Yttrium Calix[4]arene Complexes. Silylation and Silylamine Elimination Reactions on Model Oxo Surfaces

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The synthesis and the spectroscopic and structural characterization of lower-rim-silylated and rare-earth-metalated calix[4]arenes are presented. Hexamethyldisilazane, $HN(SiMe_3)_2$, reacted in a selective manner with [*p-tert*-butylcalix[4]arene]H_4 (**1**) in refluxing mesitylene to give the 1,3-silylated product [*p-tert*-butylcalix[4]arene(SiMe_3)_2]-H_2 (**2**) in high yield. The molecular structure of compound **2**, as revealed by X-ray crystallography, shows the pinched *cone* conformation of the calixarene bowl, featuring hydrogen bonding between the phenylsilyl ether and phenolic oxygen atoms (O···O, 2.838 Å). From the reaction of the sterically more crowded tetraphenyldimethyldisilazane, $HN(SiMePh_2)_2$, only starting material could be recovered. In contrast, tetramethyldisilazane, $HN(SiHMe_2)_2$, afforded the tetrakis-silylated product [*p-tert*-butylcalix[4]arene(SiHMe_2)_4] (**3**) in hexane solution at ambient temperature. A single-crystal X-ray diffraction study of compound **3** established the *1,2-alternate* conformation, which is also present in solution, as indicated by ¹H NMR spectroscopy. The yttrium complex $Y[N(SiHMe_2)_2]_3(THF)_2$ (**4**) exchanged all of its silylamide ligands when treated with an equimolar amount of **1** in toluene at ambient temperature to yield compound **5**, as indicated by IR and NMR spectroscopy. The molecular structure of **5** revealed a centrosymmetric dimer of composition [Y{*p-tert*-butylcalix[4]arene(SiHMe_2)}(THF)]_2. Three of the deprotonated phenolic oxygen atoms of the calixarene bowl bind to the metal center, two as terminal ligands and one in a bridging mode, while the fourth undergoes in situ silylation ($\nu(SiH)$ 2127 cm^{-1}). The distorted-trigonal-bipyramidal coordination geometry is completed by a THF molecule. Bis-silylated **2** reacted with **4** to form the heteroleptic complex {Y[*p-tert*-butylcalix[4]arene(SiMe_3)_2][N(SiHMe_2)_2]} (**6**). Crystal data: $C_{50}H_{72}O_4$-Si_2 (**2**), triclinic, $P\bar{1}$, $a = 12.8914(3)$ Å, $b = 14.9270(5)$ Å, $c = 15.1652(4)$ Å, $\alpha = 77.293(2)°$, $\beta = 65.019(2)°$, $\gamma = 72.234(2)°$, $Z = 2$; $C_{52}H_{80}O_4Si_4$ (**3**), triclinic, $P\bar{1}$, $a = 10.1774(2)$ Å, $b = 14.1680(2)$ Å, $c = 18.7206(2)$ Å, $\alpha = 95.8195(8)°$, $\beta = 95.5294(8)°$, $\gamma = 98.1098(7)°$, $Z = 2$; $C_{100}H_{132}O_{10}Si_2Y_2$, 2($C_6H_6$) (**5**), triclinic, $P\bar{1}$, $a = 13.2625(4)$ Å, $b = 14.5894(3)$ Å, $c = 17.0458(5)$ Å, $\alpha = 65.0986(14)°$, $\beta = 77.8786(8)°$, $\gamma = 85.5125(13)°$, $Z = 1$.

Introduction

Grafting of organometallic complexes onto oxo surfaces, often termed surface organometallic chemistry (SOMC), is a prominent route to generate novel inorganic/organometallic hybrid materials.[1,2] Such immobilized species often display unusual reactivity due to surface confinement, i.e., geometrical distortions of the metal's coordination sphere.[3,4] We[5,6] and others[7,8]

are currently pursuing SOMC on mesoporous silica materials of the M41S family.[9] Due to their structural order and mesoporosity these materials give access to a more diverse physicochemical characterization and hence can be considered as model support materials for more ordinary forms of silica. In the course of these studies, we developed a heterogeneously performed silylamide route to generate grafted metal ligand

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Scheme 1
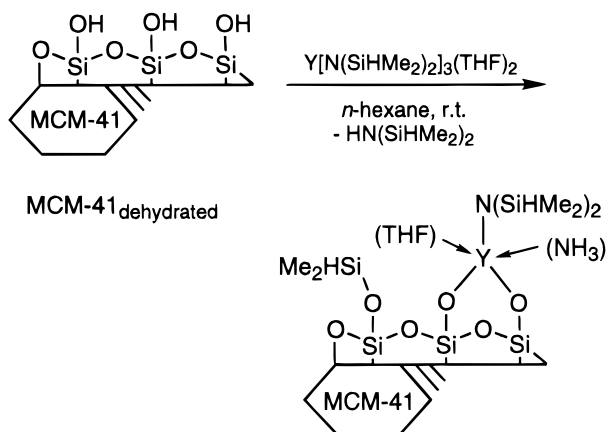
Scheme 2

species under fairly mild conditions.[4,6] A distinctive feature of this immobilization process, which is represented in Scheme 1 for trivalent lanthanide bis(dimethylsilyl)amide complexes, Ln-[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$, is the concomitant surface silylation due to the released silylamine (in situ silylation). Surface silylation was shown to compatibilize oxidic support materials for catalytic applications by hydroxyl group passivation and hydrophobization.[10−13] In particular, disilazane compounds, HN(SiR^{1}R$^2_2$)$_2$, proved to be highly efficient silylation reagents.

In this paper we describe the use of [*p-tert*-butylcalix[4]arene]-H$_4$ (**1**)[14] as a molecular silica oxo surface to model the reactivity of both various disilazane reagents and yttrium silylamide complexes. Recently, metal-driven reactions exploiting this oxo-quasiplanar environment as an oxo surface model have been extensively studied by Floriani et al.[15]

