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Published on Web 11/29/2006

Advanced Surface Functionalization of Periodic Mesoporous Silica: Kinetic Control by Trisilazane Reagents

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Abstract: The surface reactions of mesoporous silica MCM-41 with a series of new trisilylamines (trisilazanes) $(SiHMe_2)_2NSiMe_2R$ and $(SiMe_2Vin)_2NSiMe_2R$ (R = indenyl, norpinanyl, chloropropyl, 3-(*N*-morpholin)propyl; Vin = vinyl), disilylalkylamine $(SiHMe_2)$*i*$PrNSiMe_2(CH_2)_3Cl$, and monosilyldialkylamines Me_2NSiMe_2R (R = indenyl, chloropropyl, 3-(*N*-morpholin)propyl) were investigated. ^1H, ^{13}C, and ^{29}Si MAS NMR spectroscopy, nitrogen adsorption/desorption, infrared spectroscopy, and model reactions with calix[4]arene as a mimic for an oxo surface were used to clarify the chemical nature of surface-bonded silyl groups. The trisilylamines exhibited a comparatively slow surface reaction, which allowed for the adjustment of the amount of silylated and nonreacted SiOH groups and led to a stoichiometric distribution of surface functionalities. The 2:1 integral ratio of $SiHMe_2$ and $SiMe_2R$ moieties of such trisilazanes was found to be preserved on the silica surface as indicated by microanalytical as well as ^{13}C and ^{29}Si MAS NMR spectroscopic data of the hybrid materials. For example, the reaction of MCM-41 with $(SiHMe_2)_2NSiMe_2(CH_2)_3Cl$, $(SiHMe_2)$*i*$PrNSiMe_2(CH_2)_3Cl$, and $Me_2NSiMe_2(CH_2)_3Cl$ provided bi- and monofunctional hybrid materials with one-third, one-half, or all chemically accessible silanol groups derivatized by chloropropyl groups, respectively. Thus, a molecular precursor strategy was developed to efficiently control the relative amount of three different surface species, $SiHMe_2$ (or $SiVinMe_2$), $SiMe_2R$, and SiOH, in a single reaction step. The reaction behavior of indenyl-substituted monosilazanes and trisilazanes (R = Ind) with calix[4]arene proved that the indenyl substituent can act as a leaving group forming a dimethylsilyl species, which is anchored bipodally on the silica surface, that is, via two Si—O bonds.

Introduction

Surface functionalization of periodic mesoporous silica (PMS)[1−3] has given broad access to novel inorganic−organic hybrid materials of relevance for catalysis and adsorption processes.[4] Semicrystalline PMSs of the M41S and SBA families are currently investigated as versatile supports for *bioinspired* surface functionalization via tailoring of the local environment and nanoenvironment (= micro- and mesoenvironment) of catalytically active surface sites (Figure 1).[5] Such bioinspired catalysts or *mesozymes* gain enhanced catalytic activity through surface confined metal centers exhibiting steric unsaturation, highly distorted coordination environments, and site isolation.[6−9] Surface organometallic chemistry (SOMC) proved to be a favorable synthesis route for the generation of highly reactive entities.[10] The superb catalytic efficiency of

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† Universitetet i Bergen.
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§ Universität Stuttgart.

(1) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowitz, M. Z.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(2) (a) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324. (b) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(3) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(4) For review articles on the modification of mesoporous silica materials, see: (a) Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 853. (b) Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950. (c) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *111*, 56. (d) Sayari, A.; Hamoudi, S. *Chem. Mater.* **2001**, *13*, 3151. (e) De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615. (f) McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108. (g) Corriu, J. P.; Mehdi, A.; Reye, C. *J. Mater. Chem.* **2005**, *15*, 4285.

(5) Anwander, R. *Chem. Mater.* **2001**, *13*, 4419.

(6) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.

(7) Thomas, J. M.; Raja, R.; Lewis, D. W. *Angew. Chem., Int. Ed.* **2005**, *44*, 6456.

(8) *Nanostructured Catalysts*; Scott, S. L., Crudden, C. M., Jones, C. W., Eds.; Kluwer Academic/Plenum Publishers: New York, 2003.

(9) For examples, see: (a) Juvaste, H.; Pakkanen, T. T.; Iiskola, E. I. *Organometallics* **2000**, *19*, 4834. (b) McKittrick, M. W.; Jones, C. W. *Chem. Mater.* **2003**, *15*, 1132. (c) McKittrick, M. W.; Jones, C. W. *Chem. Mater.* **2005**, *17*, 4758.

(10) For recent reviews on surface organometallic chemistry see: (a) Copéret, C.; Chabanas, M.; Saint-Arroman, R. P.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156. (b) Thieuleux, C.; Coperet, C.; Dufaud, V.; Marangelli, C.; Kuntz, E.; Basset, J. M. *J. Mol. Catal. A: Chem.* **2004**, *213*, 47. (c) For a special issue on surface and interfacial organometallic chemistry, see: *Top. Organomet. Chem.* **2005**, *16*.

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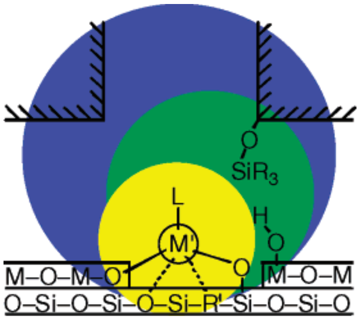


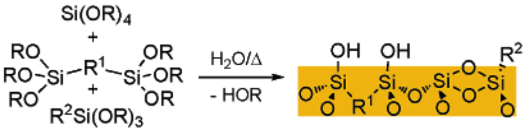
Figure 1. Various environments of surface- and pore-confined immobilized metal (M′)−ligand (L) fragments; the blue, green, and yellow areas indicate the metal's mesoenvironment, microenvironment, and local environment, respectively (adapted from ref 5).

metalloenzymes is often ascribed to a so-called *entatic state* (greek "entasis" = under tension) originating from geometrically distorted metal centers which are stabilized by hemilabile ligands and the protein environment.[11,12] Moreover, the metalloenzyme's protein environment can be "designed" via the nanoenvironment of a PMS-grafted metal center. We and others have previously shown that both the microenvironment and mesoenvironment can affect the selectivity of a catalytic transformation and the stability of highly reactive intermediates, respectively.[13−15]

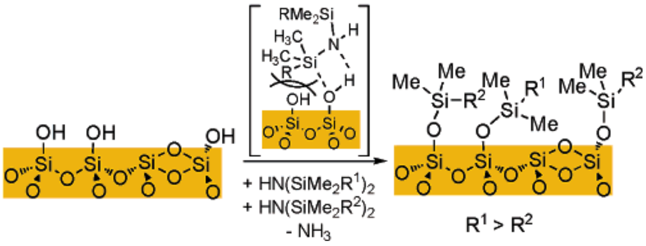
In general, two complementary strategies are pursued to tailor the microenvironment of PMS materials, that is, to decorate the pore walls with organic functionalities (Scheme 1).[4] *Direct* approach **A** utilizes various (organo)siloxane precursors in a one-pot (hydrothermal) sol−gel process.[16−21] This cocondensation (precipitation) method is particularly viable for the incorporation of organic moieties into the pore walls as shown for bifunctional periodic mesoporous organosilicas (BPMO).[22−25] Although this direct approach is proposed to afford a more uniform distribution of functional groups protruding into the channel space, the *postsynthesis* approach **B** allows, in a unique way, the grafting of chemically more precious organic functionalities, prone to hydrolysis and elimination reactions, onto calcined and dehydrated PMSs.[25−28] Another *semi-postsynthesis* method exploits the direct exchange reaction of the surfactant molecules of as-synthesized PMS with silanes.[29]

Scheme 1. General Methods for (Organo)functionalization of Silica[a]

A: *direct approach*



B: *postsynthesis approach*



[a] The bracketed feature in Scheme 1B represents the proposed rate determining reaction intermediate, that is, the formation of the size(R)-dependent S−N−H−O-four-center transposition.

We have recently shown that disilazanes (secondary silylamines or bissilylamines) act as intrinsic silylation reagents under anhydrous conditions featuring (i) mild reaction conditions, (ii) a relatively slow surface reaction, (iii) a monofunctional surface reaction, (iv) favorable atom economy, and (v) ease of thermal desorption and release of excess of silylamine and of the byproduct ammonia.[27] Additionally, *competitive* silylation reactions produced bifunctional surfaces (Scheme 1) and revealed important details of the kinetics of this very silylation reaction supporting a controlled surface functionalization due to steric constraints. Herein we describe an advanced concept of the silazane-based surface silylation exploiting trisilazanes (trisilylamines) as "single-component" precursor compounds for the generation of bifunctional silica surfaces.

Results and Discussion

Initial Reflections and Examinations. The surface reaction of disilazanes (**Dn**) of the type HN(SiR^{1}R$^2_2$)$_2$ revealed that the degree of silylation (silylation efficiency) and hence the surface hydroxyl consumption depend on the steric bulk/shape, that is, the longitudinal and lateral extension of the silyl groups.[27] For example, tetramethyldisilazane, HN(SiHMe$_2$)$_2$ **D2**, passivates all of the silanol groups of a PMS material dehydrated at 270 °C/10^{-5} Torr while the commonly employed hexamethyldisi-

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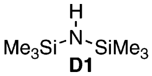
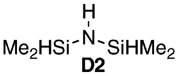
(11) Williams, R. J. P. *J. Mol. Catal.* **1985**, *30*, 1.
(12) Comba, P. *Coord. Chem. Rev.* **2000**, *200*, 217.
(13) (a) Anwander, R.; Palm, C.; Gerstberger, G.; Groeger, O.; Engelhardt, G. *Chem. Commun.* **1998**, 1811. (b) Gerstberger, G.; Anwander, R. *Chem.*—*Eur. J.* **1999**, *5*, 997. (c) Nagl, I.; Widenmeyer, M.; Grasser, S.; Köhler, K.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 1544.
(14) Dufaud, V.; Davis, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9403.
(15) (a) Huh, S.; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 1826. (b) Huh, S.; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *J. Am. Chem. Soc.* **2004**, *126*, 1010.
(16) Sutra, P.; Brunel, D. *Chem. Commun.* **1996**, 2485.
(17) (a) Burkett, S. L.; Sims, S. D.; Mann, S. *Chem. Commun.* **1996**, 1367. (b) Macquarrie, D. J. *Chem. Commun.* **1996**, 1961. (c) Lim, M. H.; Blanford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090. (d) Hall, S. R.; Fowler, C. E.; Lebeau, B.; Mann, S. *Chem. Commun.* **1999**, 201.
(18) (a) Richer, R.; Mercier, L. *Chem. Commun.* **1998**, 1775. (b) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500. (c) Richer, R.; Mercier, L. *Chem. Mater.* **2001**, *13*, 2999.
(19) Huh, S.; Chen, H.-T.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *Chem. Mater.* **2003**, *15*, 4247.
(20) Yang, Q.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 9694.
(21) Fan, H.; Lu, Y.; Stump, A.; Reed, S. T.; Baer, T.; Schunk, R.; Perez-Luna, V.; Lopez, G. P.; Brinker, C. J. *Nature* **2000**, *40*, 56.
(22) Asefa, T.; Kruk, M.; MacLachlan, M. J.; Coombs, N.; Grondey, H.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 8520.
(23) (a) Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. *Chem. Mater.* **2001**, *13*, 4760. (b) Burleigh, M. C.; Jayasundera, S.; Spector, M. S.; Thomas, C. W.; Markowitz, M. A.; Gaber, B. P. *Chem. Mater.* **2004**, *16*, 3.
(24) Xia, Y.; Wang, W.; Mokaya, R. *J. Am. Chem. Soc.* **2005**, *127*, 790.
(25) Alauzun, J.; Mehdi, A.; Reye, C.; Corriu, R. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 8718.
(26) Elings, J. A.; Ait-Meddour, R.; Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 2707.
(27) Anwander, R.; Nagl, I.; Widenmeyer, M.; Engelhardt, G.; Groeger, O.; Palm C.; Röser, T. *J. Phys. Chem. B* **2000**, *104*, 3532.
(28) Kidder, M. K.; Britt, P. F.; Zhang, Z.; Dai, S.; Hagaman, E. W.; Chaffee, A. L.; Buchanan, A. C., III. *J. Am. Chem. Soc.* **2005**, *127*, 6353.
(29) (a) Zhao, X. S.; Lu, G. Q.; Hu, X. *Chem. Commun.* **1999**, 1391. (b) Antochshuk, V.; Jaroniec, M. *Chem. Commun.* **1999**, 2373. (c) de Juan, F.; Ruiz-Hitzky, E. *Adv. Mater.* **2000**, *12*, 430. (d) Antochshuk, V.; Jaroniec, M. *Chem. Mater.* **2000**, *12*, 2496. (e) Ping, H.-P.; Yang, L.-Y.; Mou, C.-Y.; Liu, S.-B.; Lee, H.-K. *New J. Chem.* **2000**, *24*, 253.

