1** (see Experimental Section).[10]

Attempts to synthesize the analogous isopropyl-substituted silanol were not successful. Instead of the desired tris(2,4,6-triisopropylphenyl)silane, unidentified product mixtures were obtained when Cl_3SiH was reacted with (2,4,6-triisopropylphenyl)lithium.[11] Apparently, phenyl groups with *o*,*o*′-isopropyl substituents are too strongly hindered for three successive substitutions at an Si center. All further studies were thus conducted with the tris(2,4,6-trimethylphenyl)silanol **1**.

Following our initial hypothesis—that sufficiently crowded siloxy residues might stabilize mononuclear siloxalanes—we first studied the reaction of **1** with 0.5 equiv of Al_2Me_6. It was soon noted, however, that two different products are obtained from these reactions in relative amounts which change with the ratios of the reactants.

Reaction of Al_2Me_6 with 4 equiv of silanol **1** gave species **2** by 2-fold substitution at each Al center (Scheme 2). In the ^1H NMR spectra of **2** (see Experimental Section), the ortho-methyl groups at each phenyl ring give rise to two doublets centered at 2.15 and 2.45 ppm at −80 °C. These doublets coalesce to two broadened signals at −50 °C, and to one signal at −20 °C, which becomes a sharp singlet at +10 °C. Apparently, the methyl groups in *o*- and *o*′-position are diastereotopic due to an axially chiral, propeller-like arrangement into which the substituted phenyl rings of **2** are frozen at −80 °C but free to rotate with rising temperature.[12]

Scheme 2



Reaction of **1** with equivalent amounts or with excess of Al_2Me_6, on the other hand, gave the binuclear siloxalane **3**, in which two Me_2Al units are bridged by one siloxy and one Me group (Scheme 2). Low-temperature ^1H NMR spectra of this product show the Me groups in *o*- and *o*′-position of the phenyl rings as two sharp signals at 2.13 and 2.59 ppm, which broaden above −10 °C but do not coalesce up to +27 °C (see Experimental Section). Apparently, rotation of the substituted phenyl rings is even more strongly hindered here than in species **2**.[12] At −80 °C, the bridging and terminal Al-Me groups appear at 0.36 and at −0.49 and −0.54 ppm, respectively. The propeller-like chirality of the substituted phenyl rings obviously renders the terminal Al-Me groups diastereotopic. Terminal and bridging Al-Me signals coalesce with each other (and with those of residual Al_2Me_6) between −20 and −10 °C, i.e., at temperatures similar to those required for exchange between bridging and terminal Me groups in Al_2Me_6.[13]

Species **2** is completely converted to **3** by reaction with at least 1.5 equiv of Al_2Me_6 in C_6D_6 solution at room temperature within the time required to measure its NMR spectrum. This reaction is reversible: Heating of **3** to 140 °C under sublimation conditions regenerates **2** (Scheme 2). In this way, pure **2** was prepared free of residual **3**. Isolation of compound **3**, on the other hand, requires a rather judicial removal of excess Al_2Me_6, so as to avoid its conversion to **2**.

When Al_2Me_6 is reacted with 2 equiv of **1** in C_6D_6 solution at room temperature, a mixture containing equal amounts of products **2** and **3** is detected by ^1H NMR. As expected from our estimates of dimerization energies in Table 1, formation of a binuclear siloxalane with two siloxy bridges is prevented by the steric crowding at the siloxy unit, but the expected mono-

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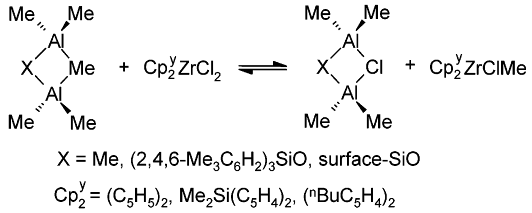
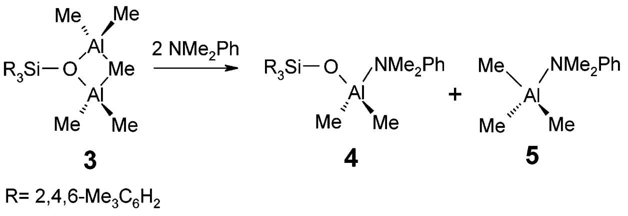
Scheme 3