Results and Discussion

Silylation of Calix[4]arene by Means of Disilazane Reagents: Structural Chemistry. Previous studies on silica materials,[10−12] including our recent investigations on mesoporous silica materials of type MCM-41,[16] revealed that disilazane compounds, HN(SiR^{1}R$^2_2$)$_2$, are efficient and versatile silylation reagents at ambient temperature. We found that the silylation efficiency markedly depends on the size of the silyl groups R^1 and R^2, respectively. For example, only 80% of the surface silanol groups of a MCM-41 sample, dehydrated at 280 °C/10^{-3} Torr, could be silylated by means of the standard silylation reagent hexamethyldisilazane, HN(SiMe$_3$)$_2$, compared to the
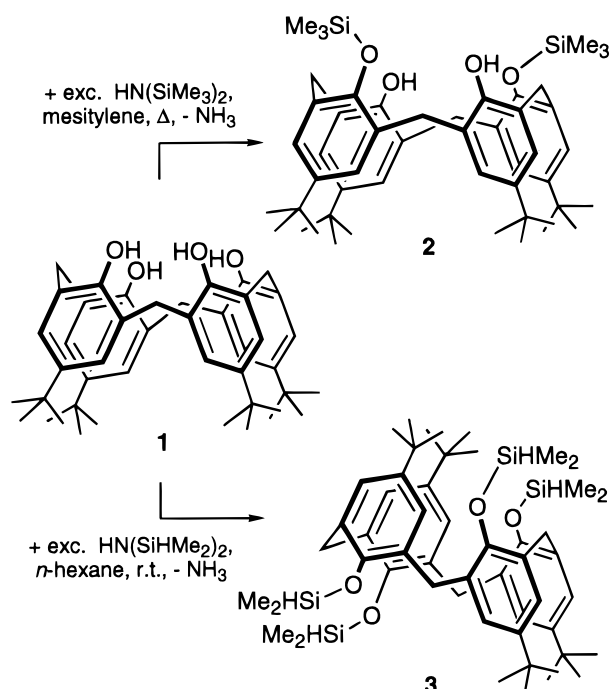
more efficient tetramethyldisilazane, HN(SiHMe$_2$)$_2$. The sterically even bulkier HN(SiMePh$_2$)$_2$ reacted with ca. 40% of the silanol groups under the same conditions. This corresponds to a surface coverage of 1.5, 1.85, and 0.75 SiR$_3$/nm^2, respectively.

In the present study, these disilazane reagents were reacted with the calix[4]arene model oxo surface under identical conditions. Treatment of a slurry of calix[4]arene **1** in hexane or toluene with excess (>20 equiv) HN(SiMe$_3$)$_2$ did not form any silylation product both at ambient temperature and under reflux conditions. However, conducting the reaction in refluxing mesitylene afforded the 1,3-disilyl ether derivative [*p-tert*-butylcalixarene(SiMe$_3$)$_2$]H$_2$ (**2**) in pure form and high yield (Scheme 2). Compound **2** could alternatively be synthesized by the consecutive reaction of **1** with NaH and freshly distilled SiMe$_3$Cl in a THF/toluene solution at ambient temperature.

The feasibility of calixarene silylation by means of standard silylation procedures using HN(SiMe$_3$)$_2$ and Me$_3$SiCl was discussed differently in the literature.[17−20] Gutsche et al. reported that only starting material was recovered from the reaction of **1** with excess of Me$_3$SiCl and HN(SiMe$_3$)$_2$ in refluxing pyridine.[17] While calix[6]arene and calix[8]arene are easily converted to the corresponding hexakis- and octakis(trimethylsilyl) derivatives, the passive reaction behavior of the cyclic tetramer was assigned to the coordinatively greater crowding of the hydroxyl groups. In contrast, when *N,O*-bis(trimethylsilyl)acetamide was used as a silylation reagent, even a tetrakis-(trimethylsilyl) derivative could be detected after prolonged

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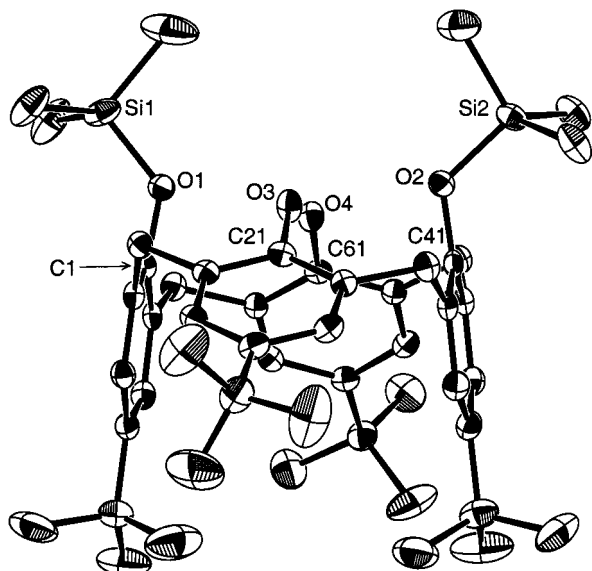
Figure 1. PLATON[48] drawing of **2**. Atoms are represented by thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. For selected distances and angles see Table 1.

Table 1. Selected Atomic Distances (Å) and Bond Angles (deg) for Compound **2**

Si1−O1	1.680(2)	Si2−O2	1.666(2)
O3−C21	1.373(3)	O4−C61	1.374(3)
O1−C1	1.390(3)	O2−C41	1.393(3)
O1···O2	4.975(2)	O1···O3	3.139(2)
O1···O4	2.878(3)	O2···O3	2.838(3)
O2···O4	3.104(2)	O3···O4	3.206(3)
Si1−O1−C1	125.0(2)	Si2−O2−C41	131.3(2)

treatment of **1** in refluxing acetonitrile. Schmutzler et al. reported the synthesis of **2** both from the reaction of **1** with HN(SiMe₃)₂ in the presence of a catalytic amount of Me₃SiCl in toluene at ambient temperature and from the reaction with Et₂NSiMe₃ in toluene (50 °C).[18] Recently, Parkin et al. also reported that the silylation reactions of calix[4]arene with both Me₃SiCl and HN-(SiMe₃)₂ were not successful.[19] Instead, they obtained compound **2** from the reaction of **1** with 2 equiv of Me₃SiI in the presence of pyridine (2 equiv).

Both *cone* and *1,3-alternate* stereoisomers can be formulated for compound **2** on the basis of the coupling pattern of the diastereotopic hydrogen atoms of the −CH₂− groups in the ¹H NMR spectrum. The two unreacted phenolic OH groups are clearly indicated by a stretching vibration at 3424 cm⁻¹ in the IR spectrum. For comparison, the calix[4]arene precursor shows a lower energy OH band at 3140 cm⁻¹ due to extended hydrogen bonding. The molecular structure of compound **2** could be additionally proven by X-ray structure analysis (Figure 1). Selected bond lengths and angles are listed in Table 1. Compound **2** adopts the *cone* conformation of the calixarene bowl, with the phenolic groups being 1,3-silylated. The two opposite silylated phenyl rings are approximately parallel to each other and almost perpendicular to the least-squares plane formed by the four carbon atoms of the methylene groups (95.15(5), 96.09(5)°). The phenolic rings are tilted against this C₄ plane by 141.60(8) and 142.02(9)°, respectively, to place the hydroxy groups inside the cavity. This "pinched cone" conformational arrangement is also revealed by the O···O distances of the silyl ether moieties (O1···O2, 4.975(2) Å) and those of the flattened phenol units (O3···O4, 3.206(3) Å). The O(phenol)−O(silyl ether) distances range from 2.838(3) to 3.139(2) Å, predicting the position of the hydrogen atoms between the neighboring

oxygen atoms O1/O4 and O2/O3, respectively. A conformationally and constitutionally identical orientation was found in dialkyl ether derivatives of compound **1**, e.g., in structurally characterized [*p-tert*-butylcalixarene(Me)₂]H₂ and [*p-tert*-butylcalixarene(Et)₂]H₂.[21,22]

