The Danishefsky Hetero Diels–Alder Reaction Mediated by Organolanthanide-Modified Mesoporous Silicate MCM-41

Gisela Gerstberger,[a] Clemens Palm,[b] and Reiner Anwander*[a]

Abstract: Silylamides are used as reactive precursors for a high-yield synthesis of β-diketonate chelates [M(fod)$_3$] (M = Sc, Y, La, Al; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate). A heterogeneously performed silylamide route is employed to graft [M{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$], including the novel aluminum derivative, onto mesoporous silicate MCM-41 through terminal silanol groups, generating stable metal siloxide linkages. Subsequent surface-confined ligand exchange with Hfod monitored by FTIR spectroscopy yields [MCM-41]M(fod)$_x$(thf)$_y$. The hybrid materials obtained, which were further characterized by nitrogen physisorption and elemental analysis, show promising activity in the catalytic hetero Diels–Alder cyclization of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene and benzaldehyde. The effects on the catalytic activity of various parameters such as the Lewis acidity of the anchored metal cation or the pore diameter of the support material are discussed. The performance of the immobilized catalyst species is compared with, and found superior to, both known homogeneous systems and materials obtained from the reaction of [Ln(fod)$_3$] with the dehydrated MCM-41 material, particularly in its deactivation behavior and reuseability.

Keywords: aluminum · catalysis · Diels–Alder reactions · immobilization · lanthanides · silylamides

Introduction

Over the past decade organolanthanide complexes have attracted considerable attention as highly efficient precatalysts for the synthesis of fine chemicals and polymers.[1, 2] As a consequence, precatalyst design and fine-tuning, through the development of more efficient synthesis procedures (e.g. the extended silylamide route)[3] and novel ligand environments (ancillary ligands),[4] have already attained a high level of sophistication. In contrast, precatalyst immobilization, which is commonly used as an attractive way of combining the advantages of both homogeneous and heterogeneous catalysis,[5] has barely been tackled in lanthanide chemistry.[6-9] We recently reported a heterogeneously performed silylamide route using lanthanide complexes as the molecular components and mesoporous MCM-41 as a siliceous support material (Scheme 1).[10] The immobilization of such rare earth metal species by reaction with isolated silanol groups to form thermodynamically stable Si-O-Ln linkages was expected to provide chemically and thermally robust, reuseable catalysts. The modification of the surface-grafted metal silylamide moieties through second-generation ligand exchange reactions is a particularly useful option with this route, as it allows the hybrid material to be individually tailored to different catalytic applications. Mesoporous MCM-41[11] seems especially well suited as a *model* support material for the commonly used silica[5] on account of its regular hexagonal pore geometry, large internal surface area (> 1000 m^{2}g^{-1}), and high number of surface silanol groups. There is also the possibility of adjusting the pore diameter from 2 to 10 nm.

The so-called Danishefsky transformation, that is the hetero Diels–Alder cyclization of an activated diene such as *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with benzaldehyde,[12, 13] is presented here as a promising reaction for evaluating the catalytic properties of grafted Lewis acidic lanthanide centers in the presence of sensitive substrate molecules (*substrate susceptibility*). This reaction is highly selective, requires mild reaction conditions, and has enormous potential in the asymmetric synthesis of organic natural products (e.g. monosaccharides).[14, 15] In this paper a comparison is made, based on leaching and recovery studies, of the catalytic activity and reuseability of molecular and immobilized 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate rare earth metal chelates [M(fod)$_x$][16] (the latter are obtained by surface ligand exchange reactions as outlined in Scheme 1).

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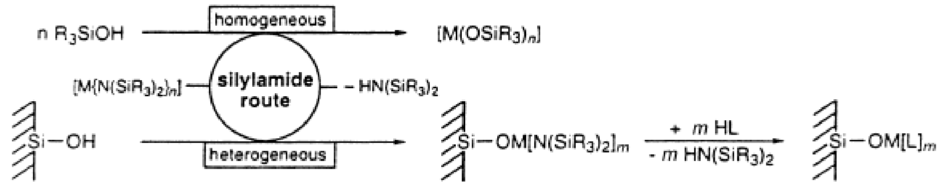


Scheme 1. Homogeneously and heterogeneously by the silylamide route—second-generation ligand exchange.

Results and Discussion

Synthesis and grafting of [M{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$]: Lanthanide silylamide precursor compounds of type [Sc{N(SiHMe$_2$)$_2$}$_3$(thf)] (**1a**) and [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (Ln = Y (**1b**), La (**1c**)) were obtained from the reaction of [LnCl$_3$(thf)$_x$] with Li[N(SiHMe$_2$)$_2$], as described previously.[10b]

In view of the similarities between Al^{3+} and the trivalent rare earth metal cations in terms of their reactivity, coordination behavior, and Lewis acidity, we decided to conduct all transformations and catalytic studies not only with the lanthanide derivatives, but also with the corresponding aluminum congeners. Thus, novel [Al{N(SiHMe$_2$)$_2$}$_3$(thf)] (**2**) was prepared by treating a suspension of AlCl$_3$ in THF with Li[N(SiHMe$_2$)$_2$] [Eq. (1)] and was isolated as a colorless, viscous oil. The ^{1}H NMR [δ(SiH) = 4.88] and IR [ν(SiH) = 2114 cm^{-1}] data of **2** are rather similar to those of the scandium derivative **1a** [δ(SiH) = 5.03; ν(SiH) = 2091 cm^{-1}] and are consistent with a less distinct metal–(SiH) interaction in solution compared with that of the larger lanthanide elements. According to ^{1}H NMR spectroscopy, elemental analysis, and mass spectrometry only one thf molecule is coordinated to the metal center in **2**.

$$\mathrm{AlCl_3} + 2.9\ \mathrm{Li[N(SiHMe_2)_2]} \xrightarrow[\text{r.t., 48 h}]{\text{THF}} \underset{\mathbf{2}}{[\mathrm{Al\{N(SiHMe_2)_2\}_3(thf)}]} \qquad (1)$$