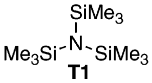
lazane, $HN(SiMe_3)_2$ **D1**, exhibited a silylation efficiency of ca. 80% only under identical conditions.



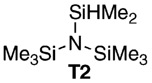
D1



D2



T1



T2

Further to investigate this kinetically controlled surface reaction, we studied trisilazanes **T1**, which is commercially available, and **T2**. The latter was synthesized from $KN(SiMe_3)_2$ and $ClSiHMe_2$ and distilled prior to use. As expected, compound **T1** reacted very slowly with the silanol groups of a dehydrated MCM-41 material. At ambient temperature, significant silylation was observed only after several weeks or at elevated temperatures. In contrast, the sterically less encumbered asymmetric compound **T2** exhibited maximum silylation efficiency (ca. 80%) after 20 h. Interestingly, ^1H MAS NMR spectroscopy (the spectrum is not shown) revealed a highly selective reaction behavior of trisilazane **T2**. Although an excess of **T2** has been employed, the silyl group ratio $SiMe_3/SiHMe_2$ was found to be the same as that of the precursor compound **T2**. Therefore, we rationalized the following surface reactivity for differently substituted (asymmetric) trisilazanes of type $N(SiHMe_2)(SiR^1Me_2)(SiR^2Me_2)$ depending on the steric bulk of the silyl groups ($R^2 > R^1 > H$):

$$\textit{slow}: \quad \text{N(SiHMe}_2)(\text{SiR}^1\text{Me}_2)(\text{SiR}^2\text{Me}_2) + \equiv\text{SiOH} \rightarrow \text{HN(SiR}^1\text{Me}_2)(\text{SiR}^2\text{Me}_2) + \equiv\text{SiOSiHMe}_2 \quad (1)$$

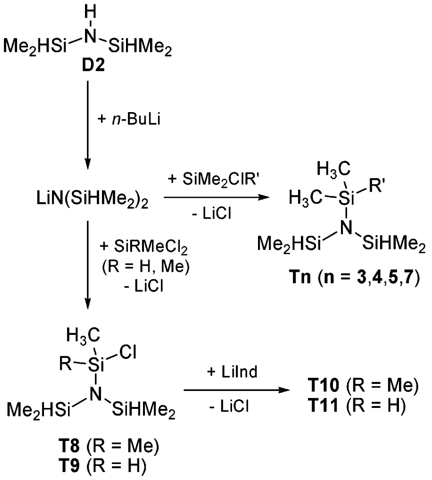
$$\textit{fast}: \quad \text{HN(SiR}^1\text{Me}_2)(\text{SiR}^2\text{Me}_2) + \equiv\text{SiOH} \rightarrow \text{H}_2\text{N(SiR}^2\text{Me}_2) + \equiv\text{SiOSiR}^1\text{Me}_2 \quad (2)$$

$$\textit{very fast}: \quad \text{H}_2\text{N(SiR}^2\text{Me}_2) + \equiv\text{SiOH} \rightarrow \text{NH}_3 + \equiv\text{SiOSiR}^2\text{Me}_2 \quad (3)$$

This way, a regular distribution of different (functional) $\equiv SiOSiRMe_2$ groups on the silica surface can be accomplished. Additionally, the inital low-rate surface reaction (1) favors a regular chemisorption of the trisilazane throughout the primary particles, counteracting an exclusive diffusion-controlled surface reaction. In the present study, we demonstrate that this approach can be also applied for trisilazane derivatives $N(SiHMe_2)_2(SiRMe_2)$ featuring chiral and chemically labile functionalities (expected silyl group surface population = 2:1).

Trisilazane and Monosilazane Library. The synthesis and reactivity of trisilazanes (**Tn**) were for the first time systematically explored by Wannagat and Niederprüm.[30] Accordingly, a large number of compounds $N(SiR_3)_3$ are known with a variety of substitution patterns (R = H, alkyl, or aryl). With increasing steric bulk of the substituents at the silicon atoms, the trisilazanes display remarkable stability toward hydrolysis. For example, tris(trimethylsilyl)amine **T1** can be treated in boiling OH^- solutions without decomposition (cf., our findings on its nonreactivity toward surface silanol groups). This inert nature allows for chemical transformations at the silicon substituents under rather harsh reaction conditions without destroying the NSi_3 moiety. The synthesis of mono- and disilazanes is usually achieved by reacting chlorosilanes $ClSiR_3$ with an excess of ammonia or primary or secondary amines. However, this route is only feasible for the smallest trisilazanes $(SiH_3)_3N$ and $(SiH_2Me)_3N$,[31] while larger silyl groups require stronger nucleophiles.

Scheme 2. Synthesis of Trisilylamines **Tn**[a]



[a] R′ = norpinanyl, 3-chloropropyl, *N*-propylmorpholine.

The use of alkali metal disilazides as nucleophiles provides an efficient entry to trisilazanes.[30] Such silylamides $LiN(SiR_3)_3$ can be obtained in nearly quantitative yield via deprotonation of the silylamine with butyllithium. The reaction of $LiN(SiR_3)_2$ with chlorosilanes $ClSiR_3$ gave the trisilazanes in high yields (Scheme 2). The synthesis of the norpinanyl-, chloropropyl-, and *N*-morpholinpropyl-substituted trisilazanes **T3**, **T4**, and **T5** was accomplished via this route, utilizing $LiN(SiHMe_2)_2$ and (3-norpinanyl)dimethylchlorosilane, (3-chloropropyl)dimethylchlorosilane, and (3-*N*-morpholinpropyl)dimethylchlorosilane as electrophiles, respectively. The latter chlorosilane was synthesized by the hydrosilylation of *N*-allylmorpholine with dimethylchlorosilane using Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex). Correspondingly, trisilazane **T6** was obtained from $LiN(SiMeVin_2)_2$[32] and (3-chloropropyl)dimethylchlorosilane. Reaction of the chloropropyl-substituted trisilazane **T4** with the nucleophilic amine diazabicyclooctane (DABCO) in toluene under reflux conditions gave ammonium chloride **T7** via precipitation from the solution.

Alternatively, secondary functional groups can be introduced as nucleophiles into a trisilazane molecule by reaction of organolithium compounds with trisilazanes $(SiHMe_2)_2NSiMe_2Cl$ **T8** and $(SiHMe_2)_2NSiHMeCl$ **T9**.[30] This approach was employed for the synthesis of trisilazanes **T10** and **T11** with indenyl lithium as a nucleophile (Scheme 2).

The monosilylamines **M1**−**M4** and the disilazane **D3** were obtained from the reaction of $LiNMe_2$ and $LiN\textit{i}Pr(SiHMe_2)$[33] with the corresponding chlorosilanes, respectively.[34]

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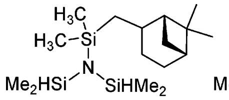
(30) Wannagat, U.; Niederprum, H. *Z. Anorg. Allg. Chem.* **1961**, *308*, 337.

(31) Ebsworth, E. A. V.; Emeleus, H. J. *J. Chem. Soc.* **1958**, 2150.

(32) Wright, J. M.; Jones, G. B. *Tetrahedron Lett.* **1999**, *40*, 7605.

(33) Wiseman, G. H.; Wheeler, D. R.; Seyferth, D. *Organometallics* **1986**, *5*, 146.

(34) For the functionalization of PMS materials with commercially available monosilazanes, see: (a) Brutchey, R. L.; Ruddy, D. A.; Andersen, L. K.; Tilley, T. D. *Langmuir* **2005**, *21*, 9576. (b) Helmy, R.; Kazakevich, Y.; Ni, C.; Fadeev, A. Y. *J. Am. Chem. Soc.* **2005**, *127*, 12446.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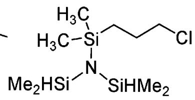
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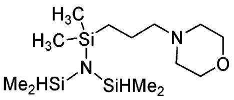
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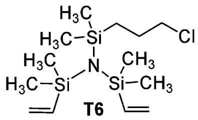
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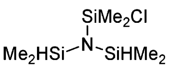
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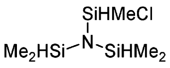
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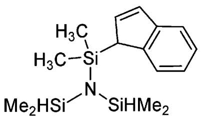
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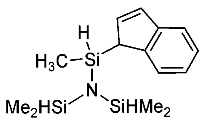
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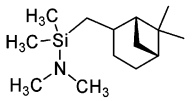
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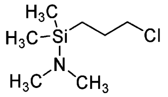
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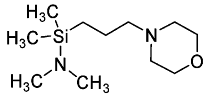
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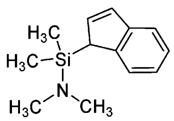
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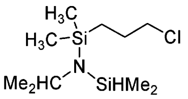
D3

Surface Reactions of Mono-, Di- and Trisilazanes. Our studies dealing with the surface reactions of disilazanes HN-$(SiMe_2R)_2$ **Dn** revealed a gradual decrease of overall reaction rate and silylating efficiency with an increasing steric bulk of R.[27] We assume that the reaction proceeds via a four-membered cyclic transition state, with the nitrogen atom abstracting a proton of a surface SiOH group and simultaneously the surface oxygen attacking as a nucleophile at one of the disilazane's silicon atoms (Scheme 1). In trisilazanes the basicity of the central nitrogen atom is reduced due to the covalent bond to a third SiR_3 moiety. The formation of a four-membered transition state on the silica surface is hampered by the larger steric demand of the molecules. Therefore the surface reactivity of trisilazanes is markedly reduced compared to mono- and disilazanes.