Scheme 4



nuclear 1:1 reaction product $R_3Si{-}O{-}AlMe_2$ obviously dismutates to the 1:2 and 2:1 reaction products.[14,15]

These observations are of direct concern for reactions of trimethyl aluminum on a silica gel surface: Isolated surface-silanol groups can be expected to react with excess Al_2Me_6 in a manner similar to that observed for the sterically obstructed silanol **1**, i.e., to form primarily a siloxalane species analogous to the monosiloxy-bridged siloxalane **3** (Scheme 3).[16] The likelihood that surface species closely related to **3** are present on Al_2Me_6-treated silica gels has motivated us to study reactions of **3** with typical components of silica-supported catalyst systems used in polymerizations of ethene and other olefins.

2. Reactions of Siloxalane 3 with Polymerization Catalyst Components. Previous studies have shown that zirconocene dichloride complexes react with Al_2Me_6 under exchange of methyl and chloride ligands according to the equilibrium described by Scheme 3, with equilibrium constants K_{EXC}, which decrease with increasing electron density at the Zr center of the zirconocene complex considered (Table 2).[17] Analogous exchange reactions with very similar K_{EXC} values were observed when the binuclear siloxalane **3** was equilibrated with a zirconocene dichloride.[18]

With doubly siloxy-bridged siloxalanes of the type $Me_2Al(\mu\text{-}OSiR_3)_2AlMe_2$, on the other hand, analogous exchange reactions did not take place to any measurable extent; that is, their K_{EXC} values are close to zero.[4] This exchange reaction thus serves as a sensitive indicator for the presence of at least one bridging Me group in a binuclear methyl aluminum species.

Table 2. Equilibrium Constants K_{EXC} for Cl/Me Exchange between Zirconocene Dichloride and Methylaluminum Compounds According to Scheme 3

	$K_{EXC}(Al_2Me_6)^a$	$K_{EXC}(\mathbf{3})$	$K_{EXC}(TMA/SiO_2)$
$(C_5H_5)_2ZrCl_2$	0.49	0.54	n.d.
$Me_2Si(C_5H_4)_2ZrCl_2$	0.22	0.37	0.033
$(^nBuC_5H_4)_2ZrCl_2$	0.13^b	0.15	0.010

[a] From ref 17. [b] For $(MeC_5H_4)_2ZrCl_2$.

Upon equilibration with an Al_2Me_6-treated silica gel,[4] zirconocene dichlorides are likewise partially converted to the respective methyl chloride complex. K_{EXC} values for two heterogeneous reactions of this type, estimated from the extents to which the respective zirconocene methyl chloride complexes are formed in the supernatant solution, are also listed in Table 2.[19] While the formal K_{EXC} values thus obtained are lower by 1 order of magnitude than those obtained with Al_2Me_6 in solution (see Experimental Section), they follow the same trend in being smaller by a factor of 2−3 for $Me_2Si(C_5H_4)_2ZrCl_2$ than for $(n\text{-}BuC_5H_4)_2ZrCl_2$. The data listed in Table 2 would therefore provide support to the notion that a siloxalane with a single siloxy bridge, such as **3**, represents a reasonable model for the species present on a Al_2Me_6-treated silica gel surface.[16]

Dimethylaniline is released into catalytic reaction systems, whenever the cationization reagent dimethylanilinium perfluorotetraphenylborate, $[PhMe_2NH]^+[B(C_6F_5)_4]^-$, is used to generate a reactive zirconocene cation, and can interact with Lewis-acidic reaction centers such as those potentially available from siloxalane **3**. Reactions of $PhMe_2N$ with the siloxalane **3** in a ratio of 2:1 or higher in C_6D_6 solution at room temperature give rise to two species, **4** and **5**, the ^1H NMR signals of which can be assigned to the structures represented in Scheme 4. The signals of species **5** are reproduced when the $Me_3Al{-}NPhMe_2$ adduct is generated by reacting dimethylaniline with Al_2Me_6. As expected from Scheme 4, the AlMe signals of species **4** and **5** always arise in a ratio of 2:3. This facile cleavage of **3** into its two moieties sets the singly siloxy-bridged siloxalane **3** apart again from its doubly siloxy-bridged congeners, which are totally adamant, due to the stability of their $(AlO)_2$ core, against attack by $PhMe_2N$.