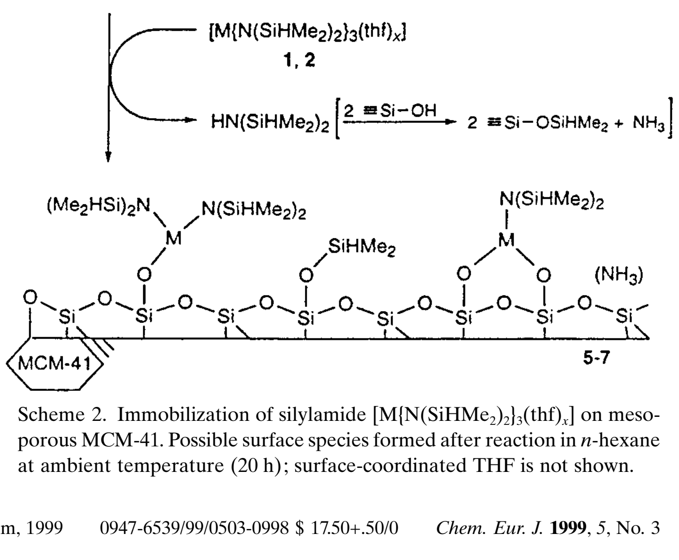
Abstract in German: *Silylamide sind reaktive Vorstufen für β-Diketonat-Chelatkomplexe [M(fod)$_3$] (M = Sc, Y, La, Nd, Er, Al; fod = 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octandionat). Mittels einer heterogen durchgeführten Silylamidroute werden [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] (Ln = Sc, Y, La) und das neue Aluminium-Derivat [Al{N(SiHMe$_2$)$_2$}$_3$(thf)] auf mesoporösem MCM-41 über isolierte Silanolgruppen unter Ausbildung einer stabilen Metallsiloxid-Gruppierung verankert. Der Immobilisierungsprozeß sowie der anschließende Silylamid/Hfod Oberflächen-Ligandenaustausch können mit Hilfe der FTIR Spektroskopie verfolgt werden. Die erhaltenen Hybridmaterialien werden durch Stickstoff-Physisorption sowie Elementaranalyse charakterisiert und bewähren sich als effiziente Katalysatoren in der hetero-Diels-Alder Reaktion von trans-1-Methoxy-3-trimethylsiloxy-1,3-butadien und Benzaldehyd. Verschiedene Einflußparameter auf die katalytische Aktivität wie z. B. die Lewis-Acidität des verankerten Metallkations oder der Porendurchmesser des Trägermaterials werden diskutiert. Die immobilisierte Katalysatorspezies wird mit den bekannten molekularen sowie chemisorbierten [Ln(fod)$_3$]-Systemen verglichen. Die Vorteile der nach dieser neuartigen Verankerungsmethode erzeugten Hybrid-Katalysatoren, wie z. B. Substratverträglichkeit und Wiedereinsetzbarkeit, konnten klar unter Beweis gestellt werden.*

The MCM-41 materials **3** and **4** used in this study were synthesized following known procedures by employing [C$_{16}$H$_{33}$NMe$_3$]Br as a template and, in the case of **4**, with mesitylene as an organic auxiliary.[11, 17, 18] Their hexagonal structure was established by powder X-ray diffraction [after calcination: d_{100} = 3.48 nm (**3**), 4.74 nm (**4**)] and the pore texture was examined by nitrogen physisorption (Table 1). To exclude any Lewis acid induced side reactions during the ligand exchange reactions and the catalytic investigations, aluminum-free synthesis gels were used. The potential of such a structurally ordered silica material to act as a versatile support material has previously been demonstrated for a few MCM-41-grafted main group[19] and organotransi-

Table 1. Analytical data, pore volume, and effective mean pore diameter.

Material	wt % M	wt % C	V_p[d] [cm^3 g^{-1}]	d_p[e] [nm]
MCM-41 (**3**)[a]	–	–	0.93	2.7
[MCM-41]SiHMe$_2$ (**3a**)[a]	–	6.45	0.58	2.1
MCM-41 (**4**)[a]	–	–	0.96	3.8
[MCM-41]SiHMe$_2$ (**4a**)[a]	–	5.29	0.55	2.9
[MCM-41]Sc[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ (**5a**)[b]	4.0	11.72	0.27	(1.7)[f]
[MCM-41]Y[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ (**5b**)[b]	7.6	12.01	–	–
[MCM-41]La[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ (**5c**)[b]	11.6	12.03	–	–
[MCM-41]Al[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ (**6**)[b]	2.5	10.48	0.31	(1.7)[f]
[MCM-41]Y[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ (**7**)[b]	6.6	11.88	0.38	2.7
[MCM-41]Sc(fod)$_x$(thf)$_y$ (**10a**)[c]	3.2	15.25	0.16	(1.5)[f]
[MCM-41]Y(fod)$_x$(thf)$_y$ (**10b**)[c]	6.5	14.43	–	–
[MCM-41]La(fod)$_x$(thf)$_y$ (**10c**)[c]	9.3	14.45	–	–
[MCM-41]Al(fod)$_x$(thf)$_y$ (**11**)[c]	1.9	14.02	0.15	(1.5)[f]
[MCM-41]Y(fod)$_x$(thf)$_y$ (**12**)[c]	5.3	12.04	0.39	2.7
[MCM-41]Y(fod)$_z$ (**13**)[c]	–	9.90	0.39	1.9

[a] Pretreatment temperature 250 °C, 3 h, 10^{-3} Torr. [b] Pretreatment temperature 25 °C, 3 h, 10^{-3} Torr. [c] Pretreatment temperature 100 °C, 3 h, 10^{-3} Torr. [d] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [e] Pore diameter according to the maximum of the pore size distribution. [f] d_p < 2.0 nm resulting from the BJH method have to be viewed critically.



Scheme 2. Immobilization of silylamide [M{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] on mesoporous MCM-41. Possible surface species formed after reaction in *n*-hexane at ambient temperature (20 h); surface-coordinated THF is not shown.

tion metal [20] species. Thus, as is shown in Scheme 2, approximately 1 mmol of silylamide was immobilized onto 1 g of MCM-41 material **3** ($d_p = 2.7$ nm)[10] through reaction with surface silanol groups, yielding hybrid materials of the type $[MCM\text{-}41]M\{N(SiHMe_2)_2\}_x(thf)_y$ (**5**, **6**). $[Y\{N(SiHMe_2)_2\}_3(thf)_x]$ (**1b**) was representatively allowed to react in an analogous manner with pore-enlarged MCM-41 material **4** ($d_p = 3.8$ nm) to afford the hybrid material **7** (Table 1).

The hybrid materials were characterized by elemental analysis and FTIR spectroscopy, and by representative X-ray diffraction and nitrogen physisorption measurements. The previously observed siloxide formation/silylation immobilization process outlined in Scheme 2 was confirmed for various lanthanide elements and for aluminum. The IR spectra of the products obtained revealed the complete consumption of the surface silanol groups and featured characteristic SiH vibration modes indicating the presence of both metal-bonded silylamide ligands (2050–2100 cm^{-1}) and $OSiHMe_2$ species (2151 cm^{-1}) (Figure 1). Interestingly, the relative intensities of the bands due to the metal-bonded species are greater for the pore-enlarged material **7**. Further studies are necessary to clarify whether this is attributable to diffusion-controlled immobilization processes or to a different surface texture imposed by differently sized mesopores. The accompanying surface silylation by the released silylamine (cf. Scheme 2) affects both the steric environment of the metal centers and the hydrophobicity of the hybrid material, which might have significant implications for the catalytic performance of future catalysts.[21, 22] Taking into consideration the metal content, which has been determined by ICP analysis, and the BET surface area of dehydrated **3** (1140 m^2g^{-1}) and **4** (920 m^2g^{-1}), the metal surface coverage is calculated to be approximately 0.45–0.50 metal atoms per nm^2. The number of reactive surface silanol sites accessible to $HN(SiHMe_2)_2$ silylation was derived as 1.42 (**3a**) and 1.44 $SiHMe_2$ moieties per nm^2 (**4a**), respectively.