A noticeable silylation of dehydrated MCM-41-**b** with $(SiMe_2H)_2NSiMe_2(C_{10}H_{17})$ **T3** could only be observed after 5 days at ambient temperature (Table 1). The reaction was easily followed by FTIR spectroscopy by examining the decrease of the sharp band of the SiOH stretching vibration at 3695 cm^{-1} and the concomitant appearance of a band at 2145 cm^{-1}, indicative of surface-bonded SiH moieties.[35] In contrast, the reaction of the monosilylamine $Me_2NSiMe_2(C_{10}H_{17})$ **M1** with MCM-41-**a** results in the silylation of ca. 86% of surface SiOH groups within 5 d (Table 1). The slow reaction rate of **T3** ensures that the norpinanyl groups are homogeneously distributed over the MCM-41 pore surface simultaneously ruling out a local enrichment of this surface functionality due to diffusion constraints. The amount and density of norpinanyl groups and of nonreacted SiOH groups can be adjusted by controlling the reaction time rather than the concentration of the silylating reagent. Many heterogeneous catalysts exhibit enhanced activity and selectivity if the catalytically active centers are highly dispersed on the support surface (single site catalysts).[36−38] One method to achieve this is the application of very large grafting precursors which act as place-marker/patterning molecules between catalytically active sites.[6−9]

A characteristic feature of our trisilazane approach is the fact that two different surface functionalities (here: the norpinanyl dimethylsiloxy and dimethylsiloxy groups) can be grafted in a single grafting step. The ^1H and ^{13}C MAS NMR spectra of **T3**@MCM-41-**b** show signals for the norpinanyl group (^{13}C: δ (ppm) = 18.89, 22.23, 25.53, 30.78, 39.52, 41.66, 49.64), for $SiHMe_2$ surface functionalities (^1H: δ (ppm) = 0.02, 4.49; ^{13}C: −2.02 ppm), and for SiOH groups (^1H: δ (ppm) = 1.78) (Figure 2).

The ^{29}Si MAS NMR spectrum of **T3**@MCM-41-**b** (Figure 2) exhibits intense signals for the SiO_4 connectivities of the MCM-41 pore walls at −108.8 (Q_4) and −99.7 ppm (Q_3) and two smaller signals, which are shifted to lower field, at 0.28 and 14.42 ppm. The latter signals can be ascribed to the silicon atoms of the *Si*HMe_2 and *Si*$Me_2(C_{10}H_{17})$ groups, respectively. The most striking feature of the silicon NMR spectrum is the integral ratio of approximately 2:1 of the $SiHMe_2$ and $SiMe_2(C_{10}H_{17})$ resonances. The relative amount of different silicon bearing moieties of the trisilazane reagent is preserved on the MCM-41 surface, even when the trisilazane reagent is used in excess relative to the surface silanol groups SiOH. Therefore, the 2:1 ratio of the different surface functionalities cannot be explained by assuming that all molecules with silylation potential, which are present in the solution, react with the surface of MCM-41. A more detailed mechanistic description must be considered. The first reaction step is the transfer of a silicon-bearing group from the chemisorbed precursor **T3** onto the silica surface. It is very likely that this group is one of the sterically less demanding $SiHMe_2$ moieties. The reaction generates a disilazane $HN(SiHMe_2)(SiMe_2C_{10}H_{17})$ which is converted to the monosilazane $H_2NSiMe_2(C_{10}H_{17})$ by attaching another $SiHMe_2$ group to the support material. Finally, the monosilazane reacts with a silanol group and liberates NH_3. According to our previous knowledge about the relative reactivity of mono-, di- and trisilazanes, the first reaction step including the trisilazane reagent **T3** is the slowest one and therefore rate determining for the entire reaction sequence. In contrast, the surface silylation of the intermediate mono- and disilazanes proceeds very fast, and the concentration of these silylamine species in solution remains low throughout the course of the reaction. Each trisilazane molecule which transfers one of its silyl groups to the MCM-41 pore surface inevitably reacts with two further SiOH groups to attach its remaining silyl groups to the silica surface. In this way, the 2:1 integral ratio of different surface functionalities is established from the very beginning of the reaction and is independent of the overall degree of surface derivatization.

To broaden the scope of this single-source precursor strategy for the synthesis of bifunctional mesoporous hybrid materials, we investigated the surface reaction of three different silylating reagents bearing chloropropyl groups: monosilylamine $Me_2NSiMe_2(CH_2)_3Cl$ **M2**, disilylamine *i*Pr$(SiHMe_2)NSiMe_2(CH_2)_3Cl$ **D3**, and trisilylamine $(SiHMe_2)_2NSiMe_2(CH_2)_3Cl$ **T4**. The chloropropyl group is widely used as a linker functionality for

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(35) Anwander, R.; Roesky, R. *J. Chem. Soc., Dalton Trans.* **1997**, *2*, 137.
(36) Jarupatrakorn, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 8380.
(37) McKittrick, M. W.; Jones, C. W. *J. Am. Chem. Soc.* **2004**, *126*, 3052.
(38) Vassylyev, O.; Chen, J.; Panarello, A. P.; Khinast, J. G. *Tetrahedron Lett.* **2005**, *46*, 6865.

Table 1. Analytical Data, Surface Area, Pore Volume, and Pore Diameter of MCM-41 Materials

		elemental analysis		N_2 physisorption		
sample[a]	silylating reagent	C/wt %	Cl/wt %	$a_{s,BET}$[b]/$m^2\ g^{-1}$	V_p[c]/$cm^3\ g^{-1}$	d_p[d]/nm
MCM-41-**a**				1110	1.23	3.6
M1@MCM-41-**a**	$Me_2NSiMe_2(C_{10}H_{17})$	25.59		510	0.41	2.8
MCM-41-**b**				1000	0.95	3.3
T3@MCM-41-**b**	$(SiHMe_2)_2NSiMe_2(C_{10}H_{17})$	8.47		810	0.66	3.0
MCM-41-**c**				1160	1.27	3.6
M2@MCM-41-**c**	$(Me_2N)SiMe_2(CH_2)_3Cl$	13.27	7.90	670	0.65	3.1
T4@MCM-41-**c**	$(SiHMe_2)_2NSiMe_2(CH_2)_3Cl$	7.02	1.79	980	0.99	3.5
D3@MCM-41-**c**	$(SiHMe_2)i PrNSiMe_2(CH_2)_3Cl$	9.80	3.07	870	0.85	3.2
T6@MCM-41-**c**	$(SiMeVin_2)_2NSiMe_2(CH_2)_3Cl$	7.59	1.84	910	0.92	3.3
MCM−41-**d**				1030	1.20	3.5
M3@MCM−41-**d**	$(Me_2N)SiMe_2(CH_2)_3(NC_4H_8O)$	18.21		590	0.58	2.9
T5@MCM−41-**d**	$(SiHMe_2)_2NSiMe_2(CH_2)_3(NC_4H_8O)$	7.45		880	0.94	3.3

[a] Pretreatment conditions: 250 °C (MCM-41)/100 °C (silylated materials), 2.5 h, 10^{-3} Torr. [b] Specific BET surface area. [c] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [d] Pore diameter according to the maximum of the BJH pore size distribution calculated from the desorption branch.

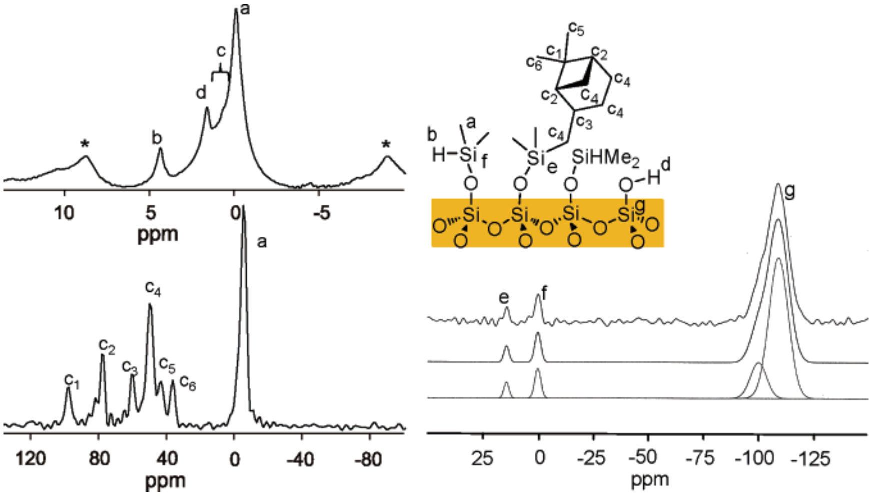

Figure 2. MAS NMR spectra of **T3**@MCM-41-**b**. (Upper left) ^1H; (lower left) ^{13}C; (right) ^{29}Si; experimental (upper trace), simulated (middle trace), Lorentzian lines (lower trace).

the immobilization of homogeneous catalysts.[39−41] As expected the monosilazane **M2** employed in a 1.5-fold excess relative to the SiOH groups reacted quantitatively with the surface of MCM-41-**c** within 48 h. The reaction of disilazane **D3** with MCM-41-**c** yielding hybrid material **D3**@MCM-41-**c** gave complete silylation of all IR-detectable silanol groups after 5 days. Trisilazane **T4** exhibited only an incomplete reaction at ambient temperature after 5 days; however, under reflux conditions in toluene as a solvent, surface silylation proceeded almost quantitatively after 6 h. The superior reactivity of *i*Pr-$(SiHMe_2)NSiMe_2(CH_2)_3Cl$ **D3** compared with trisilazane **T4** is probably due to the reduced steric bulk of the isopropyl group and the higher basicity of the nitrogen atom. The resulting hybrid materials displayed an increasing density of chloropropyl groups in the order **T4**@MCM-41-**c** < **D3**@MCM-41-**c** < **M2**@MCM-41-**c**. This is reflected in a gradual increase of the amount of chlorine found by elemental analysis (Table 1).

Nitrogen physisorption measurements of the hybrid materials as well as of the MCM-41 parent material gave adsorption and desorption isotherms of type IV according to the IUPAC nomenclature (Figure 3). This type of isotherm is characteristic of PMS materials. The functionalized hybrid materials exhibit a considerably decreased BET surface area, specific pore volume, and pore diameter (Table 1). As the spatial extension and the molar weight of the $SiMe_2(CH_2)_3Cl$ group are much higher compared to those of $SiHMe_2$, the values of the specific pore parameters decrease with increasing chloropropyl content of the hybrid materials. Hence, **M3**@MCM-41-**c**, which is completely silylated with $SiMe_2(CH_2)_3Cl$, possesses the smallest pores (3.1 nm) in this series of hybrid materials, while the channels of **D3**@MCM-41-**c** (3.2 nm) and **T4**@MCM-41-**c** (3.5 nm) are of a larger diameter corresponding to a higher amount of grafted dimethylsiloxy groups. In addition to an efficient control of total quantity, surface density, and relative amount of different grafted functional groups, the single-source precursor strategy facilitates mesopore size engineering.