Interestingly, complete silylation of **1** occurred in the presence of 4 equiv of the less sterically demanding silylamine HN-(SiHMe₂)₂ even at ambient temperature (Scheme 2). The compound [*p-tert*-butylcalixarene(SiHMe₂)₄] (**3**) was obtained in high yield and was found to readily dissolve in toluene and *n*-hexane. The SiH moiety of **3** is characterized by a stretching vibration of 2127 cm⁻¹ (cf. ≡SiOSiHMe₂ surface species, 2149 cm⁻¹;[16b] free silylamine, 2118 cm⁻¹) and a proton shift of 5.02 ppm (cf. ≡SiOSiHMe₂ surface species (¹H MAS NMR), 4.6 ppm;[16b] free silylamine, 4.40 ppm). The unusual *1,2-alternate* conformation of compound **3**, as depicted in Scheme 2, could be assigned on the basis of the signal pattern of the diastereotopic hydrogen atoms of the −CH₂− groups in the ¹H NMR spectrum, which appears as one singlet and a pair of doublets (ratio 2:1:1). As expected, the bulky SiHMe₂ group renders the *1,2-alternate* conformation immobile, i.e., an oxygen through the annulus rotation is not observable by a variable-temperature ¹H NMR study (−80 to +110 °C). Selective silylation of one, two, or three phenolic groups of calix[4]arene **1** with HN-(SiHMe₂)₂ was not successful.[23] For comparison, reaction of **1** with tris(dimethylamino)methylsilane, (Me₂N)₃SiMe, gave the tris-silylated product in high yield.[20b]

The *1,2-alternate* conformation of compound **3** could be unequivocally established by an X-ray structure determination (Figure 2, Table 2). All of the silyl groups point outward the calix[4]arene cavity. The enhanced steric crowding caused by the silyl ether substituents is particularly indicated by the cisoid O···O distances (O1···O4, 3.338(2) Å; O2···O3, 3.342(2) Å). For comparison, the O···O distances in the tris(*O*-alkylated) [*p-tert*-butylcalixarene(Me)₃]H range from 2.96 to 3.08 Å.[21] The interplanar angles of the phenyl rings with the least-squares C₄ plane formed by the four carbon atoms of the methylene groups amount to 54.22(9), 55.08(9), 73.22(10), and 74.879(9)°.

A salt metathesis procedure starting from **1**, NaH, and ClSiHMe₂ also yielded the *1,2-alternate* conformer of **3** exclusively. For comparison, the *1,2-alternate* conformer of [*p-tert*-butylcalix[4]arene(Pr)₄] could be obtained (<20% yield), along with the *partial cone* and *1,3-alternate* conformers, by direct *O*-alkylation. The *1,2-alternate* conformation of [*p-tert*-butylcalixarene(Et)₄] was formed via thermal isomerization of the *partial cone* conformer, the latter of which having been determined by an X-ray crystallographic study.[24] The *partial cone* conformation of [*p-tert*-butylcalix[4]arene(Et)₄] was also found to interconvert to the *1,2-alternate* isomer upon complexation of aluminum alkyl compounds.[25,26] Structurally characterized *1,2-alternate* conformers were also reported for the silylated compounds [*p-tert*-butylcalix[4]arene(SiMe₂)]H₂, [*p-tert*-

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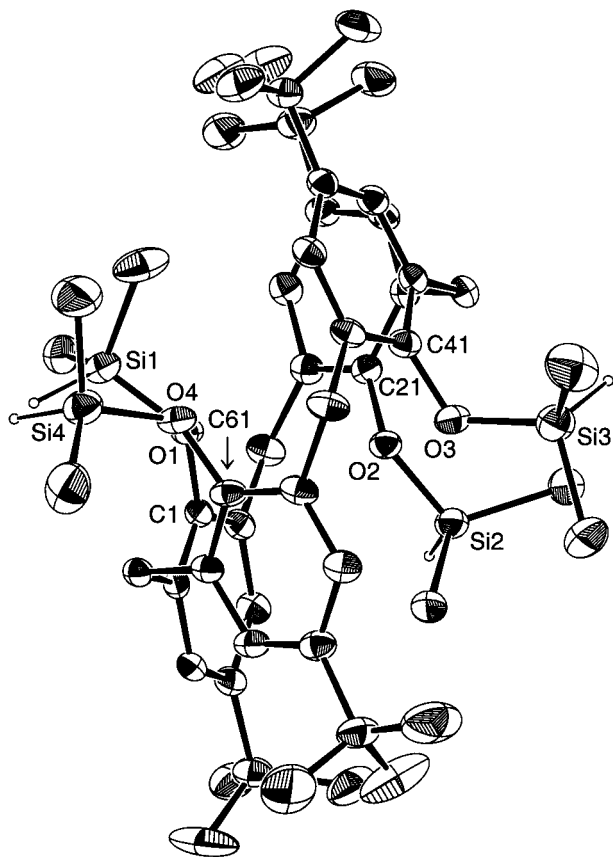
Figure 2. PLATON[48] drawing of **3**. Atoms are represented by thermal ellipsoids at the 50% probability level. Except for the silicon-bonded ones all hydrogen atoms are omitted for clarity. For selected distances and angles see Table 2.

Table 2. Selected Atomic Distances (Å) and Bond Angles (deg) for Compound **3**

Si1–O1	1.644(2)	Si2–O2	1.647(2)
Si3–O3	1.664(2)	Si4–O4	1.669(2)
O1–C1	1.368(3)	O2–C21	1.376(3)
O3–C41	1.394(3)	O4–C61	1.394(3)
O1···O2	3.105(2)	O1···O3	4.990(2)
O1···O4	3.338(2)	O2···O3	3.342(2)
O2···O4	4.908(2)	O3···O4	4.305(3)
Si1–O1–C1	130.2(2)	Si2–O2–C21	130.1(2)
Si3–O3–C41	121.4(2)	Si4–O4–C61	123.4(2)

butylcalix[4]arene(SiMe$_2$)$_2$),[20c] and [*p-tert*-butylcalix[4]arene-(SiMe$_2$)]TiCl$_2$,[27] where one and two SiMe$_2$ groups, respectively, bridge adjacent phenolic oxygen atoms.