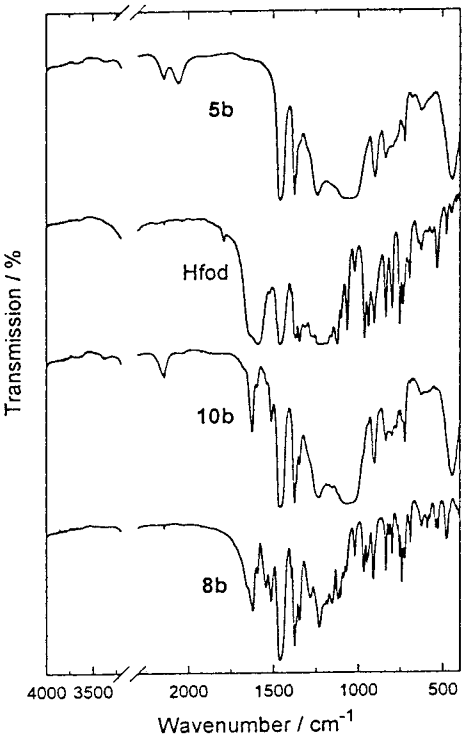


Figure 1. IR spectra (Nujol) of $[MCM\text{-}41]Y[N(SiHMe_2)_2]_x(thf)_y$ (**5b**), Hfod, $[MCM\text{-}41]Y(fod)_x(thf)_y$ (**10b**), and $[Y(fod)_3]$ (**8b**).

The extent of the pore filling caused by the silylamide immobilization was examined by nitrogen physisorption (Figures 2 and 3). The type IV isotherms of the parent support materials **3** and **4** are characterized by sharp inflection points at relative pressures p/p_0 of 0.35 and 0.45, respectively, and by the appearance of a pronounced hysteresis for the pore-enlarged material **4** due to capillary condensation (Figure 3). The grafted complexes change from the original type IV isotherm of material **3** to the almost type I isotherm in the case of the hybrid system **5a**, indicating a drastic reduction in pore volume and pore diameter (Figure 2). In contrast, the isotherm for the hybrid material **7** still shows a pronounced step at a relative pressure of about 0.3, from which a pore diameter of approximately 2.5 nm can be inferred (Figure 3). The pore diameter in materials **5** and **6** can thus be extrapolated to about 1.5 nm. In the silylated materials **3a** and **4a** obtained by treatment of **3** and **4** with $HN(SiHMe_2)_2$ the isotherms are still of type IV. The pronounced hysteresis

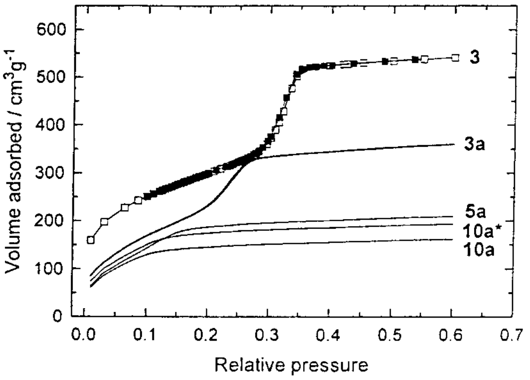


Figure 2. Nitrogen adsorption/desorption isotherms at 77.4 K of MCM-41 (**3**, filled symbols denote desorption), $[MCM\text{-}41]SiHMe_2$ (**3a**), $[MCM\text{-}41]Sc[N(SiHMe_2)_2]_x(thf)_y$ (**5a**), and $[MCM\text{-}41]Sc(fod)_x(thf)_y$ (**10a**, **10a***) (cf. Table 1, *as synthesized, activated for 3 h at 250 °C and 10^{-3} Torr).

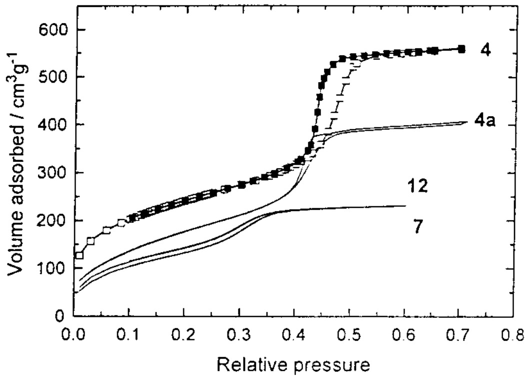


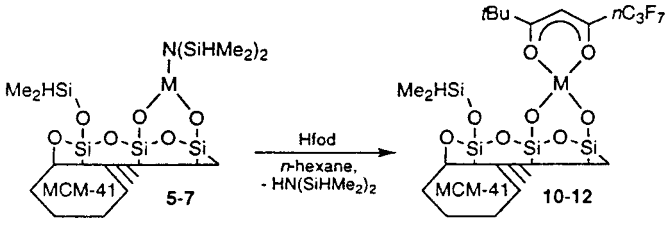
Figure 3. Nitrogen adsorption/desorption isotherms at 77.4 K of MCM-41 (**4**, filled symbols denote desorption), $[MCM\text{-}41]SiHMe_2$ (**4a**), $[MCM\text{-}41]Y[N(SiHMe_2)_2]_x(thf)_y$ (**7**), and $[MCM\text{-}41]Y(fod)_x(thf)_y$ (**12**) (cf. Table 1).

displayed by material **4** is still present in the silylated material **4a**,[18] but is not observed in the silylamide-treated material **7**.

