Surface Confined Ketyl Radicals via Samarium(II)-Grafted Mesoporous Silicas

Iris Nagl, Markus Widenmeyer, Stefan Grasser,
Klaus Köhler, and Reiner Anwander*

Anorganisch-chemisches Institut
Technische Universität München
D-85747 Garching, Lichtenbergstrasse 4, Germany

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Samarium(II) compounds display unique reductive behavior in organic transformations as evidenced by numerous individual and sequential one-electron-transfer processes involving functionalized substrate molecules.[1] The rate and selectivity of reactions induced by the standard reagent SmI_2 are markedly affected by the type of solvents and additives such as strong Lewis bases, for example, HMPA, or metal salts.[2] More recently, it was shown that the stability of ketyl radicals, which are often key intermediates in the reduction of carbonyl functionalities, depends on the ancillary anionic ligand bonded to the samarium(II) center, for example, amide, alkoxide, or cyclopentadienyl ligands.[3]

We report the grafting of samarium(II) complexes onto the internal surface of mesoporous silica materials via surface organometallic chemistry (SOMC).[4] The resulting supramolecular systems featuring mesopores accessible to an extended intraporous chemistry form stable ketyl surface radicals by one-electron reduction. Surface confinement seems to direct the reductive behavior of the Sm(II) centers yielding selectively the alcoholic product in the fluorenone/fluorenol transformation (no pinacol-coupling product could be observed).

A heterogeneously performed silylamide route was applied for the synthesis of the immobilized Sm(II) species.[5,6] This route provides mild reaction conditions and exploits both specialized molecular and support components better to monitor the surface reaction. Accordingly, black $Sm[N(SiHMe_2)_2]_2(THF)_x$ (**1**) featuring the SiH moiety as a valuable spectroscopic probe was used as a molecular precursor.[7] Samples of structurally well-ordered and poreexpanded mesoporous silicas of type MCM-41 (**2**) and MCM-48 (**3**) were employed as model support materials.[8,9] Treatment of dehydrated samples of materials **2** and **3** with excess of silylamide **1** in *n*-hexane gave a black reaction mixture, from which after several *n*-hexane washings gray-black materials **4** and **5** were isolated (Scheme 1). **Caution!** These materials ignite instantaneously and turn white upon air-exposure, indicating the presence of Sm(II) surface species.[10]

The hybrid materials were characterized by FTIR spectroscopy, elemental analysis, and nitrogen physisorption (Table 1). Approximately 2.1 and 2.4 mmol of complex **1** could be grafted onto 1 g of MCM-41 and MCM-48 material, respectively. This corresponds to a relatively high surface coverage of $\sim$1.25 and 1.40 Sm(II)/nm^2, respectively.[11] For comparison, the maximum silanol surface sites available for these materials were determined as 1.67 (**2a**) and 1.89 SiOH/nm^2 (**3a**) via tetramethyldisilazane silylation.[12] The relatively low extent of concomitant surface silylation is in accordance with the IR spectra of the Sm(II) hybrid materials which indicate a relatively small amount of $\equiv$SiOSiHMe$_2$ surface sites at 2145 cm^{-1}. However, the SiH vibration area is dominated by a broad band at 2030 cm^{-1} (1920 sh) assignable to metal-bonded silylamide ligands featuring additional agostic Sm···SiH interactions.[7] The nitrogen adsorption/desorption isotherms of material **4** and **5** clearly indicate the filling of the mesopores. Interestingly, the host-characteristic type-IV isotherm is retained as shown for the MCM-48 hybrid material **5** in Figure 1.[13] Analysis of the Barret−Joyner−Halenda (BJH) pore size distribution suggests a regular distribution of the surface species accounting for pore volumes and mean pore diameters reduced by $\sim$75 and 42%, respectively, for material **5**.