Figure 4 shows the ^1H and ^{13}C MAS NMR spectra of chloropropyl-derivatized hybrid materials **T4**@MCM-41-**c** (a), **D3**@MCM-41-**c** (b), and **M2**@MCM-41-**c** (c). A quantitative analysis of the ^1H NMR spectra is difficult because of the highly overlapping signals. However, the signal intensities of the SiH protons (4.79 ppm, $SiHMe_2$) and the protons in α-position to the chlorine atom (3.62 ppm, CH_2Cl,) can be qualitatively compared. The spectra clearly indicate a gradual increase of the integral ratio $SiHMe_2/SiMe_2(CH_2)_3Cl$ from hybrid material

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(39) Fuerte, A.; Corma, A.; Sanchez, F. *Catal. Today* **2005**, *107*, 404.
(40) Chen, H.-T.; Huh, S.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *J. Am. Chem. Soc.* **2005**, *127*, 13305.
(41) Zhang, Y.; Fei, J.; Yu, Y.; Zheng, X. *Catal. Commun.* **2004**, *5*, 643.

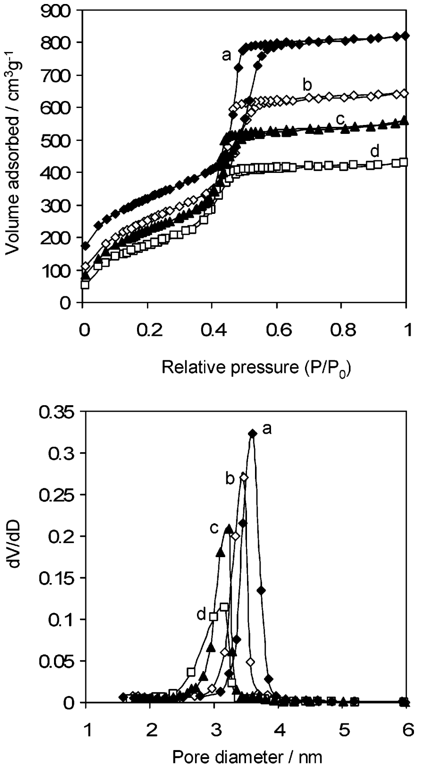

Figure 3. N_2 physisorption isotherms and corresponding pore size distributions of MCM-41-**c** (a), **T4**@MCM-41-**c** (b), **D3**@MCM-41-**c** (c), and **M2**@MCM-41-**c** (d).

D3@MCM-41-**c** (theor. 1/1) to hybrid material **T4**@MCM-41-**c** (theor. 2/1). This trend is supported by the ^{13}C NMR spectra (SiH*Me*$_2$: 0.5 ppm; *C*H$_2$*C*H$_2$*C*H$_2$Cl: 14.7, 26.5, 46.4 ppm).

The reaction of $(SiMe_2Vin)_2NSiMe_2(CH_2)_3Cl$ **T6** with MCM-41-**c** simultaneously forms two distinct synthetically versatile surface species, chloropropyl and vinyl groups, which can be independently modified by subsequent transformations.[42] Compound **T6** is the sterically most demanding trisilazane used in this study and therefore exhibited the lowest reactivity toward PMS MCM-41. Extensive surface functionalization was only achieved after 15 h in refluxing toluene; however, the IR spectrum of **T6**@MCM-41-**c** still showed a band in the region of the SiOH stretching vibration. In the ^{1}H MAS NMR spectrum of hybrid material **T6**@MCM-41-**c** (Figure 5), the signals for the protons of the C*H*C*H*$_2$ vinyl group (5.90, 6.08 ppm) and for the ClCH$_2$ fragment (3.62 ppm) appear with the expected integral ratio of approximately 3:1 (Figure 5). Accordingly, the ^{29}Si MAS NMR spectrum of **T6**@MCM-41-**c** shows signals for the different surface-bonded silicon atoms at 1.94 ppm (*Si*Me$_2$Vin) and 13.57 ppm (*Si*Me$_2$(CH$_2$)$_3$Cl) with an integral ratio of approximately 2:1 (Supporting information).

The morpholine-substituted mono- and trisilazanes **M3** and **T5** revealed similar silylating efficiency and reactivity trends as outlined above for the chloropropyl reagents (Supporting Information and Table 1).

Surface Reactions of Indenyl-Bearing Silylamines and Use of Calix[4]arene Model Surfaces. Indene compounds are widely used ligand precursors for the synthesis of metallocene complexes.[43,44] Particularly, silicon-linked indenes attract high interest in *ansa*-bridged metallocenes of the early transition metals,[45,46] which are of considerable relevance for olefin polymerization. Many commercially used polymerization catalysts are employed in immobilized form. Catalytically active metal centers may be directly grafted to a silica support via stable metal−oxygen−silicon bonds[47,48] or the metal complex is linked ("tethered") to the surface via covalent bonds between a complex ligand and the silica material.[49,51] For the latter approach surface-bonded indenyl groups are useful linker functionalities for the complexation of transition metals. As important properties of polymers like polydispersity, tacticity, and molar mass are influenced by the nature of the catalytically active metal center, the synthesis of tailor-made support materials with controlled density and surface distribution of functional groups is highly desirable.

We investigated the reaction of indene-substituted silylamines $(SiHMe_2)_2N(SiMe_2Ind)$ (**T10**), $(SiHMe_2)_2N(SiHMeInd)$ (**T11**), and $Me_2N(SiMe_2Ind)$ (**M4**) with MCM-41-**b** in order to obtain support materials with different concentrations of indene moieties. In accordance with our previous results, the monosilazane **M4** reacts with the pore surface of the mesoporous silica within 5 days to form a completely silylated hybrid material. Surprisingly, the integral ratio of the aromatic indene protons and the SiMe methyl protons in the ^{1}H MAS NMR spectrum of **M4**@MCM-41-**b** was significantly lower than expected if OSiMe$_2$Ind groups are considered as the only species present on the silica surface (Figure 6). In addition, the 16.58 wt % of carbon found by elemental analysis for **M4**@MCM-41-**b** was much lower than the theoretically predicted value of ca. 37 wt %, which can be calculated from the total amount of surface silanol groups of the MCM-41 parent material.

In order to gain more information about the chemical nature of the surface species in **M4**@MCM-41-**b**, we studied the reaction of monosilylamine **M4** with calix[4]arene **C1** as a model oxo surface.[52−55] The pK_a value of the hydroxyl groups in calix[4]arene[56] is similar to the pK_a value found for SiOH groups on silica surfaces, and a distance of 2.8−3.2 Å[57] between

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(42) For the modification of surface-bonded vinyl groups, see: (a) Asefa, T.; Kruk, M.; MacLachln, M. J.; Coombs, N.; Grondey, H.; Jaroniec, M; Ozin, G. A. *Adv. Funct. Mater.* **2001**, *11*, 447. (b) Wang, Y.; Yang, C.-M.; Schmidt, W.; Spliethoff, B.; Bill, E.; Schueth, F. *Adv. Mater.* **2005**, *17*, 53.

(43) (a) *Ziegler Catalysts*; Fink, G., Mühlhaupt, R., Brintzinger, H.-H., Eds.; Springer-Verlag: Berlin, 1995. (b) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (d) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

(44) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217.

(45) Fujita, M.; Seki, Y.; Miyatake, T. *Macromol. Chem. Phys.* **2005**, *206*, 2278.

(46) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080.

(47) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

(48) For examples, see: (a) Tudor, J.; O'Hare, D. *Chem. Commun.* **1997**, 603. (b) Van, Looveren, L. K.; Geysen, D. F. M. C.; Vercruysse, K. A. L.; Wouters, B. H. J.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 517. (c) Kageyama, K.; Tamazawa, J.; Aida, T. *Science* **1999**, *285*, 2113. (d) Anwander, R.; Nagl, I.; Zapilko, C.; Widenmeyer, M. *Tetrahedron* **2003**, *59*, 10567. (e) Fischbach, A.; Klimpel, M. G.; Widenmeyer, M.; Herdtweck, E.; Scherer, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2234.

(49) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friederichs, N. *Chem. Rev.* **2005**, *105*, 4073.

(50) Kim, I.; Han, B. H.; Kim, J. S.; Ha, C.-S. *Catal. Lett.* **2005**, *101*, 249.

(51) Britcher, L.; Rahiala, H.; Hakala, K.; Mikkola, P.; Rosenholm, J. B. *Chem. Mater.* **2004**, *16*, 5713.

(52) Floriani, C.; Floriani-Moro, R. *Adv. Organomet. Chem.* **2001**, *47*, 167.

(53) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **2000**, *122*, 538.

(54) Floriani, C. *Chem.*—*Eur. J.* **1999**, *5*, 19.

(55) Bass, J. D.; Solovyov, A.; Pascall, A. J.; Katz, A. *J. Am. Chem. Soc.* **2006**, *128*, 3737.

(56) (a) Shinkai, S. *Tetrahedron* **1993**, *40*, 8933. (b) Araki, K.; Iwamoto, K.; Shinkai, S.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3480.

(57) Anwander, R.; Eppinger, J.; Nagl, I.; Scherer, W.; Tafipolsky, M.; Sirsch, P. *Inorg. Chem.* **2000**, *39*, 4713.

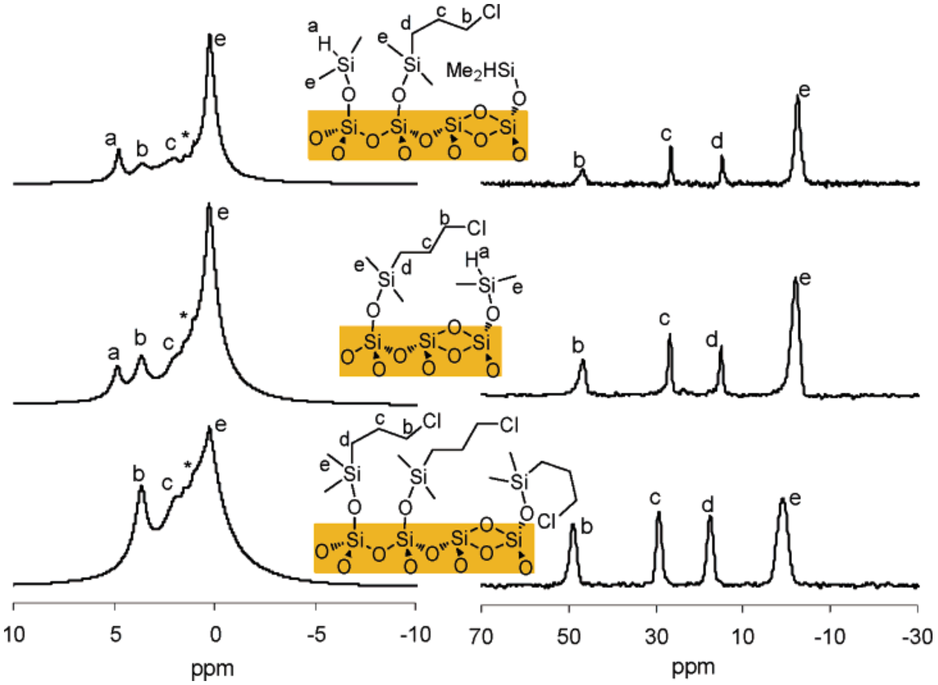

Figure 4. ^{1}H and ^{13}C MAS NMR of hybrid materials **T4**@MCM-41-**c** (a), **D3**@MCM-41-**c** (b), and **M2**@MCM-41-**c** (c) (★ = hexane).