Synthesis of [M(fod)$_3$]: In a departure from the conventional synthetic method starting with rare earth metal nitrates or chlorides,[16, 23] [Ln(fod)$_3$] (**8a–c**) and [Al(fod)$_3$] (**9**) were prepared by treating [M{N(SiMe$_3$)$_2$}$_3$][24, 25] with three equivalents of Hfod in *n*-hexane [Eq. (2)]. Compared with the traditional synthesis, yields are generally very good and the analytical data are consistent with the literature values.[23] The silylamide route has previously been applied to the synthesis of yttrium acetylacetonato complexes.[26] Complete amide/Hfod ligand exchange can also be achieved with [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] (**1b**) as a synthetic precursor. However, this leads to products containing coordinated thf molecules, which might decrease their Lewis acidity, and hence their catalytic activity.

$$[M\{N(SiMe_3)_2\}_3] + 3\ Hfod \xrightarrow[r.t.,\ 72\ h]{n\text{-hexane}} \underset{\substack{\mathbf{8a\text{-}c}\ (M = Sc, Y, La)\\ \mathbf{9}\ (M = Al)}}{[M(fod)_3]} + 3\ HN(SiMe_3)_2 \tag{2}$$

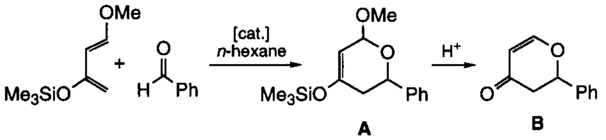
Surface ligand exchange to form immobilized [M(fod)$_x$] species: In analogy to the homogeneously performed silylamide route,[3] a suspension of the silylamide hybrid materials (**5a–c**, **6**, and **7**) in *n*-hexane was stirred for 24 h at ambient temperature with a slight excess of Hfod (Scheme 3). After washing several times with *n*-hexane, the resulting hybrid materials [MCM-41]M(fod)$_x$(thf)$_y$ (**10a–c**, **11**, and **12**), were dried under vacuum for at least 5 h (Scheme 3). The release of free silylamine was confirmed by GCMS.



Scheme 3. Formation of [MCM-41]M(fod)$_x$(thf)$_y$ by second-generation ligand exchange of [MCM-41]M[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$ with Hfod (*n*-hexane, ambient temperature, 24 h); coordinated thf is not shown.

The completeness of the surface ligand exchange was monitored by FTIR spectroscopy. In the products obtained the vibrational mode at 2151 cm^{-1} due to the OSiHMe$_2$ species formed in the silylation reaction (cf. Scheme 2) is still present, as shown in Figure 1 for hybrid material **10b**. However, all the metal-bonded silylamide moieties were replaced by chelating fod ligands, as indicated by the disappearance of the lower energy SiH vibrational modes at about 2060 cm^{-1} and concomitant appearance of the carbonyl absorptions at about 1620 cm^{-1}. Extraction experiments with an excess of Hfod showed that the metal centers cannot be degrafted under these conditions (i.e. absence of free surface silanol groups in the extracted materials). The IR spectrum of homoleptic [Y(fod)$_3$] (**8b**) is shown in Figure 1 by way of comparison. The nitrogen adsorption/desorption isotherms of materials **10a** (Figure 2) and **12** (Figure 3) showed no significant changes relative to those of their synthetic precursors, yielding similar pore diameters of 1.5 and 2.7 nm, respectively.

Catalytic studies: The efficient and selective catalysis of some Diels–Alder reactions by lanthanide β-diketonate complexes was discovered accidentally through the use of these compounds as NMR shift reagents.[27, 28] Thus, traditionally, the rare earth metal catalysts used for the hetero Diels–Alder reaction comprised complexes of the paramagnetic elements Yb and Eu. Various approaches aimed at improving the efficiency of these Diels–Alder reactions are currently being extensively investigated,[29] and some new developments towards the introduction of air-stable lanthanide catalysts were reported very recently by Spino, Clouston, and Berg.[30] Lanthanide complexes such as [Ln(fod)$_3$] have been found to selectively catalyze the Danishefsky transformation (cyclization of the 1,3-diene *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with benzaldehyde as the dienophile) (Scheme 4) as a consequence of their postulated mild Lewis acidity.[12, 13]



Scheme 4. The Danishefsky transformation; product **B** is obtained after acidic work-up with trifluoroacetic acid (TFA).

Pure or grafted MCM-41 materials also act as catalysts for a number of organic transformations,[31] and Diels–Alder reactions catalyzed by zeolites or Lewis acid modified silica or alumina have previously been described.[32] A first use of silica-grafted β-diketonate copper chelates as catalysts for asymmetric cyclopropanation was reported by Matlin et al.[33] Polysiloxane-tethered β-diketonate complexes of the metals V, Ni, Pr, Eu, and U have been used by Schurig et al. as catalysts for the Danishefsky transformation.[34]

We tested the molecular [M(fod)$_3$] (**8**, **9**) and the hybrid materials [MCM-41]M(fod)$_x$(thf)$_y$ (**10–12**) under standard conditions as catalysts for the Danishefsky transformation: In these reactions 1.1 equivalents of benzaldehyde were allowed to react with *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene in *n*-hexane at ambient temperature unless otherwise stated. The catalysts (0.2 mol% metal) were dissolved or suspended in the solvent, respectively. Owing to their moderate Lewis acidity compared for example with BF$_3$,[35] the reaction stops at product **A** without further reaction to **B**. Product **B** can be generated directly from the reaction mixture through acidic (TFA) workup. As the amount of **A** formed increases, the originally colorless solution becomes orange to brown in color. The hybrid materials **10–12** also gradually take on a brownish color, though this does not affect their catalytic activity. Immediate and intense coloration upon addition of the substrates was observed to be indicative of some irreversible reaction with the support material.

The reactivity of the unmodified parent support material **3** towards the two oxo-functionalized substrates was also probed. Both benzaldehyde and the Danishefsky diene are strongly physisorbed at ambient temperature without any coloring of the purely siliceous material. Carbon contents in the analyzed product as high as 16.7 and 18.9%, respectively, indicate high substrate loadings. Upon prolonged treatment at 250°C and 10^{-3} Torr both of the substrate molecules desorb completely, as shown by FTIR spectroscopy, nitrogen physisorption, and elemental analysis. In contrast, an aluminosilicate of type MCM-41 (Si/Al = 18) reacts instantaneously with an excess of the Danishefsky diene to form a dark brown solution and solid. The solid material exhibits a significantly reduced pore volume of 0.40 $cm^3 g^{-1}$ upon thermal treatment and the band at 3695 cm^{-1} indicative of free silanol groups disappears almost completely. This suggests that the use of purely siliceous support materials is crucial in catalytic transformations with such activated substrate molecules.[36] Selected results of the catalytic studies are summarized in Table 2.

Table 2. Summary of the catalytic studies.[a]

Run	Precatalyst	T [°C]	Yield of **A**[b] (after 10 h)
1	$[Sc(fod)_3]$ (**8a**)	25	80
2	$[Y(fod)_3]$ (**8b**)	25	80
3	$[La(fod)_3]$ (**8c**)	25	74
4	$[Al(fod)_3]$ (**9**)	25	7
5	$[MCM\text{-}41]Sc(fod)_x(thf)_y$ (**10a**)	25	97
6	$[MCM\text{-}41]Y(fod)_x(thf)_y$ (**10b**)	25	79
7	$[MCM\text{-}41]La(fod)_x(thf)_y$ (**10c**)	25	52
8	$[MCM\text{-}41]Al(fod)_x(thf)_y$ (**11**)	25	78
9	$[MCM\text{-}41]Y(fod)_x(thf)_y$ (**12**)	25	88
10	$[MCM\text{-}41]Y(fod)_x(thf)_y$ (**10b**)	0	51
11	$[MCM\text{-}41]Y(fod)_x(thf)_y$ (**10b**)	50	89
12	$[MCM\text{-}41]Y(fod)_z$ (**13**)	25	30

[a] Conditions: 2 mmol Danishefsky diene, 2.2 mmol benzaldehyde, 0.75 mmol *n*-dodecane (internal standard for GC analysis), 0.04 mmol catalyst referred to the metal content. [b] Determined by gas chromatography.