On the basis of the reactions of doubly siloxy-bridged siloxalanes with the cationization reagent $[PhMe_2NH]^+[B(C_6F_5)_4]^-$,[4] we had expected that an analogous binuclear siloxalane cation such as $Me_2Al(\mu\text{-}OSiR_3)(\mu\text{-}Me)AlMe(NPhMe_2)^+$ would arise from the corresponding reaction with siloxalane **3** and were thus surprised to observe an entirely different course for this reaction.

When reactions of **3** with $[PhMe_2NH]^+[B(C_6F_5)_4]^-$ were followed in d_8-toluene solution at room tempera-

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[14] In this respect, siloxalane **3** differs from the otherwise related aryloxalane $Me_2Al(\mu\text{-}Me)(\mu\text{-}O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me\text{-}C_6H_2)AlMe_2$, which appears to be in equilibrium with Al_2Me_6 and monomeric $Me_2Al\text{-}O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me\text{-}C_6H_2$: Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543. Schreve, A. P.; Mühlhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

[15] Analogous reactions of **1** with excess triisobutylaluminum, $^iBu_3Al$, however, gave the mononuclear siloxalane $^iBu_2AlOSi(2,4,6\text{-}Me_3H_2C_6)_3$, as indicated by its ^1H NMR (250 MHz, C_6D_6 7.15 ppm, 300 K): δ 6.77 (s, 6H, arom.), 2.39 (s, 18H, ortho-Me), 2.11 (s, 9H, para-Me), 0.95 (d, 12H, Al-$CH_2CH(CH_3)_2$), 0.21 (d, 4H, Al-$CH_2CH(CH_3)_2$); Al-$CH_2CH(CH_3)_2$ signal not detectable, while the bis(siloxy) analogue to compound **2**, $^iBuAl(OSi(2,4,6\text{-}Me_3H_2C_6)_2$, is obtained with excess of **1**. ^1H NMR (250 MHz, C_6D_6 7.15 ppm, 300 K): δ 6.71 (s, 12H, arom.), 2.31 (s, 36H, ortho-Me), 2.12 (s, 18H, para-Me), 0.79 (d, 6H, Al-CH_2-$CH(CH_3)_2$), 0.14 (d, 2H, Al-$CH_2CH(CH_3)_2$), Al-$CH_2CH(CH_3)_2$ signal not detectable.

[16] Intermediate formation of surface species related to **3** has been observed when SiO_2 aerogels are treated with Al_2Me_6: Scott, S. L. Private communication.

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

[18] In these reaction mixtures, no signals assignable to the bissiloxy complex **2** were apparent. This indicates that **3** itself, rather than any Al_2Me_6 derived from it under formation of **2**, is responsible for the Me/Cl exchange reaction with the zirconocene dichlorides.

[19] As described in ref 4, samples of a spray-dried silica gel obtained from W.R. Grace & Co., Columbia, MA 21044, with particle size 70 μm, which had been dried at 180 °C in vacuo for 8 h, subsequently treated with Al_2Me_6 and dried again in vacuo, were used for these studies. Values of 4.3 g of Al and 38 g of Si per 100 g of silica gel were obtained by elemental analysis.

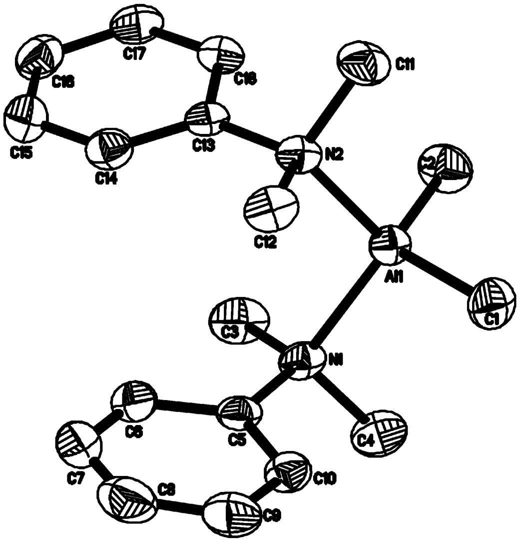


Figure 1. Structure of the cation $AlMe_2(NPhMe_2)_2^+$ (**6**). Hydrogen atoms and $B(C_6F_5)_4^-$ anion omitted for clarity; thermal ellipsoids drawn at the 50% level.