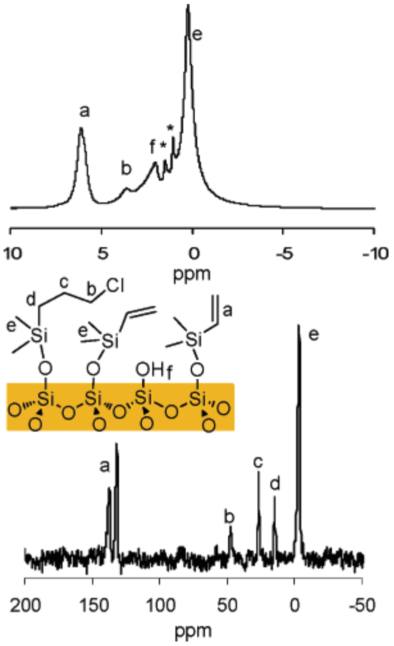

Figure 5. ^{1}H and ^{13}C MAS NMR spectra of hybrid material **T6**@MCM-41-**c** (★ = hexane).

two neighboring phenolic OH moieties is comparable to the density of silanols in dehydrated MCM-41 (1.69 OH/nm^{2}).

The reaction of Me_2NSiMe_2Ind (**M4**) with calix[4]arene **C1** yielded after 24 h at ambient temperature in hexane solution a single product in 27% yield, which was identified by NMR spectroscopy and elementary analysis as the dimethylsilyl-bridged calix[4]arene compound **C2** (Scheme 3).[58]

The formation of functionalized calix[4]arene **C2** can be rationalized by considering a two-step process: (i) Me_2NSiMe_2-Ind **M4** reacts with calix[4]arene to form the monosilylated intermediate product **C2′**. (ii) The silicon-bonded indene moiety

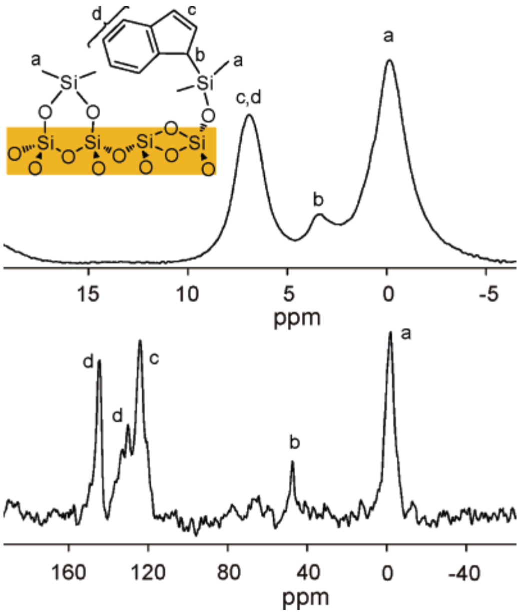

Figure 6. ^{1}H and ^{13}C MAS NMR spectra of hybrid material **M4**@MCM-41-**b**.

acts as a leaving group and is displaced by one of the neighboring hydroxyls establishing a second Si−O bond. The intermediate product **C2′** could not be isolated. It is very likely that a similar reaction takes place on the surface of MCM-41, if a silanol group is located in close proximity to an $O-SiMe_2Ind$ species. A high amount of unreacted silanol groups should favor this secondary surface reaction. Therefore, a less reactive silylamine, featuring a lower silylation efficiency, should exhibit an even more pronounced tendency for the elimination of HInd. Indeed, for the reaction of the trisilazane $(SiHMe_2)_2NSiMe_2$-Ind (**T10**) with MCM-41-**b** yielding hybrid material **T10**@MCM-41-**b**, only <50% of the trisilazane's indene groups were attached to the silica surface, as calculated from carbon analysis (Table 2).

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[58] Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216.

Scheme 3. Model Reaction of $Me_2N(SiMe_2Ind)$ **M4** with Calix[4]arene **C1**

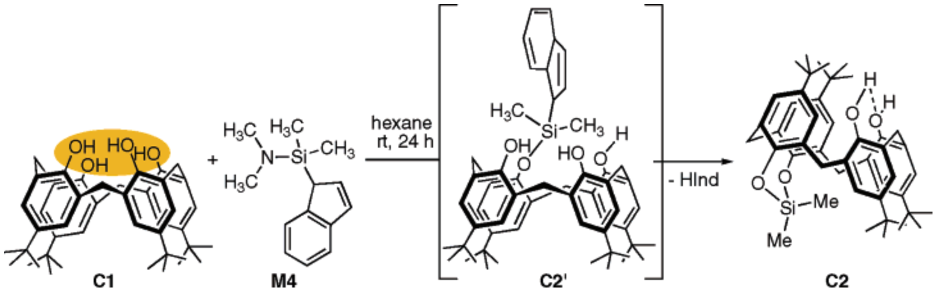

Table 2. Analytical Data, Surface Area, Pore Volume, and Pore Diameter of Indene-Grafted Hybrid Materials

		elemental analysis	N_2 physisorption		
sample[a]	silylating reagent	C/wt %	$a_{s,BET}$[b]/m^2 g^{-1}	V_p[c]/cm^3 g^{-1}	d_p[d]/nm
MCM-41-**b**			1000	0.95	3.3
M4@MCM-41-**b**	Me_2NSiMe_2Ind	16.58	670	0.47	2.6
T10@MCM-41-**b**	$(SiHMe_2)_2N(SiMe_2Ind)$	6.52	810	0.68	3.0
T11@MCM-41-**b**	$(SiHMe_2)_2N(SiMeHInd)$	5.32	920	0.77	3.1

[a] Pretreatment conditions: 250 °C (MCM-41)/100 °C (silylated materials), 2.5 h, 10^{-3} Torr. [b] Specific BET surface area. [c] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [d] Pore diameter according to the maximum of the BJH pore size distribution calculated from the desorption branch.

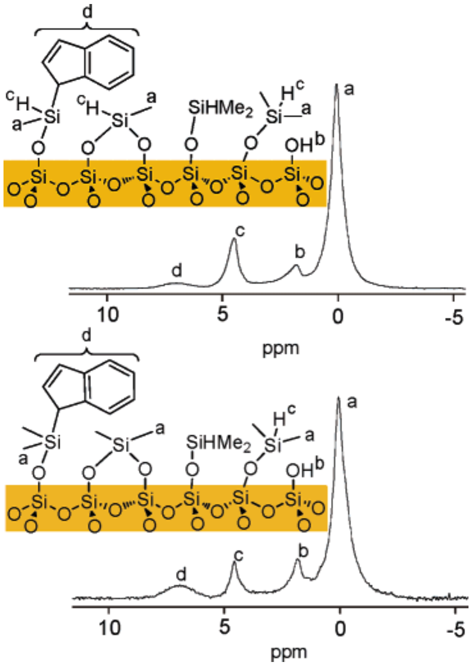

Figure 7. ^1H MAS NMR spectra of hybrid materials **T10**@MCM-41-**b** (bottom) and **T11**@MCM-41-**b** (top).

The resonance for the aromatic protons in the ^1H NMR spectrum appeared as a broad signal (Figure 7). The nucleophilic attack of a surface silanol at the silicon atom of an $OSiMe_2Ind$ group is further facilitated, if the steric bulk at the electrophilic silicon atom is decreased. This is the case for the surface reaction of $(SiHMe_2)_2N(SiHMeInd)$ **T11** with MCM-41-**b** (Scheme 4). The signal for the aromatic protons in hybrid material **T11**@MCM-41-**b** has almost vanished, indicating an efficient elimination of HInd.

It is well-known that organosilicon compounds bearing a double bond in β-position to a silicon atom are prone to cleavage of the silicon−carbon bond. A prominent example is the Lewis acid catalyzed Mukaiyama aldol reaction of allyltrimethylsilanes.[59] Shimada et al. used this kind of reactivity for the immobilization of complex organic functionalities on silica surfaces.[60] Despite the fact that immobilized indenyl groups are widely used as ligands in heterogeneous catalysis,[49,61−63] the herein described elimination reaction has not been considered until now.

Conclusion

We have developed a generally feasible single-source precursor strategy for the synthesis of bifunctional mesoporous silica materials. New trisilazane reagents $(SiR_1R_2R_3)_3N$ give broad access to a variety of surface functionalities of relevance for catalysis and adsorption/separation processes. Such trisilazanes exhibit a slow and highly selective surface reaction with the resulting bifunctionalized silica surface reflecting the relative amount of different silyl groups of the precursor. Accordingly, mesoporous silica hybrid materials with a homogeneous distribution of surface-attached dimethylsilyl, dimethyl(chloropropyl)silyl, dimethylvinylsilyl, dimethyl(*N*-morpholinpropyl)silyl, and chiral dimethylnorpinanylsilyl groups can be obtained. Particularly, the dimethyl(chloropropyl)silyl and dimethylvinylsilyl have been previously shown to be prone to secondary or subsequent Cl → X and Vin → functional group transfer. Mono- and trisilazanes with indene functionalities react with silica surfaces under partial “loss” of indene groups. This surface reaction could be clarified by means of calix[4]arene as a model oxo surface. The indene moieties of surface-bonded silyl groups act as leaving groups generating secondary siloxane bridges on the surface.

Experimental Section

All of the silylated PMS hybrid materials were synthesized from dehydrated MCM-41 silicas and manipulated with rigorous exclusion of air and water, using high-vacuum and glovebox techniques (MB

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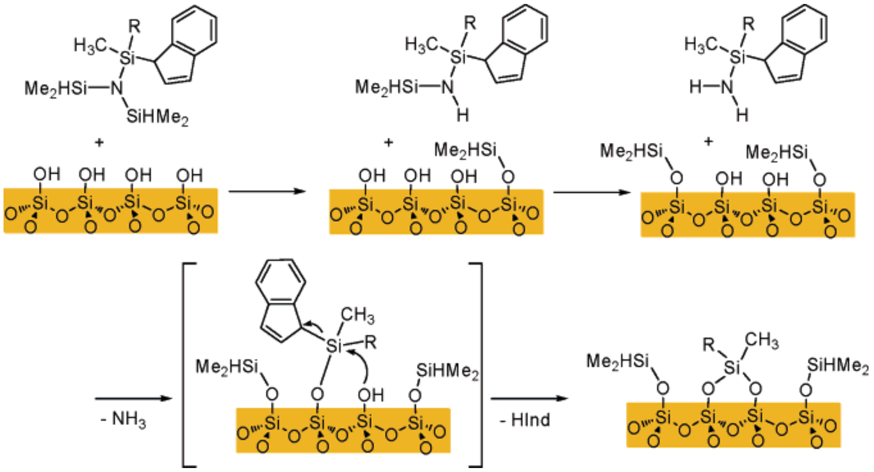
(59) Bach, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 417.
(60) Shimada, T.; Aoki, K.; Shinoda, Y.; Nakamura, T.; Tokunaga, N.; Inagaki, S.; Hayashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 4688.
(61) dos Santos, J. H. Z.; Ban, H. T.; Teranishi, T.; Uozumi, T.; Sano, T.; Soga, K. *Appl. Catal. A* **2001**, *220*, 287.
(62) Schneider, H.; Puchta, G. T.; Kaul, F. A. R.; Raudaschl-Sieber, G.; Lefebvre, F.; Saggio, G.; Mihalios, D.; Herrmann, W. A.; Basset, J. M. *J. Mol. Catal. A* **2001**, *170*, 127.
(63) Miller, C. J.; O’Hare, D. *Chem. Commun.* **2004**, *15*, 1710.