Molecular versus hybrid catalysts: A comparison of homogeneous and heterogeneous catalysis with $[Y(fod)_x]$ species **8b** and **10b** (Table 2: runs 2 and 6) (Figure 4), revealed greater stability over time as the particular advantage of the immobilized catalyst. Whereas complex **8b** is more active at the beginning of the reaction, the conversion comes to a halt after approximately 1 h. This is probably due to some kind of catalyst deactivation (e.g. poisoning, complex degradation). No further activity was observed on addition of further equivalents of the substrates. Compound **8a** reacts as rapidly as **8b**, whereas **8c** with its less Lewis acidic La^{3+} center is considerably slower, which is also consistent with the tendency of the larger lanthanide elements to expand their coordination number in solution and in the solid state by forming dinuclear β-diketonate complexes.[37] The comparatively small Al^{3+} center in the six-coordinate $[Al(fod)_3]$ (**9**) appears to suppress the Danishefsky transformation through steric constraints (no activation of the dienophile by adduct formation), resulting in almost zero conversion (run 4); the formation of approximately equal amounts of **A** and **B** is observed (each ~5%), in addition to other, unidentified, byproducts.

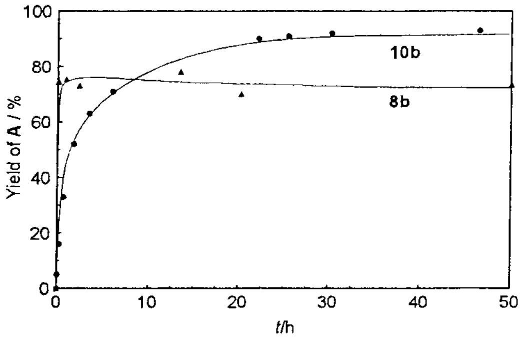


Figure 4. Catalytic activity of the complex $[Y(fod)_3]$ (**8b**) (run 2, Table 2) versus the hybrid $[MCM\text{-}41]Y(fod)_x(thf)_y$ (**10b**) (run 6, Table 2).

Although the initial activity of the hybrid catalyst **10b** is slightly lower than that of its molecular congener **8b**, almost 95% conversion is achieved after 50 h. Turnover rates are just as rapid in subsequent cycles as in the initial cycle, demonstrating the absence of any marked decrease in activity towards the end of the reaction. Furthermore, product **B** is not formed with **10b**, in contrast to the reaction with **8b**, in which increasing quantities of **B** are observed after about 30 h (ca. 8% after 67 h). The slightly lower activity of the immobilized catalyst is thought to be due mainly to restricted diffusion and to THF donor coordination (possibly resulting from the synthetic procedure). The immobilized catalyst is easily separated from the reaction mixture by centrifugation and can be reused after washing with *n*-hexane (see below). Comparison of the Al-fod species **9** (run 4) with **11** (run 8) shows the hybrid system to have unexpected catalytic activity. Whereas the molecular six-coordinate complex **9** is almost inactive, the hybrid material **11** is as active as the yttrium derivative **10b** (cf. Table 2, Figure 5). An explanation for the enhanced catalytic activity of the immobilized species might be the formation, upon surface grafting, of geometrically distorted tetra- and pentacoordinate Al centers with accessible coordination sites. A similar surface confinement was previously detected, through ^{27}Al MAS NMR studies and catalytic Meerwein–Ponndorf–Verley reductions, in MCM-41 materials containing surface-grafted methyl aluminum and isopropoxide aluminum species.[38, 39]

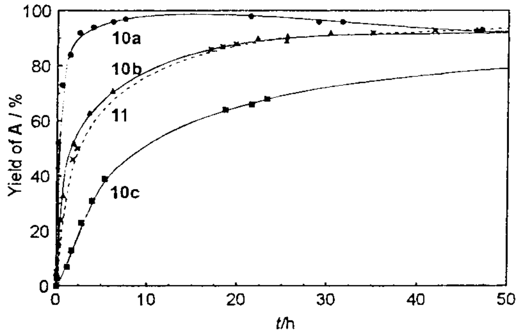


Figure 5. Comparison of the catalytic activities of $[MCM\text{-}41]M(fod)_x(thf)_y$ (**10a–c**, **11**) (runs 5–8, Table 2) as an illustration of the influence of cation size and Lewis acidity.

The effect of surface silylation was examined by testing silylated MCM-41 materials of type **3a** under the same conditions. Interestingly, products **A** and **B** are formed to a considerable extent. Maximum conversion (20%) to product **A** is obtained after 5 h, while product **B** is generated more gradually (15% after 25 h). The presence of strained Lewis acidic Si-O-Si surface species formed through calcination and dehydration[40] may contribute to the catalytic activity of the silylated materials. The consumption of all the *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene after 25 h may be a consequence of some irreversible transsilylation reaction (ca. 70% of the benzaldehyde is consumed).

Variation of the Lewis acidity: On comparing a series of trivalent metal cations of gradually increasing Lewis acidity, a clear trend in activity emerges: the more Lewis acidic the metal center, the higher its activity in our model reaction (runs 5–8, Figure 5). Hybrid material **10a** appears to be the most efficient catalyst (almost 100% conversion achieved), though with longer reaction times (>15 h), the initial product **A** is slowly converted into **B**. This transformation is not observed with materials **10b** and **10c**, in which the metal centers are less Lewis acidic. Similar Lewis acidity dependent behavior was observed for the molecular compounds (vide supra).

Variation of the temperature: The temperature dependence of the catalytic activity is exemplified by the performance of **10b** (Figure 6). At 50 °C near maximum conversion (87%) is reached after only 4.5 h, whereas at ambient temperature this takes about 20 h. The conversion is considerably slower still at 0 °C. The initial turnover frequency (TOF = [(mol product)/(mol catalyst per h)]) increases from about 10 at 0 °C to 30 at 25 °C, and to 70 at 50 °C, which, according to Arrhenius, gives an apparent activation energy of about 28 kJmol^{-1}. For comparison, the initial TOF achieved by the molecular yttrium complex **8b** was about 180 at 25 °C.