Sterically more demanding disilazane reagents seem to be inert toward calix[4]arene silylation. Only unreacted starting material was recovered from the attempted silylation of calix-arene **1** with silylamine HN(SiMePh$_2$)$_2$ in refluxing mesitylene after 48 h. However, treatment of **1** with NaH and *t*BuPh$_2$SiCl yielded ca. 6% mono-silylated product after refluxing in mesitylene for 6 h.

This study emphasizes the importance of steric factors for the disilazane-mediated silylation reaction (kinetic control). A four-centered "O···H···N···Si" transposition proposed previously as the rate-determining step for this special silylation reaction[13] seems to be favorably formed in the presence of sterically less demanding silyl groups (Figure 3). This parallels our findings obtained for disilazane silylation on siliceous
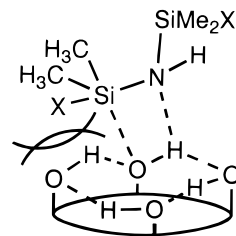
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Figure 3. Proposed "O···H···N···Si" transposition of disilazane reagents with calix[4]arene.

mesoporous materials.[16] Though tetrakis-silylated **3** documents the enhanced silylation capacity of calix[4]arene **1** toward the smallest disilazane reagent, this model oxo surface fails to mimic the rigidity of a silica surface. A putative tetrakis-silylated *cone* conformation of **3** is not formed due to steric constraints and the intrinsic conformational mobility of the calix[4]arene ring. However, the isolation of calix[4]arene derivatives of varying degree of silylation points out the feasibility of an effective oxo surface manipulation via presilylation procedures.[27]

**Reaction of Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ with Nonsilylated 1.** Complexes of rare-earth metals with deprotonated calixarene ligands featuring various ring sizes were previously obtained by salt metathesis reactions in the presence of base molecules.[28−31] Structurally characterized examples include mononuclear {Tm-[*p-tert*-butylcalix[4]arene(Me)$_2$]I(OEt$_2$)}, [Ln(L-2H)(picrate)] (Ln = Sm, Yb, Lu; L = 5,11,17,23-tetra-*tert*-butyl-25,27-bis-((diethylcarbamoyl)methoxy)-26,28-dihydroxycalix[4]arene), [Eu-{*p-tert*-butylcalix[8]arene(OH)$_6$}(NO$_3$)(DMF)$_4$]·3DMF (DMF = *N,N*-dimethylformamide), and [Eu{*p-tert*-butylcalix[6]arene-(OH)$_4$}(OH)(DMF)$_6$] and dinuclear [Eu{*p-tert*-butylcalix[4]-arene(OH)}(DMSO)]$_2$·2(acetone), [Eu{*p-tert*-butyloxacalix[4]-arene(OH)}(DMF)]$_2$·7DMF, and [Sc{*p-tert*-butyloxacalix[3]-arene}(DMSO)]$_2$·2DMSO·acetone (DMSO = dimethyl sulfoxide). Metallacalixarene complexes synthesized from organometallic precursor compounds were previously reported for main-group (Al, Ga, Ge, Sn) and d transition metals (Ti, Cr, Mo, W, Fe, Co, Zn).[32−34]

We wished to examine the reactivity of yttrium silylamide complexes toward calix[4]arene **1** via our extended silylamide route.[35] Accordingly, Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (**4**)[36] was reacted with a slurry of **1** in toluene, which completely dissolved after

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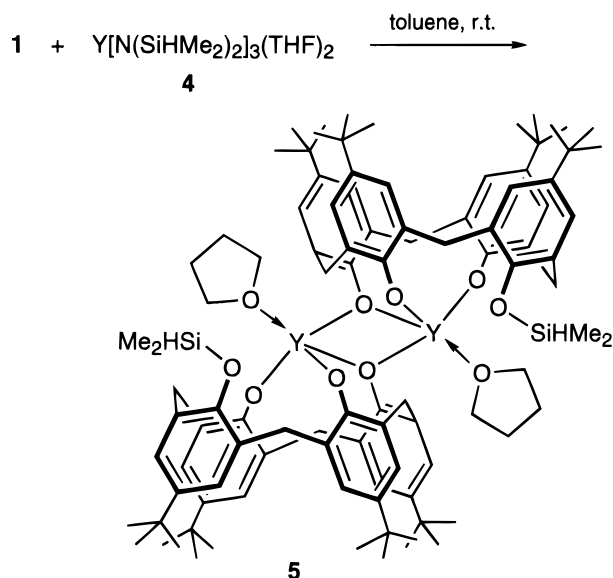
Scheme 3

a few minutes at ambient temperature (Scheme 3). Upon prolonged stirring the white precipitate **5** formed. The IR spectrum of compound **5** revealed the characteristic band pattern of the calix[4]arene ligand backbone, except for the OH stretching vibrations. Instead, a strong SiH stretching vibration at 2194 cm^{-1} appeared indicative of "OSiHMe$_2$" moieties.[37] The formation of this silyl ether moiety was also suggested by a singlet at 4.73 ppm for the SiH proton in the ^{1}H NMR spectrum. For comparison, the spectroscopic details of the SiH moiety displayed by metal-bonded amide ligands in **4** are 2072 cm^{-1} and 4.99 ppm, respectively.[36] The yield of product **5** was 85% and was reproducible. The analogous Y[N(SiMe$_3$)$_2$]$_3$ reactions gave the corresponding product only in low yield (17%).

The molecular structure of compound **5** could be unequivocally established by an X-ray diffraction study (Figure 4). Selected bond lengths and angles are summarized in Table 3.

Complex **5** crystallized from a saturated benzene solution as a centrosymmetric aryloxide dimer of composition [Y{*p-tert*-butylcalix[4]arene(SiHMe$_2$)}(THF)]$_2$. The coordination geometry at the yttrium center is best described as distorted trigonal bipyramidal. Two terminal oxygen atoms (O2, O4) and one bridging aryloxide oxygen atom (O3a) form the equatorial plane, while one THF molecule (O5) and the second bridging aryloxide oxygen atom (O3) occupy the apical positions (∠O5−Y−O3, 149.42(7)°). The terminal and bridging Y−O bond lengths