Scheme 4. Proposed Surface Reactions of Trisilazane **T10** (R = Me) and **T11** (R = H) with Dehydrated MCM-41



Braun MB150B-G-II; $O_2 < 1$ ppm, $H_2O < 1$ ppm). Hexane, THF, and toluene were purified by using Grubbs columns (MBraun SPS, solvent purification system). All solvents were stored in a glovebox. Reagents were obtained from commercial suppliers and used without further purification: tetraethylorthosilicate (Fluka), hexadecylbromide (Fluka), (3-bromopropyl)trimethylammonium bromide (Aldrich), tetramethylammonium hydroxide (Aldrich, 25 wt % solution in water), sodium water glass (Merck, 28.5 wt % SiO_2, 8.5 wt % Na_2O, rest water), cetyltrimethylammonium bromide (Aldrich) for the purely siliceous MCM-41-materials. 1,1,3,3-Tetramethyldisilazane (Gelest), *n*-butyllithium (Aldrich, 2.5 N solution in hexane), morpholine (Aldrich), chlorodimethylsilane (Aldrich), dichlorodimethylsilane (Aldrich), dichloromethylsilane (Aldrich), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst, solution in xylenes Aldrich), allylbromide (Fluka), 1,3-divinyl-1,1,3,3-tetramethyldisilazane (Gelest), diazabicyclooctane (DABCO, Aldrich), dimethylamine (Aldrich), (3-chloropropyl)dimethylchlorosilane (Gelest), dichloromethylsilane (Aldrich), 2-dimethyl[(1*S*,2*S*)-pinan-10yl]silylchloride (Gelest), and 1*H*-indene (Aldrich) for synthesis of silazane reagents.

Synthesis Procedures. A. Preparation of Silazane Precursors. Lithium dimethylamide $LiN(CH_3)_2$, lithium bis(dimethylsilyl)amide $LiN[(SiH(CH_3)_2]_2$,[64] lithium bis(dimethylvinylsilyl)amide $LiN[Si(CH_3)_2(C_2H_3)]_2$, lithium isopropyldimethylsilylamide LiN*i*Pr($SiHMe_2$),[31] and lithium indenyl $Li(C_9H_7)$[65] were prepared via deprotonation of the amines, silylamines, and *H*-indene with *n*-butyllithium according to literature procedures. Chlorodimethylsilylbis(dimethylsilyl)amine **T8** and chloromethylsilylbis(dimethylsilyl)amine **T9** were synthesized as described previously by Wannagat et al.[28] from the reaction of dichlorodimethylsilane and dichloromethylsilane with lithium bis(dimethylsilyl)amide $LiN[SiH(CH_3)_2]_2$. Chlorodimethylinden-3-ylsilane was synthesized from sodium indenyl and dichlorodimethylsilane[62] and converted into (dimethylinden-3-ylsilyl)amine M4 via reaction with lithium dimethylamide.

(3-*N*-Morpholinpropyl)dimethylchlorosilane. In a 25 mL flask, N-allylmorpholine (2.00 g, 15.72 mmol) and dimethylchlorosilane (2.97 g, 31.40 mmol) were mixed under an argon atmosphere and cooled to 0 °C. Karstedt's catalyst (5 μL) was added during vigorous stirring. The solution immediately turned slightly greenish and small amounts of a white precipitate formed. The mixture was stirred at 0 °C overnight, the precipitate was filtered off and an excess of dimethylchlorosilane was removed under a vacuum. The product (2.92 g, 84%) was obtained as a clear, greenish liquid. ^{1}H NMR δ (ppm): 3.55 (t, $^3J_{H,H} = 4.4$ Hz, 4H), 2.30 (t, $^3J_{H,H} = 4.4$ Hz, 4H), 2.21 (t, $^3J_{H,H} = 7.6$ Hz, 2H), 1.46 (m, 2H), 0.66 (m, 2H), 0.25 (s, 6H). ^{13}C NMR δ (ppm): 66.8, 61.5, 53.6, 20.0, 16.4, 1.6. Elemental Analysis: C, 48.24 (48.74); H, 9.39 (9.09); N, 6.01 (6.34).

B. Preparation of Monosilazanes. [Dimethyl[(1*S*,2*S*)-pinan-10yl]-silyl]dimethylamine M1. To a solution of [dimethyl[(1*S*,2*S*)-pinan-10yl]silyl]dimethylsilylchloride (1.15 g, 5.00 mmol) in tetrahydrofuran (cooled to ca. −36 °C) lithium dimethylamide (0.28 g, 5.50 mmol) was added slowly. After the solution was stirred for 2 h, the solvent was removed, and the product was extracted into hexane, which was subsequently removed in vacuo. ^{1}H NMR δ (ppm): 2.33 (s, 6H), 2.09−1.95 (m), 1.81−1.78 (m), 1.70−1.59 (m), 1.14 and 0.76 (s, 6H), 0.55 and 1.53 (d, $^3J_{H,H} = 10$ Hz, 1H), 0.01 and 0.00 (s, 6H). Elemental analysis: C, 69.21 (70.22); H, 12.80 (12.21); N, 5.35 (5.85).

(3-Chloropropyldimethylsilyl)dimethylamine M2. (3-Chloropropyl)dimethylchlorosilane (1.00 g, 5.84 mmol) was dissolved in 5 mL of hexane and the solution was cooled to 0 °C using an ice bath. A solution of 0.30 g (5.84 mmol) of lithium dimethylamide in 3 mL of tetrahydrofuran was added slowly and the resulting mixture was stirred overnight. The precipitated LiCl was filtered off, and the solvents were removed in vacuo to yield 0.86 g (82%) of a colorless oil, which was identified as **M2**.[66]

(3-*N*-Morpholinpropyldimethylsilyl)dimethylamine M3. Following the procedure for **M2**, (3-*N*-morpholinpropyl)dimethylchlorosilane (0.86 g, 3.89 mmol) in 5 mL of hexane was reacted with a tetrahydrofuran solution of lithium dimethylamide $LiNMe_2$ (0.32 g, 3.89 mmol). **M3** was obtained as a slightly brownish liquid (0.83 g, 93%). ^{1}H NMR δ (ppm): 3.62 (t, $^3J_{H,H} = 4.7$ Hz, 4H), 2.35 (s, 6H), 2.32 (t, $^3J_{H,H} = 4.7$ Hz, 4H), 2.22 (t, $^3J_{H,H} = 7.9$ Hz, 2H), 1.38 (m, 2H), 0.43 (m, 2H), −0.07 (s, 6 H). ^{13}C NMR δ (ppm): 67.0, 62.7, 53.8, 38.1, 20.8, 13.3, −3.2. FTIR: ν (cm^{-1}, Nujol): 1376 s, 1284 s, 1252 s, 1175 m, 1121 s, 1071 w, 986 s, 914 w, 869 m, 834 s, 787 m, 764 m, 699 w, 624 w. Elemental Analysis: C, 57.6 (57.34); H, 11.3 (11.37); N, 11.9 (12.16).

C. Preparation of Disilazanes. [(3-Chloropropyl)dimethylsilyl]-isopropyl(dimethylsilyl)amine D3. Following the procedure described for **M2**, chloropropyldimethylchlorosilane (2.78 g, 16.23 mmol) in 10 mL of hexane was reacted with a hexane solution of 1 equiv (2.00 g) of LiN*i*Pr($SiHMe_2$) to yield **D3** (3.72 g, 91%) as a slightly yellow oil. ^{1}H NMR δ (ppm): 4.66 (sp, $^3J_{H,H} = 4.0$ Hz, 1H), 3.18 (t, $^3J_{H,H} = 7.2$ Hz, 2H), 3.10 (sp, $^3J_{H,H} = 6.4$ Hz, 1H), 2.57 (m, 2H), 1.08 (d, $^3J_{H,H} = 6.4$ Hz, 6H), 0.49 (m, 2H), 0.16 (d, $^3J_{H,H} = 4.0$ Hz, 6H), 0.05 (s, 6H). ^{13}C NMR δ (ppm): 47.6, 47.2, 27.8, 25.6, 25.5, 1.6, −0.1. FTIR: ν (cm^{-1}, liquid film): 2958 vs, 2135 (SiH) s, 1456 w, 1362 w, 1252 s, 1146 m, 1004 s, 902 s, 763 m. Elemental Analysis: C, 47.44 (47.67); H, 10.32 (10.40); N, 5.22 (5.56).

D. Preparation of Trisilazanes. [Dimethyl[(1*S*,2*S*)-pinan-10-yl]-silyl]bisdimethylsilylamine T3. To a solution of dimethyl[(1*S*,2*S*)-pinan-10-yl]silylchloride (4.62 g, 20 mmol) in hexane (cooled to ca.

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[64] Eppinger, J.; Herdtweck, E.; Anwander, R. *Polyhedron* **1998**, *17*, 1195.

[65] Wang, H.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2004**, *23*, 875.

[66] Yoder, C. H.; Cader, B. M. *J. Organomet. Chem.* **1982**, *233*, 275.

−78 °C) $LiN[(SiH(CH_3)_2]_2$ (2.79 g, 20 mmol) dissolved in tetrahydrofuran was added. After the solution was stirred for 2 h, the solvent was removed, and the product was extracted into hexane, which was subsequently removed in vacuo. ^{1}H NMR δ (ppm): 4.86 (m, $^3J_{H,H}$ = 3.0 Hz, 2H), 2.39− 2.31 (m), 2.19 − 2.15 (m), 2.01−1.97 (m), 1.93−1.54 (m), 1.52−1.38 (m), 1.35 and 0.99 (s, 6H), 1.55 and 0.83 (d, $^3J_{H,H}$ = 10 Hz, 1H), 0.38 (m, 18H). ^{13}C NMR δ (ppm): 47.8, 39.5, 38.2, 29.6, 25.7, 25.5, 24.6, 23.7, 21.8, 18.7, 1.5, 0.9, 0.0. Elemental Analysis: C, 58.4 (58.8); H, 11.6 (11.3); N, 4.1 (4.3).

(3-Chloropropyl)dimethylsilylbis(dimethylsilyl)amine T4. Following the procedure described for **M2**, chloropropyldimethylchlorosilane (5.56 g, 40.90 mmol) in 20 mL of hexane was reacted with a tetrahydrofuran solution of $LiN(SiHMe_2)_2$ (4.52 g, 40.90 mmol) to yield **T4** (8.53 g, 98%) as a colorless oil. ^{1}H NMR δ (ppm): 4.60 (sp, $^3J_{H,H}$ = 3.5 Hz, 1H), 3.18 (t, $^3J_{H,H}$ = 6.6 Hz, 2H), 1.58 (m, 2H), 0.58 (m, 2H), 0.16 (d, $^3J_{H,H}$ = 3.5 Hz, 12H), 0.09 (s, 6H). ^{13}C NMR δ (ppm): 46.2, 26.5, 14.9, 0.4, 0.2. FTIR ν (cm^{-1}, liquid film): 2955 vs, 2126 vs, 1937 w, 1804 w, 1419 m, 1253 s, 1159 w, 952 s, 907 s, 830 m, 773 w, 693 w. Elemental Analysis: C, 40.54 (40.33); H, 9.95 (9.78); N, 5.43 (5.23).

