DALTON
COMMUNICATION

Grafting of versatile lanthanide silylamide precursors onto mesoporous MCM-41 †

Reiner Anwander* and Rainer Roesky

Institut für Technische Chemie I, Universität Stuttgart, D-70550 Stuttgart, Germany

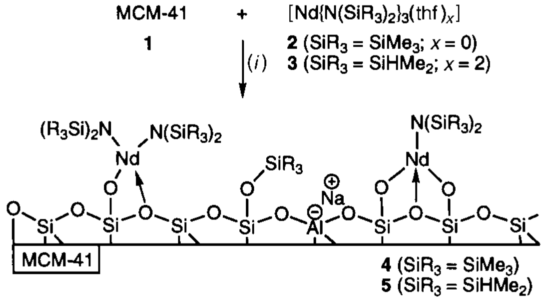
Chemical anchoring of organometallic lanthanide silylamides onto the internal walls of dehydrated MCM-41 in *n*-hexane at ambient temperature was monitored by FTIR spectroscopy and nitrogen adsorption/desorption.

In the past decade surface organometallic chemistry[1] has been challenged by the discovery of the intriguing class of mesoporous support materials composed of, for example, aluminosilicates and metal oxides.[2,3] Like the commonly used silica and alumina supports[4] the new systems are capable of surface reactions *via* terminal silanol groups. However, the prevailing structural patterns such as hexagonally arranged, uniform mesopores ensure a more detailed characterization by means of nitrogen adsorption/desorption, X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).[5] Furthermore, the interplay of the proposed readily tunable pore radius (20–100 Å) and the accommodation of both bulky metal complexes and reactants might even allow substrate transformations in a regime of stereo- and shape-selectivity.[6] Given the current high interest in the field of 'stereoselective catalysis by organolanthanide complexes'[7] we anticipated the grafting of such reactive moieties onto mesoporous material MCM-41 *via* formation of a thermodynamically stable lanthanide–siloxide σ bond.[8] MCM-41-derived hybrids containing main-group-[9] and d-transition-organometallics[10] have recently been described.

Herein, we report our initial results on a heterogeneously performed silylamide route employing MCM-41 **1** and amides of type $[Nd\{N(SiMe_3)_2\}_3]$ **2** and $[Nd\{N(SiHMe_2)_2\}_3(thf)_2]$ (thf = tetrahydrofuran) **3**. Such highly soluble, monomeric silylamides are known to act as key precursors in homogeneous, protolytic exchange reactions under mild conditions.[11]

Dehydrated MCM-41 was synthesized according to the literature employing $[N(C_{14}H_{29})Me_3]Br$ as a templating agent.[2] After calcination (N_2: 500 °C, 5 h, heating rate 1.5 °C min^{-1}; air: 500 °C, 5 h) and dehydration (10^{-5} Torr: 280 °C, 4 h, heating rate 1 °C min^{-1}),‡ **1** was characterized by XRD, nitrogen adsorption and desorption isotherms (BET surface area: 1005 m^2 g^{-1}; pore diameter: 26 Å (desorption); pore volume: 0.78 cm^3 g^{-1}), elemental analysis (ICP, Si : Al ≈ 18), and IR spectroscopy [ν(OH): 3695 cm^{-1}].[12] The grafting procedure involves the addition of silylamide desolved in *n*-hexane to a suspension of MCM-41 in *n*-hexane within a period of 5 min (Scheme 1). Upon stirring for 2 h, followed by several *n*-hexane washings, the resulting bluish hybridic materials were dried under vacuum for at least 5 h.§ This way, approximately 1 mmol of silylamide per g of **1** could be loaded. However, quantitative gas chromatography allowed the detection of only 0.3–0.4 mmol of released silylamine ligand probably due to retention in the mesopores by metal complexation or silylation reaction.¶