Table 3. Selected Bond Distances (pm) and Angles (deg) for Complex 6

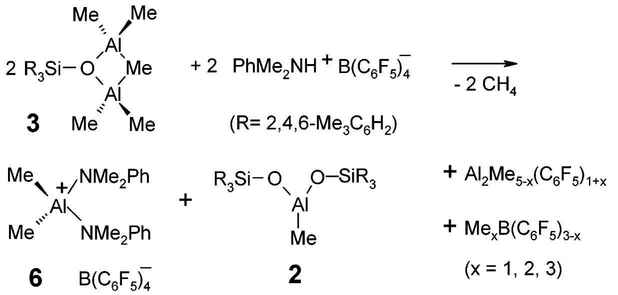
Al1−N1	205.1(2)
Al1−N2	203.8(2)
Al1−C1	195.8(2)
Al1−C2	195.4(2)
C2−Al1−C1	115.4(1)
C1−Al1−N1	109.4(1)
C1−Al1−N2	105.8(1)
C2−Al1−N1	106.7(1)
C2−Al1−N2	111.0(1)

ture, methane evolution was observed within a few minutes. ^{1}H NMR spectra of these reaction mixtures (see Experimental Section) indicate formation of the bis-siloxy AlMe compound **2** and of another hitherto unencountered species. This species was isolated in crystalline form from larger-scale reactions and was revealed by an X-ray structure determination (see Experimental Section) to be the $[B(C_6F_5)_4]^-$ salt of the mononuclear cation $[AlMe_2(NPhMe_2)_2]^+$, **6**.

The geometry of cation **6**, which no longer contains any siloxy function (Figure 1, Table 3), is as expected for a tetracoordinated alkyl aluminum species and in fact rather similar to that of the recently described cation $[AlMe_2(OEt_2)_2]^+$, which was shown to activate $Me_2Si(Me_4C_5)(t\text{-BuN})Ti$ (1,3-pentadiene) for ethene polymerization catalysis.[20] Analogous reactions between Al_2Me_6 and $[PhMe_2NH]^+[B(C_6F_5)_4]^-$ likewise lead to the formation of $[AlMe_2(NPhMe_2)_2]^+[B(C_6F_5)_4]^-$, as indicated by the appearance of its ^{1}H NMR signals, but in the presence of an excess of Al_2Me_6 decomposition is observed within a short time. When prepared from **3** as described above, however, no decomposition is noticeable in benzene solution even after several days.

As for the course of the reaction leading to the formation of the dimethylaniline-stabilzed cation **6**, no indication for the appearance of any intermediates was obtained by NMR spectroscopy, even at temperatures of −30 °C. From the stoichiometry of the reaction, i.e., from the consumption of two $[PhMe_2NH]^+[B(C_6F_5)_4]^-$ units concomitant with formation of only one cation−anion pair, it is clear that some neutral aluminum and boron organyl compounds must be formed by C_6F_5 transfer from B to Al. In accord with the reaction sequence represented in Scheme 5, we observe in these reaction systems at −0.08 ppm the ^{1}H NMR signal of $[AlMe_2(C_6F_5)]_2$, previously observed by Bochmann and Sarsfield to arise by organyl exchange in reaction mixtures containing Al_2Me_6 and $[CPh_3]^+[B(C_6F_5)_4]^-$.[21]

Scheme 5



How reactions with $[PhMe_2NH]^+[B(C_6F_5)_4]^-$ proceed on Al_2Me_6-treated silica surfaces, i.e., whether the mononuclear cation $[AlMe_2(NPhMe_2)_2]^+$ (**6**) arises also under these conditions or whether binuclear cations of the type $Me_2Al(\mu\text{-OSiX}_3)(\mu\text{-Me})AlMe(NPhMe_2)^+$ are prevented from dismutation reactions of type represented in Scheme 5 by the mutual spatial isolation of the surface-bound siloxy groups, and how this would affect the ensuing reactions with zirconocene precatalysts, remains a challenging question.