The presence of Sm(II) surface species in materials **4** and **5** could be proven by their reactivity toward fluorenone. After addition of an equimolar amount of fluorenone to black suspensions of materials **4** and **5** in *n*-hexane, brown materials **6** and **7** could be isolated.[14] According to GC analyses of the supernatants $\sim$85% of the ketone was consumed. Assuming a quantitative immobilization of Sm(II) surface species, not all of these sites seem to be accessible for the conformationally rigid fluorenone. Moreover, the high carbon contents and apparent total loss of pore volume of materials **6** and **7** could not be expected (Table 1), pointing out pore blocking and solvent inclusion. The unequivocal formation of surface ketyl radicals was revealed by their X-band EPR spectra.[15,16] The room-temperature EPR spectra of the dry powders (Figure 2,a) consist of five lines at $g = 2.0033$. The spectra are symmetric (no g or hf anisotropy) and can well be interpreted as due to the hyperfine (hf) interaction of the unpaired electron with four groups of two equivalent protons (two of them are not resolved) as expected according to the literature.[16] Computer simulation using the hyperfine coupling constants derived from EPR/ENDOR experiments of a fluorenone radical anion solution[16] reproduce the experimental spectrum very well (a_i (^{1}H): 0.31, 0.2, 0.07, and 0.01 mT, line width $\Delta B_{pp} = 0.18$ mT, the last two couplings are not resolved). No qualitative changes were observed in the spectra for recording temperatures

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* Corresponding author. Fax: +49 89 289 13473. E-mail: reiner.anwander@ch.tum.de.

[1] For a recent review, see: Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307−338.

[2] Kagan, H. B.; Namy, J.-L. *Top. Organomet. Chem.* **1999**, *2*, 155−198.

[3] (a) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754−766 and references therein. (b) Takats, J. *J. Alloys Compd.* **1997**, *249*, 52−55. (c) Clegg, W.; Eaborn, C.; Izod, K.; O'Shaughnessy, P.; Smith, J. D. *Angew. Chem.* **1997**, *109*, 2925−2926; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2815−2817.

[4] Basset, J.-M.; Gates, B. C.; Candy, J. P.; Choplin, A.; Leconte, M.; Quignard, F.; Santini, C. C. *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Kluwer: Dordrecht, 1988.

[5] Anwander, R.; Roesky, R. *J. Chem. Soc., Dalton Trans.* **1997**, 137−138.

[6] Preliminary studies of the reactivity of SmI_2 with siliceous support materials in THF indicated that in the absence of any base molecules and upon prolonged contacting complete oxidation of the samarium centers occurred; Nagl, I.; Anwander, R., unpublished results.

[7] Nagl, I.; Scherer, W.; Tafipolsky, M.; Anwander, R. *Eur. J. Inorg. Chem.* **1999**, 1405−1407.

[8] The mesoporous silicas were synthesized according to slightly modified literature procedures: (a) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834−10843. (b) Van Der Voort, P.; Morey, M.; Stucky, G. D.; Mathieu, M.; Vansant, E. F. *J. Phys. Chem.* **1998**, *102*, 585−590.

[9] For a recent review article on the modification of mesoporous silica materials, see: Moller, K.; Bein, T. *Chem. Mater.* **1998**, *10*, 2950−2963.

[10] Sm(II)-doped silicate glasses prepared according to a sol gel process and subsequent heating in the presence of hydrogen were reported to be colorless; see: Nogami, M.; Abe, Y. *Appl. Phys. Lett.* **1994**, *65*, 1227−1229.

[11] For comparison, homoleptic Ln(III) silylamides yield a metal surface coverage of approximate 0.8 Ln/nm^2, while the alkyl amide Nd(N*i*Pr$_2$)$_3$(THF) produces a similar surface coverage.[5]

[12] Anwander, R.; Palm, C.; Stelzer, J.; Groeger, O.; Engelhardt, G. *Stud. Surf. Sci. Catal.* **1998**, *117*, 135−142.

[13] Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquérol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603−619.