The consumption of all terminal silanol groups and the disappearance of the SiO mode at 980 cm^{-1} (strained Si–O–Si bonds) were unequivocally proven by Fourier-transform IR spectroscopy (Fig. 1). Type-**3** silylamide was employed not only for reasons of changed reactivity during immobilization and following ligand exchange reactions, but also for its unique behaviour as an IR probe. Two ν(Si–H) stretches appear in the spectra of hybrid material **5**. The lower energy one at 2058 cm^{-1} can be assigned to metal bonded amide moieties.[11] Independently performed reactions of the silylamines $HN(SiMe_3)_2$ and $HN(SiHMe_2)_2$ with **1** in *n*-hexane revealed formation of silylated **6a** and **6b** under these mild conditions and allowed the assignment of the Si–H stretching frequency at 2144 cm^{-1} to **6b**-analogous '$OSiHMe_2$' moieties. The competing silylation reaction is in agreement with the findings from quantitative gas chromatography and points out a self-supported spacing of the lanthanide centres by steric restrictions or diffusion-controlled reactions within the mesopores. For comparison, silylation reactions along the homogeneously performed silylamide route are observed only when an *excess* of more acidic alcohols such as $HOCH(CF_3)_2$[14] or $HOSiBu^t_3$[15] are employed. Calculations from the elemental analysis of **6a** reveal that approximately 13% of the MCM-41 silicon atoms are carrying reactive sites available for silylation.‖ Also, elemental analyses of the hybrid materials **4** and **5** favour the formation of '$MCM\text{-}41{-}O_2Ln[N(SiMe_3)_2]$' over bis(amide) moieties.



Scheme 1 Possible surface species of the immobilization of neodymium silylamides on MCM-41: (*i*) hexane, room temperature, 20 h; thf is not shown for **5**

---

† *Non-SI unit employed:* Torr ≈ 133.322 Pa.

‡ Dehydration at temperatures >350 °C led to partial collapse of the mesopores as indicated by nitrogen adsorption and desorption isotherms (recorded on a micromeritics ASAP 2000).

§ All manipulations were performed in a dinitrogen-filled glove box (MB Braun MB150B-G-II). The initial grafting runs were carried out with coloured silylamide solutions of neodymium to visualize completeness of the reactions (titration). Prolonged reaction times (> 24 h) gave no further immobilization. Also, after prolonged Soxhlet extractions with thf only traces of what we assume to be a non-chemically anchored complex were isolated. X-Ray diffraction spectra of air-exposed hybrid materials showed the characteristic pattern of **1**, however, with decreased intensity. For **1** (stirred in *n*-hexane, evacuated for 5 h, N_2-filled) (Found: C, 0.28; H, 0.27; N, 0.41%. Synthesis of **4** from **2**: **2** (0.300 g, 0.48 mmol) in *n*-hexane (10 cm^3) was added to **1** (0.368 g) in *n*-hexane (10 cm^3) over 5 min. The mixture was stirred for 20 h, **4** was separated by centrifugation, washed with *n*-hexane (20 cm^3) and dried *in vacuo* for at least 5 h (Found: C, 9.45; H, 2.45; N, 1.95; Nd, 11.1%). IR (Nujol): 831s, 771m, 661m, 604m cm^{-1} $[N(SiMe_3)_2]$. Synthesis of **5** from **3**: as above using **3** (0.330 g, 0.48 mmol) and **1** (0.248 g) (Found: C, 10.0; H, 2.35; N, 2.00; Nd, 8.8%). IR (Nujol): 2144m, 2058m, 902s, 836s, 681m, 626m cm^{-1} $[N(SiHMe_2)_2]$.

¶ Hexamethyldisilazane was thoroughly studied as a trimethylsilylating agent for silica (gels).[13]

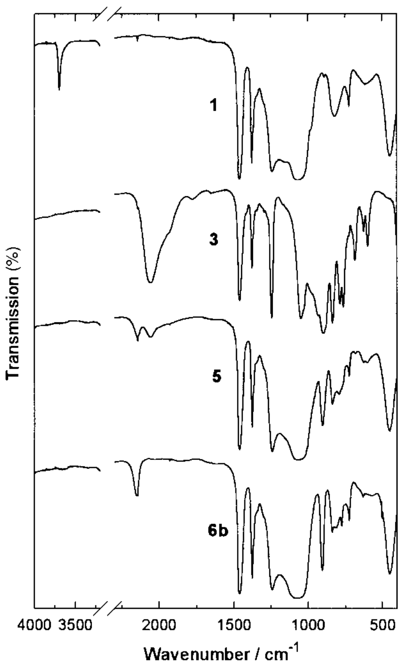


Fig. 1 FTIR spectra (Nujol). MCM-41 (**1**), $[Nd\{N(SiHMe_2)_2\}_3(thf)_2]$ (**3**), MCM-41 + $[Nd\{N(SiHMe_2)_2\}_3(thf)_2]$ (**5**), MCM-41 + $HN(SiHMe_2)_2$ (**6b**, 10^{-3} Torr, 2 h, 250 °C)