Experimental Section

Because of the high air and moisture sensitivity of the methyl siloxalanes descibed below (especially of cation **6**), all reactions were performed under argon with Schlenk-line techniques or under nitrogen in a glovebox. Solvents were dried prior to use by refluxing over and distillation from sodium or calcium hydride. Deuterated solvents were dried over 4 Å molecular sieves and used without further purification.

Zirconocene dichloride complexes were synthesized according to literature reports.[22] Other chemicals were purchased from commercial suppliers and used without further purification. Samples of $[PhMe_2NH]^+[B(C_6F_5)_4]^-$ were obtained as gifts from Targor GmbH. The synthesis of tris(2,4,6-trimethylphenyl)siliyl chloride was performed according to published procedures.[9]

Tris(2,4,6-trimethylphenyl)silanol (1). To 150 mL of an ethanol solution of 0.50 g (1.19 mmol) of tris(2,4,6-trimethylphenyl)silyl chloride were added 10.3 g of KOH (183 mmol) and 70 mL of H_2O. The solution was slightly turbid, since the silyl chloride is not completely soluble under these conditions. The reaction mixture was heated to reflux while a clear solution is formed. After 12 h of reflux, the solution is concentrated by evaporating most of the ethanol. The resulting suspension is extracted twice with 100 mL of pentane, and the combined organic layers are washed several times with water until the water layer has a neutral pH value. After drying over $MgSO_4$, filtration, and removal of the solvent by evaporation, 0.43 g (1.02 mmol, yield 86%) of pure **1** is obtained

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in the form of colorless crystals. ^{1}H NMR (250 MHz, $CDCl_3$, 7.24 ppm, 300 K): δ 6.77 (s, 6H, Ph), 2.24 (s, 9H, para-Me), 2.15 (s, 18H, ortho-Me), 2.08 (s, 1H, Si-OH). ^{1}H NMR (250 MHz, C_6D_6, 7.15 ppm, 300 K): δ 6.73 (s, 6H, Ph), 2.31 (s, 18H, ortho-Me), 2.10 (s, 9H, para-Me), 1.90 (s, 1H, Si-OH).^{13}C NMR (250 MHz, C_6D_6, 128.0 ppm, 300 K): δ 144.6 (Ph, ortho-C), 139.2 (Ph, para-C), 135.4 (Ph, ipso-C), 130.0 (Ph, meta-C), 24.6 (ortho-Me), 21.1 (para-Me). EI-MS: 401 (M^+), 282, 267, 264, 235, 163. Anal. Calcd for $C_{27}H_{34}OSi$: C, 80.54; H, 8.51. Found: C, 80.27; H, 8.30.

Bis[tris(2,4,6-trimethylphenyl)siloxy]aluminummethyl (2). To a stirred solution of 0.054 g (0.375 mmol) of Al_2Me_6 in 15 mL of toluene was added dropwise 0.50 g (1.24 mmol) of tris(2,4,6-trimethylphenyl)silanol **1** in 5 mL of toluene during 5 min at room temperature. After the evolution of methane had ceased, the solution was stirred for another 30 min and the solvent then removed under vacuo. The remaining white powder was heated to 140 °C for 18 h in vacuo to remove any residual Al_2Me_6. In this manner 0.42 g (0.50 mmol, 81% yield) of pure **2** was obtained in the form of a colorless powder. ^{1}H NMR (250 MHz, C_6D_6, 7.15 ppm, 300 K): δ 6.71 (s, 12H, Ph), 2.29 (s, 36H, ortho-Me), 2.11 (s, 18H, para-Me), −0.55 (s, 3H, Al-Me). ^{1}H NMR (250 MHz, $C_6D_5CH_3$, 7.17/7.09/7.00 ppm, 213 K): δ 6.70 and 6.61 (two br s, together 12H, Ph), 2.51 und 2.42 (two br s, together 18H, ortho-Me), 2.16 (s, 18H, para-Me), 2.14 (overlapping with the signals at 2.05) and 2.05 (two br s, together 18H, ortho-Me), −0.45 ppm (s, 3H, Al-Me). ^{13}C NMR (250 MHz, C_6D_6, 128.0 ppm, 300 K): δ 144.1 (Ph, ortho-C), 138.6 (Ph, para-C), 137.2 (Ph, ipso-C), 130.0 (Ph, meta-C), 25.0 (ortho-Me), 21.1 (para-Me), −10.9 (Al-Me). ^{27}Al NMR (400 MHz, C_6H_5F, 358 K): no resolved signal detectable. EI-MS: 844 (M^+), 829 ($M^+ - Me$), 710, 605, 589, 485, 282, 265, 163, 133, 120, 105.