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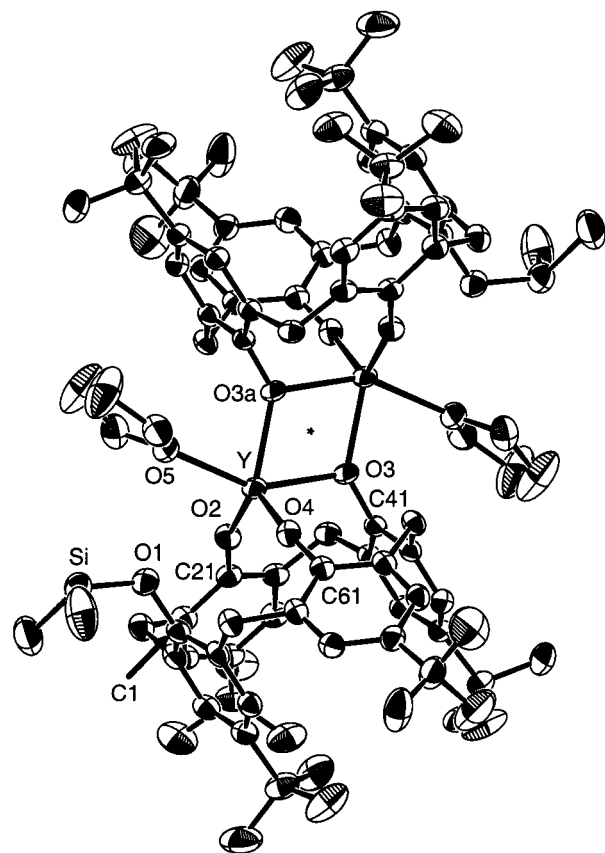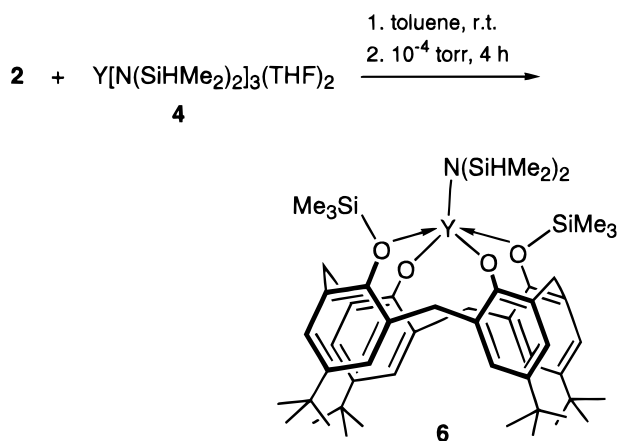

Figure 4. PLATON[48] drawing of **5**. Atoms are represented by thermal ellipsoids at the 50% level (the asterisk indicates the center of symmetry). All hydrogen atoms and one benzene solvent molecule are omitted for clarity. For selected distances and angles see Table 3.

Table 3. Selected Atomic Distances (Å) and Bond Angles (deg) for Compound **5**·2C$_6$H$_6$

Y−O2	2.069(2)	Y−O3	2.265(2)
Y−O3a	2.256(2)	Y−O4	2.061(2)
Y−O5	2.342(2)	Y···O1	3.430(2)
Si−O1	1.665(2)	O1−C1	1.388(4)
O2−C21	1.341(4)	O3−C41	1.373(4)
O4−C61	1.347(3)	O1···O2	3.452(3)
O1···O3	5.511(3)	O1···O4	3.474(3)
O2···O3	3.109(2)	O2···O4	3.538(3)
O3···O4	3.122(3)		
O2−Y−O3	91.56(7)	O2−Y−O3a	120.66(7)
O2−Y−O4	117.86(8)	O2−Y−O5	103.47(8)
O3−Y−O4	92.27(7)	O3−Y−O5	149.42(7)
O3−Y−O3a	68.96(7)	O3a−Y−O4	118.37(7)
O3a−Y−O5	80.48(7)	O4−Y−O5	103.50(8)
Si−O1−C1	121.1(2)	Y−O2−C21	162.7(2)
Y−O3−C41	112.2(1)	Y−O4−C61	160.8(2)
Y−O3−Ya	111.04(8)	Ya-O3−C41	136.7(2)

average 2.065 and 2.260 Å, respectively, and are comparable to those found in other formally 5-coordinate yttrium aryloxide complexes, e.g., (C$_5$Me$_5$)Y(OC$_6$H$_3$*t*Bu$_2$-2,6)$_2$ (2.096(4), 2.059(3) Å).[38] The distance between the OSiHMe$_2$ group (O1) and yttrium of 3.430(2) Å indicates no additional interaction. The calix[4]arene ligand backbone adopts a *pinched cone* conformation. The bridging phenolate and the silyl ether phenolate rings are parallel to each other, forming interplanar angles of 97.47(6) and 99.14(6)° with the least-squares plane spanned by the four carbon atoms of the four methylene groups. The terminally bonded phenolate oxygen atoms O2 and O4 belong to the aryl units, displaying interplanar angles of 136.88(7) and 139.45(8)°.

Scheme 4. Synthesis and Proposed Structure of Complex **6**

The molecular structure of **5** is "isostructural" with [Fe{*p-tert*-butylcalix[4]arene(SiMe₃)}(NH₃)]₂, which was obtained from the reaction of excess Fe[N(SiMe₃)₂]₃ with **1** in toluene.[33a] In the iron complex the NH₃ molecule occupies one of the apical positions. Structural similarities are also detected in other dinuclear lanthanide complexes, including the europium calix[4]arene complexes mentioned above.[28]

The most interesting structural feature of complex **5** is the presence of both yttrium aryloxide and arylsilyl ether bonds, which impressively parallels our findings on mesoporous silica materials.[6] We propose an initial fast amide/aryloxide exchange reaction involving three phenolic positions of the tetravalent model oxo surface. The fourth phenolic position seems to be not readily accessible to another bulky silylamide complex. This was further examined by the reaction of **1** with excess yttrium complex **4**, from which also product **5** could be isolated. Under these conditions the released silylamine favorably competes for this remaining site, as already pointed out by the formation of [*p-tert*-butylcalix[4]arene(SiHMe₂)₄] (**3**). Power et al. discussed an N→OSiMe₃ shift originating from the anionic N(SiMe₃)₂ ligand to explain the partial silylation detected in [Fe{*p-tert*-butylcalix[4]arene(SiMe₃)}(NH₃)]₂ and [Co₃{*p-tert*-butylcalix[4]arene(SiMe₃)₂}₂(THF)]₂.[33a]

Tetravalent calixarene ligands seem to qualify as superior model systems to mimic the reactivity of metal silylamide complexes on oxo surfaces, i.e., a scenario involving both metal−oxygen bond formation and in situ silylation (Scheme 1). For comparison, only metal−siloxide bonds were formed by the reaction of Y[N(SiMe₃)₂]₃ with a trivalent oligosilasesquioxane,[39] which represents another class of promising model systems.[40] However, both of these model systems emphasize the kinetic and thermodynamic limitations of multivalent molecular oxo model surfaces. Particularly, in the presence of oxophilic, electron-deficient metal centers agglomerization or rearrangement to dimeric and hence higher coordinated metal centers is a predominant reaction pathway in solution.