[14] Similarly O, N-ligated mononuclear Sm(II) complexes reveal the formation of dinuclear Sm(III) pinacolate complexes after change of solvent from THF to hexane or after removal of any solvent; in contrast, C_5Me_5-supported Sm(III) ketyl complexes stay intact in apolar solvents.[3a]

[15] Molecular mono ketyl systems were reported to display no EPR signal due to antiferromagnetic superexchange interaction between the ketyl radical and the lanthanide(II) spins and/or spin−lattice relaxation of the ketyl radical via paramagnetic lanthanide(III) ions; in contrast, Sm(III) tris(ketyl) showed a strong EPR signal with $g = 2.0027$.[3a]

[16] (a) Dehl, R.; Fraenkel, G. K. *J. Chem. Phys.* **1963**, *39*, 1793−1802. (b) Evans, J. C.; Rowlands, C. C.; Herold, B. J.; Empis, J. M. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 389−394.

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Scheme 1. Proposed Surface Species

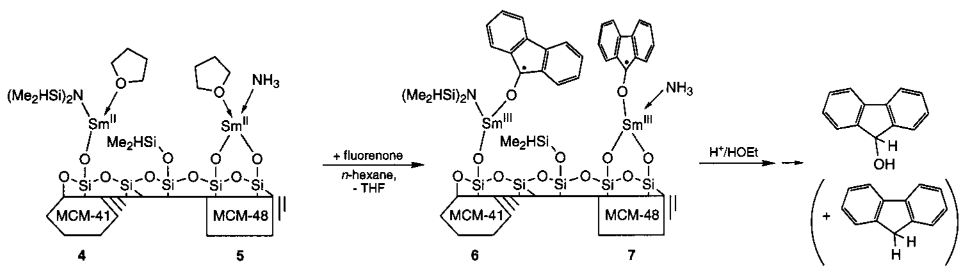

Table 1. Analytical Data, Surface Area, Pore Volume, and Effective Mean Pore Diameter

material[a]	wt % C	a_s[b]/ $m^2\ g^{-1}$	V_p[c]/ $cm^3\ g^{-1}$	d_p[d]/ nm
MCM-41 (**2**)		1010	0.95	3.3
[MCM-41]$SiHMe_2$ (**2a**)[e]	5.8	883	0.70	2.9
[MCM-41]$Sm[N(SiHMe_2)_2]_x(THF)_y$ (**4**)	10.2	434	0.26	2.3
[MCM-41]$Sm[N(SiHMe_2)_2]_x$(fluorenyl) (**6**)	28.9	48	–	–
[MCM-41]$Sm(OH)_x$ (**8**, recovered material)	4.7	813	0.72	3.0
MCM-48 (**3**)		1044	1.21	3.3
[MCM-48]$SiHMe_2$ (**3a**)[e]	6.6	819	0.77	2.7
[MCM-48]$Sm[N(SiHMe_2)_2]_x(THF)_y$ (**5**)	10.4	512	0.30	1.9
[MCM-48]$Sm[N(SiHMe_2)_2]_x$(fluorenyl) (**7**)	30.6	22	–	–
[MCM-48]$Sm(OH)_x$ (**9**, recovered material)	3.7	734	0.65	3.0

[a] Pretreatment temperature: 280 °C, 4 h, 10^{-3} Torr for **2** and **3**; 250 °C, 3 h, 10^{-3} Torr for **2a**, **3a**, **8**, and **9**; 25 °C, >5 h, 10^{-3} Torr for **4**, **5**, **6**, and **7**. [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 (d_p < 2.0 nm have to be viewed critically). [e] Dehydrated mesoporous material reacted with excess of $HN(SiHMe_2)_2$.