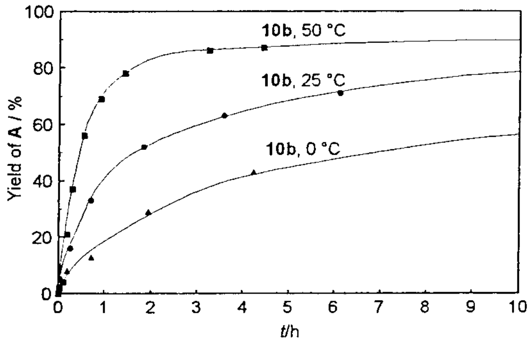


Figure 6. Influence of the temperature on the catalytic activity of [MCM-41]Y(fod)$_x$(thf)$_y$ (**10b**) (runs 6, 10, 11, Table 2).

Variation of the pore diameter: Nitrogen physisorption studies showed the pore diameters of materials **10b** (like **10a**) and **12** to be 1.5 and 2.7 nm, respectively (cf. Figures 2 and 3). Material **12** (run 9) exhibits a higher initial catalytic activity than **10b** (run 6), though in both cases the concentrations of the product **A** ultimately converge to a final yield of almost 95% (Figure 7). This means that a limiting factor in this reaction is still the rate of diffusion, which can be increased by using support materials with larger pore diameters. Hence, the tailoring of the pore radius by the addition of organic auxiliaries during hydrothermal synthesis or by post-synthetic silylation combined with the immobilization of substituents of varying bulk thus seems to be a promising approach to stereo- and shape-selective transformations.[41]

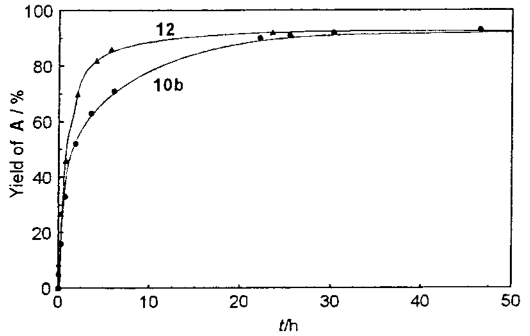
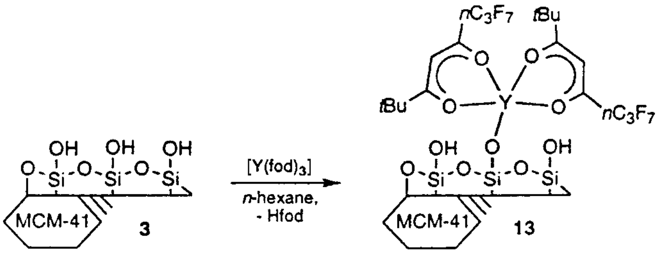


Figure 7. Influence of the pore radius on the catalytic activity of the hybrid system [MCM-41]Y(fod)$_x$(thf)$_y$; **10b**: 1.5 nm pore diameter (run 6, Table 2), **12**: 2.7 nm pore diameter (run 9, Table 2).

Leaching and catalyst recovery experiments: When the reaction solution of run 6 was separated from the catalyst and treated with fresh equivalents of the substrates, the solution itself showed no catalytic activity. Conversely, on starting a new catalytic run with the separated, *n*-hexane-washed **10b**, about the same total conversion was reached after 24 h. Even after six catalytic runs no significant decrease in activity was observed. These experiments therefore demonstrate that leaching of the hybrid materials **10** does not occur under the conditions of our catalytic runs. Equally importantly, the used catalyst can be easily separated and quantitatively recovered.

Synthesis and catalytic performance of [Ln(fod)$_3$]-grafted MCM-41 materials: Material **13** was generated by treating the MCM-41 material **3** with an excess of [Y(fod)$_3$] (**8b**) in *n*-hexane for 24 h, omitting the "detour" via the grafted silylamide intermediate (Scheme 5). A surface reaction (chemisorption) with [Y(fod)$_3$] is indicated in the IR spectrum of **13** by a considerable weakening of the absorption band of the isolated silanol groups. In addition, elemental analysis



Scheme 5. Formation of [MCM-41]Y(fod)$_z$ (**13**) by chemisorption of [Y(fod)$_3$] onto dehydrated MCM-41 (*n*-hexane, ambient temperature, 24 h).

revealed that the number of grafted metal centers present (ca. 3.4% Y) is only about half that in material **10b**, while the metal/fod ratio is approximately 2. Material **13** also displays a significantly higher pore volume and mean pore diameter compared to material **10b** (Table 1, Figure 8).

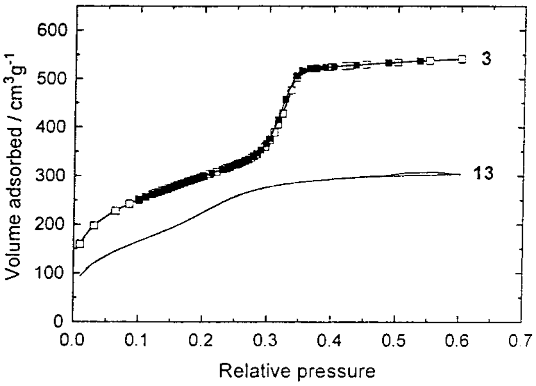


Figure 8. Nitrogen adsorption/desorption isotherms at 77.4 K of materials MCM-41(**3**, filled symbols denote desorption) and [MCM-41]Y(fod)$_z$ (**13**) (cf. Table 1).

The catalytic performance of material **13** was examined to elucidate whether the silylamide grafting process is in fact necessary, and what advantages it offers (run 6 versus run 12, Figure 9). The initial (5 min) catalytic activity of **13** was quite high, and was even comparable to that of the homogeneous catalyst **8b**. In this reaction product **B** is, however, generated from the outset. After 20 h all of product **A** had been transformed into the elimination product **B**, the yield of which was in excess of 95% after 40 h. This reaction behavior is totally different from that of the molecular compound [Y(fod)$_3$] (**8b**) and the in situ silylated hybrid material **10b**. It is rather reminiscent of the reactivity of the parent material **3** and the aluminum-containing MCM-41 materials in this catalytic transformation, in which product **B** is also generated from the outset with a combined yield of 30% of both of the Diels–Alder products (**A** and **B**) and complete consumption of the Danishefsky diene. Surface sites of enhanced Lewis acidity thus appear to be present in material **13**. Additional silylation might therefore be necessary to selectively poison residual silanol groups,[42] and thus facilitate the isolation of **A**. Recovered **13** from run 12 exhibits the same pattern of reactivity, and shows no significant decrease in activity when reused in subsequent runs. However, the observation of some residual catalytic activity in the separated reaction solution is indicative of the leaching of some physisorbed [Y(fod)$_3$] from the hybrid catalyst. Thus, on the basis of these results, silylamide grafting by reaction with isolated surface silanol groups and consumption of the remaining free silanol groups by in situ silazane silylation (Scheme 2) seems to prevent unwanted side reactions of the substrates and support material during these catalytic transformations.