Nitrogen adsorption and desorption isotherms of **4** and **5** clearly demonstrate the filling of the mesopores (Fig. 2). The host-characteristic type-IV isotherm (**1**) is replaced by type-I isotherms (**4**, **5**) indicating the presence of microporous materials. The original pore volume of 0.78 $cm^3\ g^{-1}$ is reduced to approximately 0.30 $cm^3\ g^{-1}$ (after activation at 100 °C under high vacuum).[16] The silylated materials still display type-IV isotherms and the pore characteristics reveal effective pore-size engineering [BET surface area: ≈840 $m^2\ g^{-1}$ (**6a**, **6b**); pore diameter (desorption): 21 Å (**6a**, **6b**); pore volume: 0.53 $cm^3\ g^{-1}$ (**6a**), 0.54 $cm^3\ g^{-1}$ (**6b**)]. Further evidence for a competing silylation reaction stems from the reaction of monomeric $[Nd(NPr^i_2)_3(thf)]$[17] **7** with **1**.* Evaluation of the free isopropylamine results in complete desorption at $T < 150$ °C under high vacuum. As a result, approximately 2 mmol of **7** can be immobilized to yield hybrid material **8** [17.3% Nd (m/m) detected by ICP analysis]. The pore volume is decreased to 0.10 $cm^3\ g^{-1}$ (Fig. 2). All anchored amide complexes can be 'degrafted' as alkoxide complexes by treatment with $HOC(CF_3)_3$ (pK_a 5.7)[18]–thf solutions. The support residues display nitrogen adsorption and desorption isotherms which are similar to the silylated materials (**4**, **5**) and to original **1** (**8**).

A direct conclusion of these findings is that by varying the ratio of silylamide to silylamine different metal loadings will be available by simultaneous consumption of all terminal silanol groups, and hence the spacing of the metal centres will be effected. Preliminary ligand exchange reactions with less acidic alcohols such as ethanol and binaphthol (stoichiometric) reveal that we can direct future investigations towards the generation of both unsaturated lanthanide centres (small ligand chemistry) and 'immobilized chirality', two main features of organolanthanides and stereoselective catalysis.

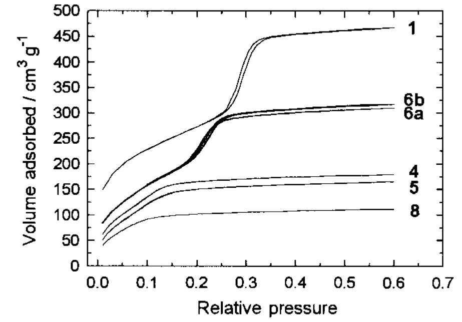


Fig. 2 Nitrogen adsorption and desorption isotherms (77.4 K): **1**, **4**, **5**, **8** (10^{-3} Torr, >5 h, room temperature); **6a**, **6b** (10^{-3} Torr, >5 h, room temperature and 2 h, 250 °C)

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) and Hoechst AG for financial support of this research project and the DFG for the award of a fellowship to R. A. Additionally, generous support from Professor J. Weitkamp is gratefully acknowledged. We are also grateful to Dr. Thomas Röser for valuable technical assistance.