Reaction of Y[N(SiHMe₂)₂]₃(THF)₂ with Presilylated 2. The reaction of [*p-tert*-butylcalix[4]arene(SiMe₃)₂]H₂ (**2**) with an equimolar amount of Y[N(SiHMe₂)₂]₃(THF)₂ (**4**) in toluene proceeds under fairly mild conditions to give complex **6** as a white powder (Scheme 4). The yield of the hexane-soluble product was ca. 90% based on a molecular composition of {Y[*p-tert*-butylcalix[4]arene(SiMe₃)₂][N(SiHMe₂)₂]}. All of the

THF molecules separated off upon prolonged treatment in vacuo at ambient temperature.

The yttrium-bonded bis(dimethylsilyl)amide ligand is clearly indicated by the SiH stretching vibration at 2069 cm⁻¹ in the IR spectrum and a SiH proton at 5.45 ppm considerably downshifted compared to its synthetic precursor **4** (δ_{SiH} 4.99 ppm). The ¹H NMR spectrum of complex **6** is in agreement with a *cone* (as depicted in Scheme 4) or an *1,3-alternate* conformation. The yttrium-bonded bulky silylamide ligand is supportive of an *exo* isomer; i.e., the yttrium atom is located away from the lower rim of the macrocycle and not into the calixarene cavity. *exo* and *endo* isomers were recently structurally characterized for the mononuclear divalent germanium complex Ge[*p-tert*-butylcalix[4]arene(SiMe₃)₂], displaying a *cone* conformation.[19] A mononuclear structure for **6** could also be rationalized on the basis of structurally characterized {Tm[*p-tert*-butylcalix[4]arene(Me)₂]I(OEt₂)}, which was obtained from the reaction of [*p-tert*-butylcalixarene(Me)₂]H₂ with TmI₂(DME)₃ in THF.[31] This thulium complex also adopts the *cone* conformation. Monocalixarene species were also reported in the case of partially *O*-alkylated analogues, e.g., {Al[*p-tert*-butylcalix[4]arene(Me)₂]Me}[32b] and {Zr[*p-tert*-butylcalix[4]arene(Me)₂]X₂}.[41]

Conclusions

We have shown that silylation and metalation reactions previously observed on silica surfaces can be qualitatively modeled by employing unmodified and modified calix[4]arene as model oxo surfaces. The silylation efficiency on both the model oxo surface and the "real" oxo surface decreases in the order HN(SiHMe₂)₂ > HN(SiMe₃)₂ > HN(SiMePh₂)₂, depending on the steric bulk of the disilazane reagent. Hence, these disilazane silylation experiments are an effective tool to manipulate the calix[4]arene surface for subsequent derivatization reactions. The multifunctional surface reaction of metal silylamides involving silylation and siloxide formation occurs also with the hydroxyl groups of the calix[4]arene platform. As represented for the yttrium amide Y[N(SiHMe₂)₂]₃(THF)₂, silylamine elimination generates adjacent aryloxide and silyl ether moieties. However, the conformational mobility of the calix[4]arene macrocycle decisively limits its applicability as a model for a rigid oxo surface. This was demonstrated for the exclusive isolation of the *1,2-alternate* conformer of [*p-tert*-butylcalixarene(SiHMe₂)₄]. In addition, oxophilic, electron-deficient metal centers tend to agglomerize in solution, forming higher coordinated metal centers as shown for dinuclear [Y{*p-tert*-butylcalix[4]arene(SiHMe₂)}(THF)]₂. Note that it is often the presence of geometrically constrained and coordinatively unsaturated metal centers on a rigid oxo surface which cause enhanced or novel catalytic activity. However, the modeling of mononuclear, nonagglomerated surface metal sites featuring reactive metal ligand moieties seems to be feasible after initial manipulation of the oxo model surface. We consider heteroleptic complexes of the type {Ln[*p-tert*-butylcalix[4]arene(SiMe₃)₂][N(SiHMe₂)₂]} as promising precursor compounds to study secondary surface ligand (silylamide) exchange reactions.

Experimental Section

General Considerations. All compounds were handled with the rigorous exclusion of oxygen and moisture in flame-dried (180 °C) Schlenk-type glassware using standard high-vacuum-line techniques

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or an argon-filled glovebox (MBraun) with O_2/H_2O < 1 ppm. The solvents were dried and distilled by standard methods and stored in a glovebox. Deuterated solvents were obtained from Deutero GmbH and degassed and dried over Na/K alloy. NMR spectra were recorded either on a Bruker DPX-400 (FT, 400 MHz, ^{1}H; 100 MHz, ^{13}C) or on a JEOL JNM-GX-400 (FT, 400 MHz, ^{1}H; 100 MHz, ^{13}C) spectrometer. ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin-Elmer 1650-FTIR spectrophotometer as Nujol mulls. Mass spectra (CI, ionization agent isobutene) were obtained on a Finnigan MAT-90 spectrometer. Elemental analyses were performed in the institute's microanalytical laboratory. *tert*-Butylcalix[4]arene (**1**), 1,1,1,3,3,3-hexamethyldisilazane, and 1,1,3,3-tetramethyldisilazane were purchased from Aldrich. 1,1,3,3-Tetraphenyldimethyldisilazane was acquired from GELEST. All of the disilazane reagents were degassed (freeze–pump–thaw if a liquid) prior to use. Y[N(SiHMe₂)₂]₃(THF)₂ (**4**) and Y[N(SiMe₃)₂]₃ were synthesized according to published procedures.[36]

Synthesis of 25,27-Bis(trimethylsiloxy)-4-*tert*-butylcalix[4]arene (2). Method A. In a glovebox, compound **1** (0.583 g, 0.900 mmol), hexamethyldisilazane (2.905 g, 18.00 mmol), and mesitylene (10 mL) were placed together in a flask equipped with a fused reflux condenser and blow-off valve. After the mixture was stirred for 6 h under reflux conditions (170 °C), the volatiles were removed in vacuo. Subsequent drying under high vacuum (10^{-3} Torr) for 5 h and recrystallization from hexane afforded bis-silylated **2** in the form of colorless crystals suitable for X-ray analysis (0.6172 g, 0.778 mmol, 86%). Anal. Calcd (found) for $C_{50}H_{72}O_4Si_2$: C, 75.70 (75.88); H, 9.15 (9.04) (N, <0.1). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 8.16 (s, 2H, OH), 7.26 (s, 4 H, aromatic H), 6.93 (s, 4 H, aromatic H), 4.56 (d, $^3J_{H-H}$ = 13.0 Hz, 4 H, CH₂), 3.38 (d, $^3J_{H-H}$ = 13.0 Hz, 4 H, CH₂), 1.49 (s, 18 H, *tert*-butyl H), 0.83 (s, 18 H, *tert*-butyl H, 0.38 (s, 18 H, SiCH₃). ^{13}C{^{1}H} NMR (100.5 MHz, benzene-d_6, 25 °C): δ 151.9/145.7/144.9/141.5/130.8/125.8/125.3/125.3 (s, aromatic C), 34.1 (s, *tert*-butyl-C), 33.9 (s, *tert*-butyl-C), 33.5 (s, CH₂), 32.1 (s, *tert*-butyl-CH₃), 30.9 (s, *tert*-butyl-CH₃), 0.48 (s, SiMe). IR (Nujol): 3424 br s, 1598 w, 1363 m, 1303 m, 1285 w, 1261 w, 1252 m, 1201 m, 1125 m, 1100 m, 1026 w, 979 w, 951 w, 942 w, 924 m, 893 s, 871 m, 842 s, 777 m, 752 m, 646 m, 583 w, 554 w, 518 w, 496 w, 440 w cm^{-1}.