(3-*N*-Morpholinpropyldimethylsilyl)bis(dimethylsilyl)amine T5. (3-*N*-Morpholinpropyl)dimethylchlorosilane (2.00 g, 9.02 mmol) was dissolved in 5 mL of hexane, and a solution of $LiN(SiHMe_2)_2$ (1.25 g, 9.02 mmol) in 5 mL tetrahydrofuran was slowly added. LiCl immediately precipitated from the solution and after 2 h of stirring at room temperature was removed by centrifugation. The solvents were removed from the remaining solution under a vacuum to yield **T5** (2.27 g, 79%) as a slightly yellow, viscous oil. ^{1}H NMR δ (ppm): 4.69 (sp, $^3J_{H,H}$ = 3.6, 2H), 3.61 (t, $^3J_{H,H}$ = 4.0 Hz, 4H), 2.23 (t, $^3J_{H,H}$ = 4.0 Hz, 4H), 2.18 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 1.45 (m, 2H), 0.66 (m, 2H), 0.20 (d,$^3J_{H,H}$ = 3.6 Hz, 12H), 0.18 (s, 6H). ^{13}C NMR δ (ppm): 67.0, 62.3, 53.9, 21.1, 16.2, 1.3, 1.1. FTIR ν(cm^{-1}, liquid film): 2931 vs, 2853 vs, 2125 s, 1459 s, 1376 s, 1251 s, 1121 m, 979 m, 951 m, 911 s, 886 s, 833 m, 772 w. Elemental Analysis: C, 48.84 (49.00); H, 10.44 (10.75); N, 8.34 (8.79).

(3-Chloropropyl)dimethylsilylbis(dimethylvinylsilyl)amine T6. Following the procedure described for **M2**, chloropropyldimethylchlorosilane (1.50 g, 8.77 mmol) in 10 mL of hexane was reacted with a tetrahydrofuran solution of $LiN(SiMe_2Vin)_2$ (1.68 g, 8.77 mmol) to yield **T6** (2.41 g, 86%) as a colorless oil. ^{1}H NMR δ (ppm): 6.23 (dd, $^3J_{H,H}$ = 18.3 Hz, 20.2 Hz, 2H), 5.83 (dd, $^2J_{H,H}$ = 3.5 Hz, $^3J_{H,H}$ = 18.3 Hz, 2H), 5.63 (dd, $^2J_{H,H}$ = 3.5 Hz, $^3J_{H,H}$ = 20.2 Hz, 2H), 3.17 (t, $^3J_{H,H}$ = 6.4 Hz, 2H), 0.63 (m, 2H), 1.59 (m, 2H), 0.26 (s, 12H), 0.16 (s, 6H). ^{13}C NMR δ (ppm): 143.3, 131.0, 47.8, 28.0, 17.1, 2.8, 2.5. FTIR ν (cm^{-1}, liquid film): 3047 s, 2954 vs, 1591 m, 1403 s, 1255 vs, 1176 m, 1009 s, 839 vs, 683 vs, 608 m, 534 m. Elemental Analysis: C, 48.29 (48.78); H, 9.64 (9.45); N, 4.12 (4.38).

{**[(*N*-Diazabicyclooctane)propyldimethylsilyl]bis(dimethylsilyl)-amine**}**chloride T7.** $(SiHMe_2)_2NSiMe_2(CH_2)_3Cl$ **T4** (1.00 g,3.73 mmol) and diazabicyclooctane (0.84 g, 7.46 mmol) were dissolved in 15 mL of toluene and heated to reflux for 18 h. A white solid precipitates from the solution which was separated by centrifugation, repeatedly washed with tetrahydrofuran (4 × 3 mL), and dried under reduced pressure to yield **T7** (0.96 g, 68%). ^{1}H NMR δ (ppm): 4.42 (sp, $^3J_{H,H}$ = 3.46 Hz, 2H), 3.64 (m, 6H), 3.42 (m, 2H), 3.23 (m, 6H), 1.63 (m, 2H), 0.56 (m, 2H), 0.15 (d, $^3J_{H,H}$ = 3.46 Hz, 12H), 0.13 (s, 6H). ^{13}C NMR δ (ppm): 67.2, 52.5, 45.6, 17.0, 15.1, 1.4, 0.9. FTIR: ν (cm^{-1}, Nujol): 2131 m, 1313 w, 1250 s, 1168 w, 1093 w, 1056 m, 984 s, 956 s, 906 s, 877 s, 840 w, 773 m, 632 w. Elemental Analysis: C, 47.91 (47.38); H, 10.7 (9.99); N, 11.23 (11.05).

(Indenyldimethylsilyl)bis(dimethylsilyl)amine T10. To a solution of chlorodimethylsilylbis(dimethylsilyl)amine **T8** (2.50 g, 11.00 mmol) in hexane (cooled to ca. −78 °C) lithiumindenyl (1.22 g, 10.00 mmol) was added. The reaction was started by adding a few drops of tetrahydrofuran and the solution was allowed to warm up to ambient temperature. When the reaction was completed (GC−MS analysis) the solvent was removed in vacuo. The oily product was redissolved in hexane and heated for 30 min under reflux, and LiCl was filtered off. The solvent was evaporated, and all volatile impurities were removed under a vacuum (10^{-5} Torr, 60 °C). ^{1}H NMR δ (ppm): 7.51, 7.44, 7.24, 7.17 (4H), 6.89 (d, $^3J_{H,H}$ = 5.0 Hz, 1H), 6.62 (dd, 1H), 4.73 (sp, $^3J_{H,H}$ = 3.2 Hz, 2H), 3.81 (s, 1H), 0.12−0.08 ppm (s, 6H), 0.17 (d, $^3J_{H,H}$ = 3.2 Hz, 12H). Elemental Analysis: C, 57.85 (58.96); H, 8.59 (8.91); N, 4.46 (4.58).

(Indenylmethylsilyl)bis(dimethylsilyl)amine T11. Following the procedure described for **T10**, chloromethylsilylbis(dimethylsilyl)amine **T9** (2.33 g, 11.00 mmol) was reacted with lithiumindenyl (1.22 g, 10.00 mmol) to yield **T11**. ^{1}H NMR (2 diastereomers) δ (ppm): 7.44 (d, $^3J_{H,H}$ = 8.5 Hz), 7.37−7.30 and 7.15, −7.03 (m, 3H), 6.80 and 6.76 and 6.56 (d, $^3J_{H,H}$ = 7 Hz, 1H), 6.47 (dd, 1H), 4.56 (m, $^3J_{H,H}$ = 3.0 Hz, 2H), 4.30 and 4.00 (m, $^3J_{H,H}$ = 3.0 Hz, 1H), 3.53 and 3.48 (d, $^3J_{H,H}$ = 2 Hz, 1H), 0.20 and −0.14 (d, $^3J_{H,H}$ = 3.0 Hz, 3H), 0.04 and −0.01 (t, $^3J_{H,H}$ = 3.0 Hz, 1H). ^{13}C NMR δ (ppm): 144.5, 144.0, 143.5, 135.1, 134.0, 130.0, 129.2, 125.1, 123.7, 123.2, 123.1, 121.0, 46.4, 0.2, 0.0, −1.5, −3.5. FTIR: ν (cm^{-1}, Nujol): 2120 (Si−H). Elemental Analysis: C, 57.30 (57.78); H, 8.62 (8.66); N, 4.52 (4.81).

E. Synthesis of MCM-41 Materials. All as-synthesized materials were calcined in air at 540 °C for 5 h, dehydrated under a high vacuum (10^{-5} Torr) at 270 °C for 4 h, and stored in a glovebox.

MCM-41-a,c,d. Cetyltrimethylammoniumbromide (CTAB, 4.27 g, 11.71 mmol) and *N*-(3-trimethylammoniumpropyl)hexadecyldimethylammoniumdibromide (C_{16-3-1}, 5.51 g, 10.30 mmol) were dissolved in distilled water (281 g, 15.60 mol), and tetramethylammonium hydroxide (TMAOH, 25 wt % in water, 23.65 g, 64.88 mmol) was added. Tetraethylorthosilicate (TEOS, 27.00 g, 130 mmol) was added, and the resulting gel was stirred for 40 min at ambient temperature. The white precipitate was filtered off and immediately resuspended in 350 mL of distilled water. This mixture was loaded into a 500 mL Teflon autoclave and heated without stirring at 100 °C for 6 days. The solid product was recovered by filtration, extensively washed with distilled water, and dried overnight at ambient temperature. Molar composition of the synthesis gel: 0.08 CTAB:0.09 C_{16-3-1}:1 TEOS:0.5 TMAOH: 120 H_2O.

MCM-41-b. CTAB (69.20 g, 243 mmol) was dissolved in distilled water (300 g, 16.67 mol). Sodium water glass (72 g) was diluted with distilled water (40 g, 2.22 mol) and slowly added while vigorous stirring. The resulting gel was stirred for 20 min, and trimethylbenzene (TMB, 21.20 g, 0.18 mol), concd H_2SO_4 (4.80 g, 48.93 mmol), and distilled water (20 g), and sodium chloride (20 g, 342 mmol) were added subsequently. The mixture was loaded into a 500 mL Teflon autoclave and heated without stirring at 100 °C for 20 h. The product was recovered by filtration, washed with distilled water and ethanol, and dried at ambient temperature overnight. Molar composition of the synthesis gel: 1 Si:0.585 CTAB:67 H_2O:0.145 H_2SO_4:0.55 TMB:1.08 NaCl.

F. Silylation Experiments. The silylation reactions were carried out by adding an excess of the silylating reagent dissolved in 3 mL of hexane or toluene to 5 mL of a hexane or toluene suspension of the dehydrated MCM-41 material. After the reaction mixture was stirred for a desired period of time at ambient temperature or in refluxing toluene, nonreacted silylating reagent was separated by several hexane washings via centrifugation. The silylated materials were dried under a vacuum for 2.5 h.

G. Hybrid Materials. M1@MCM-41-a. Following the procedure described above, **M1** (185 mg, 0.77 mmol) was reacted with MCM-41-**a** (200 mg,3.51 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 510$ m^2 g^{-1}, $V_{tot} = 0.41$ cm^3 g^{-1}, $d_{BJH,des} = 2.8$ nm. Elemental Analysis: C, 25.59; H, 3.9; N, <0.1.

M2@MCM-41-c. Following the procedure described above, $Me_2NSiMe_2(CH_2)_3Cl$ **M2** (539 mg, 3.00 mmol) was reacted with MCM-41-**c** (500 mg, 3.62 mmol SiOH groups/g) at 25 °C for 48 h in hexane. N_2 physisorption: $a_s = 670$ m^2 g^{-1}, $V_{tot} = 0.65$ cm^3 g^{-1}, $d_{BJH,des} = 3.1$

nm. ^{1}H MAS NMR δ (ppm): 3.62, 1.86 (1.44, 0.99; solvent, hexane), 0.25. ^{13}C CPMAS NMR δ (ppm): 48.9, 29.3, 17.5, 0.9. ^{29}Si MAS NMR δ (ppm): 14.8, −109.3. Elemental Analysis: C, 13.27; H, 2.42; N, <0.3; Cl, 7.90.