References

1 J. M. Basset, B. C. Gates, J. P. Candy, A. Choplin, H. Leconte, F. Quignard and C. Santini, (Editors), *Surface Organometallic Chemistry, Molecular Approaches to Surface Catalysis*, Kluwer, Dordrecht, 1988.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature* (*London*), 1992, **359**, 710; J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3 D. M. Antonelli, A. Nakahira and J. Ying, *Inorg. Chem.*, 1996, **35**, 3126.
4 W. C. Finch, R. D. Gillespie, D. Hedden and T. J. Marks, *J. Am. Chem. Soc.*, 1990, **112**, 6221.
5 F. Schüth, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 1306.
6 See, for example, A. Corma, M. Iglesias and F. Sánchez, *J. Chem. Soc., Chem. Commun.*, 1995, 1635.
7 M. A. Giardello, V. P. Conticelli, L. Brard, M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10241; H. Tsukube, H. Shiba and J.-I. Uenishi, *J. Chem. Soc., Dalton Trans.*, 1995, 181; H. Sasai, T. Arai, Y. Satow, K. N. Houk and M. Shibassaki, *J. Am. Chem. Soc.*, 1995, **117**, 6194.
8 J. L. Sessler, B. L. Iverson, V. Kral, R. E. Thomas, D. A. Smith and D. Magda, *PCT Int. Appl.*, WO 95 29,702 (Cl. A61K47/48), 1995; N. E. Drysdale and N. Herron (du Pont de Nemours, E. I. and Co.), *PCT Int. Appl.*, WO 95 02,625 (Cl. CO8G65/10), 1995.
9 C. Huber, K. Moller and T. Bein, *J. Chem. Soc., Chem. Commun.*, 1994, 2619.
10 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature* (*London*), 1995, **378**, 159.
11 W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber and G. R. J. Artus, *Z. Naturforsch., Teil B*, 1994, **49**, 1789; W. A. Herrmann, R. Anwander, V. Dufaud and W. Scherer, *Angew. Chem.*, 1994, **106**, 1338; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1285; J. P. Kinney and R. H. Staley, *J. Phys. Chem.*, 1983, **87**, 3735.
12 J. Chen. Q. Li, R. Xu and F. Xiao, *Angew. Chem.*, 1995, **107**, 2898; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2898.
13 W. Hertl and M. L. Hair, *J. Phys. Chem.*, 1971, **75**, 2181; D. W. Sindorf and G. E. Maciel, *J. Phys. Chem.*, 1982, **86**, 5208.
14 D. C. Bradley, H. Chudzynska, M. E. Hammond, M. B. Hursthouse, M. Motevalli and W. Ruowen, *Polyhedron*, 1992, **11**, 375.
15 K. J. Covert, D. R. Neithammer, M. C. Zonnevylle, R. E. LaPointe, C. P. Schaller and P. T. Wolczanski, *Inorg. Chem.*, 1991, **30**, 2494.
16 A. C. Greenwald, W. S. Rees jun. and U. W. Lay, in *Rare Earth Doped Semiconductors*, eds. G. S. Pomrenke, P. B. Klein and D. W. Langer, MRS, Pittsburgh, PA, 1993.
17 H. C. Aspinell and M. R. Tillotson, *Polyhedron*, 1994, **13**, 3229.
18 C. J. Willis, *Coord. Chem. Rev.*, 1988, **88**, 133.

Received 30*th October* 1996; *Communication* 6/07391C

---

* Synthesis of **6a** from **1**: to a suspension of **1** (0.490 g) in *n*-hexane was added $HN(SiMe_3)_2$ (excess, 0.5 cm^3). After stirring for 20 h the unreacted silylamine and *n*-hexane were removed *in vacuo*. Material **6a** was dried *in vacuo* for at least 5 h at 20 °C, then heated at 250 °C under high vacuum for 2 h (Found: C, 6.50; H, 1.60%). IR (Nujol): 864s, 846s, 757m, 563m cm^{-1} $[N(SiMe_3)_2]$. Synthesis of **6b** from **1**: as above using **1** (0.247 g) and $HN(SiHMe_2)_2$ (excess, 0.3 cm^3) (Found: C, 5.15; H, 1.50%). IR (Nujol): 2145m, 904s, 837s, 773m, 629m cm^{-1} $[N(SiHMe_2)_2]$. Synthesis of **8** from **7**: **7** (0.185 g, 0.36 mmol) was added to **1** (0.342 g) in *n*-hexane (10 cm^3). The mixture was stirred for 2 h and additional **7** (0.182 g, 0.35 mmol) added. More **7** (0.104 g, 0.20 mmol) was added and the solution stirred for 20 h, **8** was separated by centrifugation, the residue washed with *n*-hexane (20 cm^3) and dried *in vacuo* for at least 5 h (Found: C, 14.50; H, 2.65; N, 2.20; Nd, 17.3%). IR (Nujol): 918m, 823m, 799m cm^{-1} (NPr^i_2). Only small amounts of silylamide complexes could be grafted on pre-silylated material, probably reflecting some non-silylated bridging OH-moieties.