Method B. In a round-bottom flask, to a slurry of compound **1** (1.296 g, 2.000 mmol) in 20 mL of toluene was added chlorosilane (0.435 g, 4.000 mmol) dissolved in 10 mL of toluene. Then, NaH (0.096 g, 4.000 mmol) was added in small portions with vigorous stirring. After it was stirred for an additional 24 h at ambient temperature, the reaction mixture was filtrated and the volatiles removed in vacuo. Another sequence of redissolving in toluene, filtering, and drying under vacuum resulted in a white powder, which was recrystallized from toluene to give compound **2** (1.090 g, 1.374 mmol, 68%).

Synthesis of 25,26,27,28-Tetrakis(dimethylsiloxy)-4-*tert*-butylcalix-[4]arene (3). Method A. In a glovebox, compound **1** (0.324 g, 0.500 mmol), tetramethyldisilazane (0.267 g, 2.000 mmol), and toluene (10 mL) were placed together in a flask equipped with a fused reflux condenser and blow-off valve. After the mixture was stirred for 16 h at ambient tmperature, the volatiles were removed in vacuo. Additional drying under high vacuum (10^{-3} Torr) for 5 h and recrystallization from hexane afforded tetrakis-silylated **3** in the form of colorless crystals suitable for X-ray analysis (0.320 g, 0.362 mmol, 72%). Anal. Calcd (found) for $C_{52}H_{80}O_4Si_4$: C, 70.85 (71.04); H, 9.15 (9.11) (N, <0.1). ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ 7.40 (d, $^4J_{H-H}$ = 2.6 Hz, 4 H, aromatic H), 7.16 (d, $^4J_{H-H}$ = 1.8 Hz, 4 H, aromatic H), 5.02 (sp, $^1J_{H-H}$ = 188.3 Hz, $^3J_{H-H}$ = 2.6 Hz, 4 H, SiH), 4.53 (d, $^3J_{H-H}$ = 12.8 Hz, 4 H, CH₂), 4.08 (s, 2 H, CH₂), 3.24 (d, $^3J_{H-H}$ = 12.8 Hz, 2 H, CH₂), 1.42 (s, 36 H, *tert*-butyl-H), 0.01 (d, $^3J_{H-H}$ = 2.6 Hz, 12 H, SiCH₃), −0.17 (d, $^3J_{H-H}$ = 2.6 Hz, 12 H, SiCH₃). ^{13}C{^{1}H} NMR (100.5 MHz, benzene-d_6, 25 °C): δ 149.4/142.4/132.2/130.1/126.3/125.9 (s, aromatic C), 40.0 (s, *tert*-butyl-C), 33.9 (s, *tert*-butyl-C), 33.9 (s, CH₂), 31.6 (s, *tert*-butyl-CH₃), 1.22 (s, SiMe). IR (Nujol): 2126 m (ν_{Si-H}), 1315 w, 1252 m, 1201 m, 1128 w, 952 m, 935 s, 909 s, 864 w, 833 m, 788 m, 772 w, 749 w, 690 w, 668 w, 624 w cm^{-1}. MS (CI): *m/z* 881 (22) [M$^+$], 879 (54) [M$^+$ − H₂], 824 (14) [M$^+$ − SiHMe₂], 821 (100) [M$^+$ − SiH₂Me₂ − H₂], 764 (33) [M$^+$ − 2 SiH₂Me₂ − H₂], 706 (16) [M$^+$ − 3 SiH₂Me₂ − H₂], 648 (7) [M$^+$ − 4 SiH₂Me₂ − H₂].

Method B. In a Schlenk flask, compound **1** (0.649 g, 1.000 mmol) was suspended in 20 mL of toluene and chlorosilane (0.379 g, 4.000 mmol) dissolved in 10 mL of toluene added. Then, NaH (0.0960 g, 4.000 mmol) was added in small portions under vigorous stirring. After it was stirred for an additional 24 h at ambient temperature, the reaction mixture was filtered and the volatiles removed in vacuo. The resulting white powder was recrystallized form toluene to give compound **3** (0.471 g, 0.534 mmol, 53%).

Synthesis of Bis[25-(dimethylsiloxy)-26,27,28′-trioxy-μ₃-(tetrahy-drofuranyttrium(III))-4-*tert*-butylcalix[4]arene] (5). In a glovebox, **1** (1.298 g, 2.000 mmol), **4** (1.260 g, 2.000 mmol), and 40 mL of toluene were placed together in a flask equipped with a fused reflux condenser and blow-off valve. After the mixture was stirred for 4 days, a white precipitate formed, which was separated by filtration and washed with 10 mL of *n*-hexane and 10 mL of toluene. The solid was collected and dried overnight under high vacuum to give 84% of **5** (1.461 g, 1.685 mmol) as a white powder. Anal. Calcd (found) for $C_{50}H_{69}O_5SiY$: C, 79.26 (80.15); H, 4.01 (4.18). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.35 (d, $^4J_{H-H}$ = 2.5 Hz, 2 H, aromatic H), 7.31 (d, $^4J_{H-H}$ = 2.5 Hz, 2 H, aromatic H), 7.00 (s, 2 H, aromatic H), 6.91 (s, 2 H, aromatic H), 5.10 (d, $^3J_{H-H}$ = 17.8 Hz, 2 H, CH₂), 4.73 (br s, 1H, SiH), 4.41 (d, $^3J_{H-H}$ = 18.7 Hz, 2 H, CH₂), 3.68 (br s, 4H, THF), 3.35 (d, $^3J_{H-H}$ = 16.8 Hz, 2 H, CH₂), 3.25 (d, $^3J_{H-H}$ = 17.6 Hz, 2 H, CH₂), 1.50 (s, 18 H, C(CH₃)₃), 1.34 (br s, 4H, THF), 1.04 (s, 9 H, C(CH₃)₃), 0.91 (s, 9 H, C(CH₃)₃), 0.06 (d, 6 H, $^3J_{H-H}$ = 3.7 Hz, SiCH₃). A ^{13}C NMR spectrum of compound **5** could not be recorded due to its low solubility. IR (Nujol): 2194 m (ν_{Si-H}), 1605 w, 1312 m, 1275 w, 1255 w, 1212 m, 1198 m, 1171 w, 1125 w, 1096 w, 1026 w, 969 w, 919 w, 902 m, 872 m, 840 m, 820 w, 794 m, 742 m, 688 w, 555 w, 538 m, 506 w, 449 w, 435 w cm^{-1}.