M3@MCM-41-d. Following the procedure described above, **M3** (1.35 g, 3.92 mmol) was reacted with MCM-41-**d** (1.00 g, 3.92 mmol SiOH groups/g) at 25 °C for 2 days in hexane. N_2 physisorption: $a_s = 590$ m^2 g^{-1}, $V_{tot} = 0.58$ cm^3 g^{-1}, $d_{BJH,des} = 2.9$ nm. ^{1}H MAS NMR δ (ppm): 3.50, 2.27 (1.44 and 0.97; solvent, hexane), 0.26. ^{13}C CPMAS NMR δ (ppm): 66.8, 62.3, 54.3, 20.4, 15.3, −0.4. Elemental Analysis: C, 18.21; H, 3.39; N, 2.35.

M4@MCM-41-b. Following the procedure described above, **M4** (163 mg, 0.75 mmol) was reacted with MCM-41-**b** (300 mg, 2.80 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 670$ m^2 g^{-1}, $V_{tot} = 0.47$ cm^3 g^{-1}, $d_{BJH,des} = 2.6$ nm. ^{1}H MAS NMR δ (ppm): 6.84, 3.44, 0.22. ^{13}C CPMAS NMR δ (ppm): 145.0, 131.5, 124.2, 47.6, 1.5. Elemental Analysis: C, 16.58; H, 1.97; N, <0.1.

D3@MCM-41-c. Following the procedure described above, **D3** (684 mg, 2.72 mmol) was reacted with MCM-41-**c** (500 mg, 3.62 mmol SiOH groups/g) at 25 °C for 5 days in hexane to yield 520 mg of the hybrid material. N_2 physisorption: $a_s = 870$ m^2 g^{-1}, $V_{tot} = 0.85$ cm^3 g^{-1}, $d_{BJH,des} = 3.2$ nm. ^{1}H MAS NMR δ (ppm): 4.79, 3.62, 1.95 (1.45, 1.03; solvent, hexane), 0.25. ^{13}C CPMAS NMR δ (ppm) 46.5, 26.7, 14.9, −2.2. ^{29}Si MAS NMR δ (ppm): 14.5, −1.1, −109.0. Elemental Analysis: C, 9.80; H, 1.96; N, <0.1; Cl, 3.07.

T3@MCM-41-b. Following the procedure described above, **T3** (250 mg, 0.76 mmol) was reacted with MCM-41-**b** (500 mg, 2.80 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 810$ m^2 g^{-1}, $V_{tot} = 0.66$ cm^3 g^{-1}, $d_{BJH,des} = 3.0$ nm. ^{1}H MAS NMR δ (ppm): 4.49, 2.95, 1.78, 1.15, 0.84, 0.02. ^{13}C CPMAS NMR δ (ppm): 49.6, 41.7, 39.5, 30.8, 25.5, 22.2, 18.9, 2.0. ^{29}Si MAS NMR δ (ppm): 14.4, 0.3, −99.7, −108.8. Elemental Analysis: C, 8.47; H, 1.73; N, <0.1.

T4@MCM-41-c. Following the procedure described above, **T4** (268 mg, 0.91 mmol) was reacted with MCM-41-**c** (166 mg, 3.62 mmol SiOH groups/g) at 109 °C for 6 h in toluene. N_2 physisorption: $a_s = 980$ m^2 g^{-1}, $V_{tot} = 0.99$ cm^3 g^{-1}, $d_{BJH,des} = 3.5$ nm. ^{1}H MAS NMR δ (ppm): 4.74, 3.57, 2.01 (1.44, 1.00; solvent, hexane), 0.23. ^{13}C CPMAS NMR δ (ppm): 46.6, 26.7, 14.7, −2.6. ^{29}Si MAS NMR δ (ppm): 14.4, 1.6, −109.3. Elemental Analysis: C, 7.02; H, 1.49; N, <0.1; Cl, 1.79.

T5@MCM-41-d. Following the procedure described above, **T5** (1.11 g, 3.49 mmol) was reacted with MCM-41-**d** (2.00 g, 3.92 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 880$ m^2 g^{-1}, $V_{tot} = 0.94$ cm^3 g^{-1}, $d_{BJH,des} = 3.3$ nm. ^{1}H MAS NMR δ (ppm): 4.66, 3.84, 1.87 (1.43 and 1.00; solvent, hexane), 0.25. ^{13}C CPMAS NMR δ (ppm): 67.6, 62.9, 25.1, 18.6, 11.9, −2.2. Elemental Analysis: C, 7.45; H, 1.84; N, 0.70.

T6@MCM-41-c. Following the procedure described above, **T6** (860 mg, 2.7 mmol) was reacted with MCM-41-**c** (500 mg, 3.62 mmol SiOH groups/g) at 109 °C for 15 h in toluene. N_2 physisorption: $a_s = 910$ m^2 g^{-1}, $V_{tot} = 0.92$ cm^3 g^{-1}, $d_{BJH,des} = 3.3$ nm. ^{1}H MAS NMR δ (ppm): 6.08, 5.90, 3.59, 2.02 (1.47, 1.05; solvent, hexane), 0.24. ^{13}C CPMAS NMR δ (ppm): 137.1, 131.6, 47.3, 26.5, 14.8, −3.3. ^{29}Si MAS NMR δ (ppm): 14.3, 2.1, −108.0. Elemental Analysis: C, 7.59; H, 1.50; N, <0.1; Cl, 1.84.

T10@MCM-41-b. Following the procedure described above, **T10** (243 mg, 0.79 mmol) was reacted with MCM-41-**b** (500 mg, 2.80 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 810$ m^2 g^{-1}, $V_{tot} = 0.68$ cm^3 g^{-1}, $d_{BJH,des} = 3.0$ nm. ^{1}H MAS NMR δ (ppm): 7.09, 4.59, 3.56, 2.01, 1.80, 0.06. Elemental Analysis: C, 6.52; H, 1.37; N, 0.1.

T11@MCM-41-b. Following the procedure described above, **T11** (266 mg, 0.75 mmol) was reacted with MCM-41-**b** (500 mg, 2.80 mmol SiOH groups/g) at 25 °C for 5 days in hexane. N_2 physisorption: $a_s = 920$ m^2 g^{-1}, $V_{tot} = 0.77$ cm^3 g^{-1}, $d_{BJH,des} = 3.1$ nm. ^{1}H MAS NMR δ (ppm): 7.34, 4.54, 2.10, 0.06. Elemental Analysis: C, 5.32; H, 1.34; N, 0.40.

Surface Model: 25,26-μ_2-Dimethylsiloxy-4-*tert*-butylcalix[4]arene C2. Calix[4]arene **C1** (306 mg, 0.47 mmol) and **M4** (102 mg, 0.47 mmol) were dissolved in 10 mL of hexane and stirred for 24 h at ambient temperature under an argon atmosphere. All volatiles were removed under a vacuum, and the resulting crude product was extracted with 10 mL of hexane. The solvent was evaporated from the hexane fractions to yield 90 mg (0.13 mmol, 27%) of **C2**. ^{1}H NMR δ (ppm): 7.19−7.00 (m, 8H), 6.32 (s, 2H), 4.37 (d, $^2J_{H,H} = 14$ Hz, 1H), 4.27 (d, $^2J_{H,H} = 16$ Hz, 2H), 4.07 (d, $^2J_{H,H} = 14$ Hz, 1H), 3.79 (d, $^2J_{H,H} = 16$ Hz, 2H), 3.54 (d, $^2J_{H,H} = 14$ Hz, 1H), 3.37 (d, $^2J_{H,H} = 14$ Hz, 1H), 1.28 (s, 18H), 1.23 (s, 18H), 0.32 (s, 3H), −0.81 (s, 3H). ^{13}C NMR δ (ppm): 149.4, 149.3, 144.6, 143.2, 129.3, 128.6, 128.5, 126.6, 126.3, 125.5, 125.3, 125.0, 34.0, 33.9, 31.7, 31.5, 31.4, 2.5, −3.1. The hexane insoluble residue was identified as nonreacted calix[4]arene **C1** by NMR spectroscopy.

Characterization. Powder X-ray diffraction (PXRD) patterns were recorded on a Philips X'pert PRO instrument in the step/scan mode (step width, 0.034; accumulation time, 30 s/step; range (2Θ), 0.31°−9.96°) using monochromatic Cu K_α radiation ($\lambda = 1.5418$ Å). IR spectra of the parent and silylated materials were recorded on a Perkin-Elmer Fourier transform infrared (FTIR) spectrometer 1760X using Nujol mulls sandwiched between CsI plates. ^{1}H, ^{13}C, and ^{29}Si MAS NMR spectra were obtained at ambient temperature on a Bruker AV300 instrument (resonance frequencies were 300.13, 75.46, and 47.73 MHz; conditions: ^{1}H, pulse repetition 2.0 s, spinning speed 8 kHz; ^{13}C, pulse repetition 5.0 s, spinning speed 8 kHz; referenced to adamantane (^{1}H, 2.00 ppm; ^{13}C, 29.46 ppm); ^{29}Si, pulse repetition 60.0 s, spinning speed 5 kHz) and a Bruker MSL-400 spectrometer (resonance frequencies were 400.13 and 100.63 MHz; conditions: ^{1}H, pulse repetition 5.0 s, $\pi/2$ pulse, spinning speed 10 kHz; ^{13}C, pulse repetition 10.0 s, $\pi/2$ pulse, spinning speed 10 kHz; referenced to $Si(CH_3)_4$) equipped with standard 4 mm MAS probes. Single pulse excitation has been applied, and ^{13}C NMR spectra were recorded using cross polarization and high power proton decoupling. Nitrogen adsorption−desorption isotherms were measured with an ASAP 2020 volumetric adsorption apparatus (Micromeritics) at 77.4 K for relative pressures from 10^{-2} to 0.99 [$a_m(N_2$, 77 K) 0.162 nm^2]. Prior to analysis, the samples were outgassed in the degas port of the adsorption analyzer at 523 K for 3 h. The BET specific surface area was obtained from the nitrogen adsorption data in the relative pressure range from 0.04 to 0.20. The pore size distributions were derived from the desorption branch using the Barrett−Joyner−Halenda (BJH) method.[67] Elemental analyses were performed on an Elementar VarioEL/Perkin-Elmer instrument. The surface silanol population was obtained from the surface coverage $\alpha(SiR_3)$ of activated silylated samples as described previously.[23]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. This research is currently supported by the NANOSCIENCE program of the Universitetet i Bergen. M.W. and F.E. thank the Fonds der Chemischen Industrie for the award of a fellowship.

Supporting Information Available: Figures of PXRD patterns, physisorption isotherms and NMR spectra of materials MCM-41-**a**−**d**, **T3**@MCM-41-**b**, **T4**@MCM-41-**c**, **T5**@MCM-41-**d**, **T6**@MCM-41-**c**, **T10**@MCM-41-**b**, **M1**@MCM-41-**a**, **M2**@MCM-41-**c**, **M3**@MCM-41-**d**, **M4**@MCM-41-**b**, and **D2**@MCM-41-**c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA065444V

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(67) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.