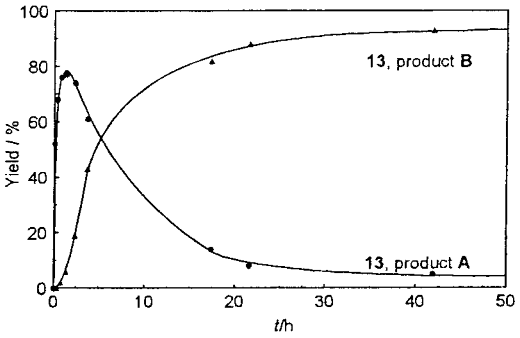


Figure 9. Catalytic behavior of chemisorbed [Y(fod)$_3$] (**13**, run 12, Table 2)

Conclusion

Lanthanide and aluminum silylamides of type [M{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] have proved versatile as reagents for tailoring silica support materials for catalytic applications. With our heterogeneous silylamide route high surface coverage is achieved. The formation of reactive metal ligand moieties, such as [MCM-41]M[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$, combined with in situ silylation by the released silylamine to form additional [MCM-41]SiHMe$_2$ sites, allows the coordination sphere of the metal to be tuned in a subsequent silylamine elimination reaction, thereby adapting the surface properties of the support material to sensitive organic substrates (*substrate susceptibility*). The peculiarities of this novel immobilization sequence were demonstrated by the catalytic performance of the ligand-exchanged materials [MCM-41]M(fod)$_x$(thf)$_y$ in the hetero Diels–Alder Danishefsky transformation of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with benzaldehyde. The immobilized species performed extremely well compared to the molecular [M(fod)$_3$] derivatives, especially in terms of stability and handling. In addition, the Lewis acidity (i.e. cation size) and pore diameter of the support material were shown to be important parameters influencing catalytic performance. The MCM-41 hybrid catalysts are not subject to leaching and can be easily recovered and reused in several further catalytic runs. Product formation is sensitive to the changes in metal surface coverage and surface environment arising from different grafting techniques.

Our current plans involve the incorporation of chiral ligands to tailor the support for enantioselective Lewis acid catalysis. This approach seems to hold much promise as a way of promoting asymmetric induction by adjusting the steric and electronic situation at the MCM-41 surface/metal-ligand interface.

Experimental Section

General: All syntheses and manipulations of compounds and hybrid materials were performed with rigorous exclusion of air and moisture, using high-vacuum and glove-box techniques (MBraun MB 150B-G-II; $O_2 <$ 1 ppm, $H_2O < 1$ ppm). Solvents were freshly distilled under argon from Na/K alloy. 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedionate (Aldrich) and *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Fluka) were dried over 4 Å molecular sieves, and benzaldehyde (Aldrich) was distilled and stored over 4 Å molecular sieves prior to use. $AlCl_3$ (Aldrich) was used without further purification. [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] **1a–c**,[10b] Ln[N(SiMe$_3$)$_2$]$_3$,[24] and Al[N(SiMe$_3$)$_2$]$_3$[25] were prepared according to literature methods. The dehydrated MCM-41 samples **3** and **4** were synthesized according to reference [18]. Tetramethyldisilazane was purchased from

Aldrich and degassed (freeze-pump-thaw cycles) before use. The silylated materials [MCM-41]SiHMe$_2$ (**3a** and **4a**) were prepared by solution impregnation with the disilazane agent according to reference [18]. FTIR spectra were recorded on Perkin-Elmer 1600 series and 1760X spectrometers as Nujol mulls sandwiched between CsI plates. NMR spectra were recorded at ambient temperature on JEOL-JMN-GX 400 (399.77 MHz ^{1}H; 100.54 MHz ^{13}C) and Bruker DPX 400 (400.13 MHz ^{1}H; 100.63 MHz ^{13}C) instruments at ambient temperature in C_6D_6. Elemental analyses were performed on an Elementar VarioEL and a plasma 400 emission spectrometer (Perkin-Elmer). Mass spectra were measured on a Finnigan MAT 90 instrument. Nitrogen physisorption measurements were performed on an ASAP 2010 volumetric adsorption apparatus (Micromeritics) at 77.4 K and relative pressures of between 10^{-2} and 0.70 [$a_m(N_2, 77\,K) = 0.162\,nm^2$]. Unless otherwise stated in Table 1, samples were degassed prior to analysis under vacuum (about 10^{-3} Torr) for 5 h at ambient temperature. Specific surface areas were determined by the BET method. Pore size distributions were calculated according to the BJH method, using the Kelvin equation to calculate the mean pore diameter d_p.[43] The catalytic reactions were monitored by gas chromatography, using a HP 5890 series II FID instrument equipped with a 12.5 m × 0.33 mm 100% polysiloxane column (temperature program: 80 °C initial temperature for 2.5 min; heating rate 10 °C min^{-1}; final temperature 240 °C for 0.5 min). The integrator was calibrated on *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene and benzaldehyde with *n*-dodecane as internal standard. Yields of product **A** were calculated on this basis, assuming the course of reaction to be normal. For better reliability, each sample was measured twice.

[Al{N(SiHMe$_2$)$_2$}$_3$(thf)] (2): AlCl$_3$ (0.495 g, 3.71 mmol) was dissolved in THF (20 mL) and the solution was stirred at ambient temperature for 48 h. Li[N(SiHMe$_2$)$_2$] (1.50 g, 10.8 mmol) was added in small portions, and the reaction mixture was stirred for another 48 h at ambient temperature. The solvent was then removed in vacuo, the residue was extracted with *n*-hexane (15 mL), and separated from the precipitated LiCl using a cannula. Evaporation of the extract for 48 h at 10^{-4} Torr gave the product as a clear, colorless oil (1.637 g, 90%). ^{1}H NMR (400.1 MHz, 25 °C, C_6D_6): $\delta = 4.88$ (h, 6H, $^3J(H,H) = 2.9$ Hz; SiH), 3.98 (m, 4H; thf), 1.25 (m, 4H; thf), 0.41 (d, 36H, $^3J(H,H) = 2.9$ Hz; SiCH$_3$); ^{13}C NMR (100.6 MHz, 25 °C, C_6D_6): $\delta = 72.7$ (thf), 24.8 (thf), 3.4 (SiCH$_3$); MS (CI): *m/z* (%): 496 (31, [*M*]$^+$), 423 (4, [$M^+ -$ thf]), 320 (100, [H$M^+ - 3$SiHMe$_2$]), 265 (23, [N(SiHMe$_2$)$_2$]$_2$H), 133 (23, [HN(SiHMe$_2$)$_2$]); IR: $\tilde{\nu} = 2114$s (SiH), 1461s, 1377s, 1249s, 1039w, 1001m, 976s, 937vs, 905vs, 878vs, 856s, 826m, 768m, 726w, 683w, 668w, 492w, 417w cm^{-1}. $C_{16}H_{50}AlN_3OSi_6$ (496.1) (%): calcd C 38.7, H 10.2, N, 8.5; found C 36.8, H 10.2, N, 7.8.