Synthesis of 25,27-Bis(trimethylsiloxy)-26,27-μ₂-(yttrium(III) bis-(dimethylsilyl)amide)-4-*tert*-butylcalix[4]arene (6). In a glovebox, **2** (0.555 g, 0.700 mmol), **4** (0.441 g, 0.700 mmol), and 20 mL of toluene were placed together in a flask equipped with a fused reflux condenser and blow-off valve. After the mixture was stirred overnight at ambient temperature, the volatiles were evaporated in vacuo. The solid was collected and dried under high vacuum to give 89% of **6** (0.632 g, 0.624 mmol) as a white powder. Anal. Calcd (found) for $C_{54}H_{84}NO_4$-Si₄Y: C, 64.06 (63.87); H, 8.36 (9.50); N, 1.38 (1.48). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.23 (s, 4 H, aromatic H), 6.79 (s, 4 H, aromatic H), 5.45 (sp, $^1J_{Si-H}$ = 174 Hz, $^3J_{H-H}$ = 2.8 Hz, 2 H, SiH), 4.35 (d, $^3J_{H-H}$ = 12.0 Hz, 4 H, CH₂), 3.06 (d, $^3J_{H-H}$ = 12.0 Hz, 4 H, CH₂), 1.48 (s, 18 H, C(CH₃)₃), 0.97 (s, 18 H, C(CH₃)₃), 0.60 (d, $^3J_{H-H}$ = 2.9 Hz, 12 H, NSiCH₃), 0.38 (s, 18 H, OSiCH₃). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 132.8/132.6/130.2/129.5/126.4/126.1/125.2/123.9 (s, aromatic C), 34.1 (s, C(CH₃)₃), 33.9 (s, C(CH₃)₃), 33.5 (s, CH₂), 32.0 (s, C(CH₃)₃), 31.1 (s, C(CH₃)₃), 3.34 (s, NSiCH₃), 0.48 (s, OSiCH₃). IR (Nujol): 2120 (sh) w, 2069 w (ν_{Si-H}), 1335 m, 1321 s, 1258 s, 1213 m, 1169 m, 1120 m, 1090 m, 1021 m, 950 w, 918 s, 893 s, 872 s, 846 s, 824 w, 795 m, 735 w, 681 w, 647 w, 608 w, 541 w, 491 w, 470 w, 439 w, 404 w cm^{-1}.

X-ray Crystallography. General Procedure. Suitable single crystals for the X-ray diffraction studies were grown by standard techniques from saturated solutions of **2** and **3** in hexane at −35 °C and from a saturated solution of **5** in benzene at ambient temperature. Crystal color, shape, and size were colorless, cubic, and 0.25 × 0.25 × 0.25 mm, repectively, for **2** (colorless, plate, and 0.62 × 0.46 × 0.19 mm for **3**; colorless, plate, and 0.50 × 0.40 × 0.15 mm for **5**). All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares calculations. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 42. All calculations were performed on a Linux-PC using the programs Collect,[43] Denzo,[44] SORTAV,[45] Sir92,[46] SHELXL-97,[47] and PLA-TON99.[48] A summary of the crystal and experimental data is reported in Table 4.

(42) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500–502), 4.2.6.8 (pp 219–222), and 4.2.4.2 (pp 193–199),
(43) "Collect" Data Collection Software; Nonius BV, 1998.

Table 4. Crystal Data and Details of the Data Collection and of the Final Structure Refinements for Complexes **2**, **3**, and **5**

	2	**3**	**5**
chem formula	$C_{50}H_{72}O_4Si_2$	$C_{52}H_{80}O_4Si_4$	$C_{100}H_{132}O_{10}Si_2Y_2 \cdot 2C_6H_6$
a (Å)	12.8914(3)	10.1774(2)	13.2625(4)
b (Å)	14.9270(5)	14.1680(2)	14.5894(3)
c (Å)	15.1652(4)	18.7206(2)	17.0458(5)
α (deg)	77.293(2)	95.8195(8)	65.0986(14)
β (deg)	65.019(2)	95.5294(8)	77.8786(8)
γ (deg)	72.234(2)	98.1098(7)	85.5125(13)
V (Å^3)	2505.01(13)	2641.78(7)	2924.71(14)
Z	2	2	1
fw	793.26	881.52	1886.29
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T (°C)	−130(1)	−103(1)	−80(1)
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.052	1.108	1.070
μ (mm^{-1})	0.11	0.15	1.06
R1^a (obsd/all)	0.051/0.064	0.061/0.076	0.051/0.059
wR2^b (all)	0.140	0.168	0.147

^{a} R1 $= \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} wR2 $= [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Crystal Structure Determinations of 2, 3, and 5. Preliminary examinations and data collections were carried out on a Kappa CCD area detecting diffraction system (Nonius; MACH 3) equipped with a rotating anode and Mo Kα radiation (graphite monochromator) using mixed φ- and ω-scans for **2** and **3** (φ-scans for **5**). The unit cell parameters were obtained by full-matrix least-squares refinements of 19 914 (38 419, 23 664) reflections. Data for compounds **3** and **5** are respectively given in parentheses. A total number of 19 914 (38 419, 23 664) reflections were collected. Raw data were reduced and scaled with the program DENZO.[44] Data were corrected for Lorentz and polarization effects. Corrections for absorption effects were applied using SORTAV.[45] After merging a total of 7140 (9838, 11 858) independent reflections remained and were used for all refinements. The θ range was 1.4−27.6° (2.2−25.7, 4.5−28.3°). All "heavy atoms" of the asymmetric unit were refined anisotropically. All hydrogen atoms were placed in calculated positions and included in the structure factor calculations but not refined for **3** and **5**. In the case of compound **2**, all hydrogen atoms were found in the difference map and were refined with restrained isotropic atomic displacement parameters. The number of refinement parameters was 721 (541, 571). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ using the SHELXL-97[47] weighting scheme and stopped at shift/error < 0.001. A potentially accessible area of 487 Å^3 has been calculated for **5**. Due to severe disorder no solvent molecule could be located. Thus, the BYPASS method[49] was applied to account for the disordered solvent contribution to the structure factor in the final refinement. In **3** high residual electron densities of +1.56/−0.70 e Å^{-3} have been observed in close proximity to the silicon atoms Si3 and Si4, indicating an unresolved disorder problem in the corresponding SiHMe$_2$ groups. In **2** and **5** residual electron densities of +0.35/−0.35 and +0.43/−1.06 e Å^{-3} have been observed, respectively.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of compounds **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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