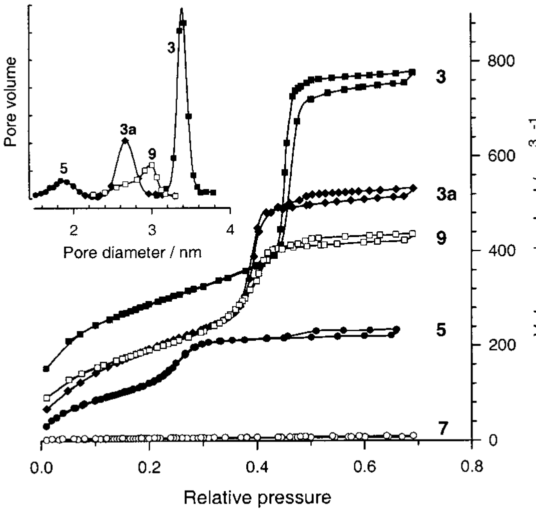

Figure 1. Nitrogen adsorption/desorption isotherms at 77.4 K and the corresponding BJH pore size distributions of the parent and modified MCM-48 materials **3**, **3a**, **3**, **5**, **7**, and **9** (cf. Table 1).

between 130 and 323 K indicating the rigid bonding of the radical to the surface.

Treatment of the hybrid materials **6** and **7** with both aqueous HCl (2 N) and ethanolic HCl (99:1) under inert gas yielded fluorenol as the main product of reduction, although a small amount of fluorene could be detected. This contradicts the findings in homogeneous solutions where organosamarium(II) complexes treated with equimolar amounts of ketone hydrolyze to give the pinacol product exclusively.[3a] The presence of sterically separated, surface-bound Sm(II) species in hybrid materials **4** and **5** seems to drastically modify the selectivity of this transformation.[17] The sligthly yellow recovered materials **8** and **9** display a pronounced OH stretch vibration at 3690 cm^{-1} in the IR spectrum and show the original type-IV isotherm (Figure 1). For comparison, a dehydrated ordinary silica material (Aerosil-200, Degussa-Hüls, surface area 200 $m^2\ g^{-1}$) gave similar hybrid materials [AS200]-$Sm[N(SiHMe_2)_2]_x(THF)_y$ (**10**, loading = 0.3 Sm(II)/nm^2, a_s = 148 $m^2\ g^{-1}$) and [AS200]$Sm[N(SiHMe_2)_2]_x$(fluorenyl) (**11**, a_s = 141 $m^2\ g^{-1}$) which showed qualitatively analogous reaction behavior. However, the ketyl radicals on material **11** seem to be increasingly prone to hydrogen radical abstraction as indicated by a significant amount of fluorenol in the supernatant solution. We ascribe this ketyl destabilization to the lack of pore confinement (protective effect of the intrapore arrangement) and the changed morphology of the Aerosil-200 silica material (presence of bulk silanol groups). As a consequence, material **11** displayed a weak EPR signal (Figure 2,b). The effect of surface silylation on both possible radical stabilization and the control of the concentration/spacing of the metal centers as well as the presence of different pore radii are currently examined.

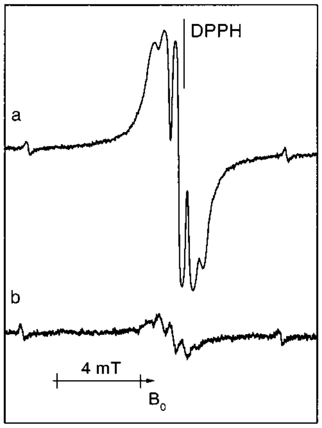

Figure 2. X-band EPR spectrum (T = 293 K) observed for M41S materials **6** and **7** (a) and Aerosil material **11** (b) under argon atmosphere.

Given the rich chemistry of carbon coupling reactions induced by molecular Sm(II) reagents quite a new chemistry should evolve from such surface-confined “monometallic” Sm(II) centers.[18] This kind of surface chemistry might also have significant implications for the reactivity pattern of other low-valent, highly reductive metal centers.

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Supporting Information Available: Experimental procedures for the preparation of all new materials including physicochemical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For comparison, homoleptic Ti(III) complexes carrying bulky tBu_3-SiO ligands allowed the direct EPR observation of a diphenyl carboxy radical, however, also dimerization occurred between the carbonyl and phenyl *para* carbon atoms of separate Ph_2CO units, see: Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66–78.

(18) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.