Tris(2,4,6-trimethylphenyl)siloxydialuminumpentamethyl (3). To a stirred solution of 0.12 g (1.66 mmol) of Al_2Me_6 in 15 mL of toluene was added dropwise 0.30 g (0.75 mmol) of tris(2,4,6-trimethylphenyl)silanol **1** in 5 mL of toluene during 5 min at room temperature. After the evolution of methane had ceased, the solution was stirred for another 15 min and the solvent then removed in vacuo. Residual toluene and excess Al_2Me_6 were removed from the resulting colorless foam by coevaporation with 10 mL of pentane to yield 0.38 g (0.72 mmol, 97% yield) of **3** in the form of a colorless powder. Although rapid methyl exchange between **3** and Al_2Me_6 leads to coalescence of their respective ^{1}H NMR signals, the absence of significant amounts of Al_2Me_6 is indicated by the ^{1}H NMR integral ratios obtained for this product. ^{1}H NMR (250 MHz, C_6D_6, 7.15 ppm, 300 K): δ 6.67 (s, 6H, Ph), 2.59 (br s, 9H, ortho-Me), 2.18 (br s, 9H, ortho-Me), 2.05 (s, 9H, para-Me), −0.39 (br s, 15H, Al-Me). ^{1}H NMR (250 MHz, $C_6D_5CH_3$, 7.17/7.09/7.00 ppm, 213 K): δ 6.57 (s, 3H, Ph), 6.50 (s, 3H, Ph), 2.59 (s, 9H, ortho-Me), 2.13 (s, 9H, ortho-Me), 2.06 (s, 9H, para-Me), 0.36 (s, 3H, Al-μ-Me), −0.49 (s, 6H, terminal Al-Me), −0.54 (s, 6H, terminal Al-Me). ^{13}C NMR (250 MHz, C_6D_6, 128.0 ppm, 300 K): δ 144.8 (Ph, ortho-C), 139.9 (Ph, para-C), 134.6 (Ph, ipso-C), 130.4 (Ph, meta-C), 26.7 (ortho-Me) 25.0−24.7 (ortho-Me), 20.9 (para-Me), −2.6 to −4.1 (Al-Me). ^{27}Al NMR (400 MHz, C_6H_5F, 358 K): δ 158.0 ($w_{1/2}$ ca. 2500 Hz).

$[AlMe_2(NPhMe_2)_2]^+[B(C_6F_5)_4]^-$ (6). To a stirred solution of 0.40 g (0.99 mmol) of tris(2,4,6-trimethylphenyl)silanol **1** in 40 mL of toluene was added dropwise 0.16 g (1.12 mmol) of Al_2Me_6 in 20 mL of toluene during 5 min. To the resulting solution of tris(2,4,6-trimethylphenyl)siloxydialuminumpentamethyl **3** was added 0.40 g (0.5 mmol) of solid $[PhMe_2NH]^+$-$[B(C_6F_5)_4]^-$, and the suspension was stirred for 48 h at ambient temperature. The solvent and all volatile components were removed in vacuo, and the resulting powder was washed several times with 20 mL portions of pentane. Addition of 10 mL of toluene, filtration, and drying of the collected residue in vacuo provided 0.05 g (0.05 mmol, 20% yield) of **6** in NMR-pure quality as a sligthly brownish powder. Crystals suitable for X-ray structure determination were isolated from a concentrated solution of **6** in chlorobenzene into which pentane was slowly allowed to diffuse at room temperature. ^{1}H NMR (250 MHz, C_6D_6 7.15 ppm, 300 K): δ 6.87 (m, 6H, Ph), 6.35 (m, 4H, Ph), 1.65 (s, 12H, N-Me), −0.92 (s, 6H, Al-Me).