General procedure for the synthesis of [M(fod)$_3$] (M = Sc (8a), Y (8b), La (8c), Al (9)): The silylamide complex [M{N(SiMe$_3$)$_2$}$_3$] was dissolved in *n*-hexane (10 mL per mmol) and Hfod (3 equiv) was added dropwise. After stirring the mixture for 72 h, the solvent and released silylamine were removed in vacuo (10^{-4} Torr), and the residue was sublimed at ~100 °C and 10^{-4} Torr or recrystallized to give the product in almost quantitative yield. The analytical data of compounds **8a–c** and **9** are consistent with literature values.[16, 23]

General procedure for the synthesis of [MCM-41]M{N(SiHMe$_2$)$_2$}$_x$(thf)$_y$ (5–7): The silylamide [M{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] (**1–2**) was dissolved in *n*-hexane (10 mL), and the solution was quickly added (<1 min) to a suspension of the dehydrated MCM-41 material (**3**, **4**) in *n*-hexane (10 mL). The reaction mixture was stirred for 20 h at ambient temperature and the solid product was then centrifuged off and washed several times with *n*-hexane (20 mL). The *n*-hexane fractions were collected and the solvent evaporated to determine the amount of unreacted silylamide complex present. The colorless hybrid materials **5–7** were dried in vacuo for at least 5 h.

5a: **1a** (0.566 g, 1.10 mmol) + **3** (0.899 g). 0.005 g unreacted **1a**. IR: $\tilde{\nu} =$ 2151m (SiH), 2076m (SiH), 899s, 836m, 678m, 626m cm^{-1}. Found C 11.7, H 2.9, N 2.3, Sc 4.0.

5b: **1b** (0.613 g, 0.97 mmol) + **3** (0.833 g). No unreacted **1b**. IR: $\tilde{\nu} = 2151$m, 2061m cm^{-1} (SiH). Found C 12.0, H 2.7, N 1.8, Y 7.6.

5c: **1c** (0.594 g, 0.87 mmol) + **3** (0.714 g). No unreacted **1c**. IR: $\tilde{\nu} = 2151$m, 2054m cm^{-1} (SiH). Found C 12.0, H 2.8, N 2.0, La 11.6.

6: **2** (0.393 g, 0.79 mmol) + **3** (0.685 g). 0.029 g unreacted **2**. IR: $\tilde{\nu} = 2151$m, 2102m cm^{-1} (SiH). Found C 10.5, H 2.8, N 2.7, Al 2.5.

7: **1b** (0.393 g, 0.63 mmol) + **4** (0.567 g). 0.015 g unreacted **1b**. IR: $\tilde{\nu} =$ 2151m, 2063m cm^{-1} (SiH). Found C 11.9, H 2.4, N 1.9, Y 6.6.

General procedure for the synthesis of [MCM-41]M(fod)$_x$(thf)$_y$ (10–12): Hfod (slight excess relative to the metal content) was diluted with *n*-hexane (5 mL) and added to a suspension of the silylamide hybrid species **5–7** in *n*-hexane (15 mL). After stirring the mixture for 20 h at ambient temperature, the colorless solids were separated by centrifugation and washed several times with *n*-hexane. The combined *n*-hexane fractions were colorless and contained no metal species. The resulting fod hybrid materials **10–12** were dried in vacuo at ambient temperature for at least 5 h.

10a: **5a** (0.540 g, 0.47 mmol Sc) + Hfod (0.144 g, 0.49 mmol). IR: $\tilde{\nu} =$ 2151m (SiH), 1627m, 1598w, 1514m cm^{-1} (C=O). Found C 15.3, H 2.4, N 1.2, Sc 3.2.

10b: **5b** (0.500 g, 0.41 mmol Y) + Hfod (0.121 g, 0.42 mmol). IR: $\tilde{\nu} = 2151$m (SiH), 1624m, 1598w, 1512m cm^{-1} (C=O). Found C 14.4, H 2.3, N 1.1, Y 6.5.

10c: **5c** (0.506 g, 0.38 mmol La) + Hfod (0.115 g, 0.39 mmol). IR: $\tilde{\nu} =$ 2151m (SiH), 1622m, 1594w, 1509m cm^{-1} (C=O). Found C 14.5, H 2.3, N 1.2, La 9.3.

11: **6** (0.481 g, 0.45 mmol Al) + Hfod (0.144 g, 0.49 mmol). IR: $\tilde{\nu} = 2151$m (SiH), 1641m, 1622m, 1523m cm^{-1} (C=O). Found C 14.0, H 2.4, N 1.3, Al 1.9.

12: **5b** (0.301 g, 0.22 mmol Y) + Hfod (0.083 g, 0.28 mmol). IR: $\tilde{\nu} = 2151$m (SiH), 1623m, 1598w, 1513m cm^{-1} (C=O). Found C 12.0, H 2.0, N 0.6, Y 5.3.

Reaction of [Y(fod)$_3$] with MCM-41: [Y(fod)$_3$] (0.168 g, 0.17 mmol) was dissolved in *n*-hexane (5 mL), and the solution was added to a suspension of **3** (0.210 g) in *n*-hexane (10 mL). After stirring the mixture at ambient temperature for 28 h, unreacted [Y(fod)$_3$] and liberated Hfod were removed by centrifuging off the solid material and washing it several times with *n*-hexane (30 mL). This solid was dried in vacuo at ambient temperature for at least 5 h to yield hybrid **13** as a colorless powder (0.260 g). IR: $\tilde{\nu} = 3695$m (OH), 1622m, 1591w, 1514m cm^{-1} (C=O). Found C 13.6 , H 1.7 (after activation at 100 °C and 10^{-3} Torr: C 9.9, H 1.3).

Catalytic experiments: All catalytic runs (1–12, Table 2) were carried out in a glove box as follows: 0.04 mmol catalyst (2 mol%) was dissolved or suspended in *n*-hexane (3 mL), and *n*-dodecane (127.8 mg, 0.75 mmol) was added as an inert internal standard. A freshly prepared solution of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (344.6 mg, 2 mmol) and benzaldehyde (233.5 mg, 2.2 mmol) in *n*-hexane (2 mL) was then immediately added. The mixture was left to stir at the given temperature until no further conversion was observed. Samples (0.1 mL) were withdrawn at regular intervals, centrifuged in the case of the hybrid materials, and immediately analyzed by GC. In the leaching experiment with the hybrid material **10b** the reaction mixture was centrifuged once no further conversion was observed, **10b** was separated off, and another equivalent of each of the two substrates was added to the solution. Samples were again taken and analyzed to test the solution for catalytic activity due to cleaved metal complex: No catalytic activity was observed. In the long-term activity/recovery experiment with a sample of **10b**, the catalyst was centrifuged off once conversion was complete, washed twice with *n*-hexane, dried, and then reused in further, identical runs. The degree of conversion was measured as described above.

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