Table 4. Crystallographic and Experimental Data[a] for Complex 6

formula	$C_{42}H_{28}AlBF_{20}N_2$
cryst color and form	colorless prisms
cryst syst, space group	triclinic, $P\bar{1}$
a [Å]	12.4159(14)
b [Å]	13.6012(14)
c [Å]	14.6254(19)
α [deg]	66.390(8)
β [deg]	65.179(9)
γ [deg]	84.685(8)
Z; V [Å^3]	2; 2045.5(4)
cryst size [mm]	0.65 × 0.3 × 0.25
T [K]; d_{calcd}, [g/cm^3]	173; 1.589
μ [mm^{-1}], F(000)	0.177; 984
scan mode; θ range [deg]	ω, 1.6−27°
no. of reflns collected	9826
no. of ind reflns	8724 (R_{int} = 2.04%)
no. of obsd reflns ($I > 2\sigma(I)$)	6969
no. of params; GOF	595; 1.015
$R(F)$, $R_w(F^2)^a$ (obsd data)	3.98%; 9.84%
$R(F)$, $R_w(F^2)^a$ (all data)	5.39%; 10.7%
largest diff peak [e/Å^3]	0.363

[a] Weighting scheme: $w^{-1} = \sigma^2(F_o{}^2) + (0.049P)^2 + 0.9727P$, with $P = (F_0{}^2 + 2F_c{}^2)/3$.

Reactivity Studies on the NMR Scale. Since all compounds studied were stable in C_6D_6, reactivity studies were performed in that solvent. 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. NMR tubes were sealed and kept at −80 °C until the first measurement. Reactions were followed by ^{1}H NMR spectroscopy at room temperature.

Methyl/Chloride Exchange with Zirconocene Dichloride Complexes. To study reactions of siloxalane **3** with the zirconocene dichlorides listed in Table 2, 500 μL of a 5 mM stock solution of the respective zirconocene dichloride was mixed with 50−200 μL of a 50 mM stock solution of **3**, directly in a NMR tube, so as to obtain initial, nominal $[\mathbf{3}]_{init}$:$[Zr]_{tot}$ ratios I in the range of 1:1 to 4:1. The solutions were stored for 24 h at room temperature, after which their ^{1}H NMR were taken on a 250 MHz NMR spectrometer. Concentration ratios $Q = [Cp_2ZrMeCl]$:$[Cp_2ZrCl_2]$ were obtained from the respective signal intensities of these species. Initial concentration ratios $I = [\mathbf{3}]_{init}$:$[Zr]_{tot}$ were experimentally determined by comparing 1/15 of the total signal intensities of all Al- and Zr-bound methyl groups with 1/10 (for $(C_5H_5)_2ZrCl_2$) or 1/8 (for (n-$BuC_5H_4)_2ZrCl_2$ and $Me_2Si(C_5H_4)_2ZrCl_2$) of the total signal intensities of all Cp protons. From the data thus obtained (Supporting Information), the equilibrium constants listed in Table 2 were evaluated by use of the relationship $K_{EXC} = Q/[I(1 + 1/Q) - 1]$.[17]

Nominal equilibrium constants for the heterogeneous reaction systems containing Al_2Me_6-treated silica gel were evaluated from the data reported in ref 4 by assuming that the Al content of the samples used (4.3%) would be entirely due to the presence of a surface species analogous to **3**.[18] If other, less reactive Al-containing surface species were also present in addition to a singly siloxy-bridged species, apparent K_{EXC} values would be underestimated by a factor corresponding to the proportion of the latter.

Semiempirical Calculations of Dimerization Energies. Energy differences between the dinuclear complexes and their two mononuclear halves, each with optimized geometries, were calculated for the siloxalanes and alkoxalanes listed in Table

1 by means of the MNDO program contained in the HYPERCHEM program package, using the standard parameters provided with the 1996 version 5.01 of this program package. In preparation for these studies, it had been noted that the geometries of several known siloxalanes and alkoxalanes were reproduced significantly better by MNDO than by the AM1 and PM3 programs contained in the HYPERCHEM package.[23]

Crystal Structure Determinations. X-ray diffraction analysis of complex **6** was carried out on a Siemens P4 four-circle diffractometer using Mo Kα radiation (71.073 pm) and a graphite monochromator (Table 4). Crystal decay was monitored by measuring three standard reflections every 100 reflections. The structures were solved using direct methods.[24] Hydrogen atoms were refined on calculated positions with fixed isotropic *U*, using riding model techniques.[24] Absorption corrections were applied using psi-scan data. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 202605. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.)

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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