DALTON
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Grafting of bulky rare earth metal complexes onto mesoporous silica MCM-41 †

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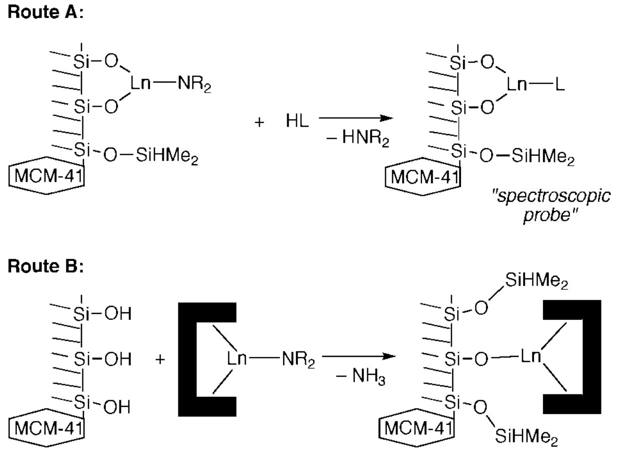
Received 19th April 1999, Accepted 6th September 1999

Heteroleptic yttrium bis(dimethylsilyl)amide complexes featuring chelating *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-ethane-1,2-diamine (H_2L^1) and *trans*-1,2-bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane (H_2L^2) ligands were immobilized on mesoporous silica MCM-41 according to a heterogeneously performed silylamide route. FTIR Spectroscopy revealed a novel grafting sequence involving amine elimination and subsequent metal siloxide formation and surface silylation. Nitrogen adsorption/desorption isotherms of the resulting hybrid materials obtained at 77.4 K indicated peculiarities of the immobilization process such as the presence of differently modified mesopores. According to preliminary catalytic investigations, the hybrid materials exhibit promising catalytic activity in a hetero Diels–Alder reaction (Danishefsky transformation). Molecular model complexes were synthesized *via* amine elimination reactions with triphenylsilanol and fully characterized by means of spectroscopy (FTIR, ^{1}H, ^{13}C, ^{29}Si NMR). Mononuclear [$YL^1(OSiPh_3)(thf)(CH_3CN)$] adopts a slightly distorted pentagonal bipyramidal geometry in the solid state, with the (planar) L^1 and acetonitrile ligands located in the equatorial plane.

Mesoporous (alumino-)silicas of the M41S family are currently discussed as attractive support materials in catalysis and material sciences.[1] We and others envisaged MCM-41, the pore diameter of which can be adjusted in the range of 15 to 100 Å,[2] as a unique platform to study the grafting of highly reactive metalorganic compounds.[3] Scheme 1 outlines two strategies which we are presently pursuing to generate novel catalytically relevant hybrid materials of the rare earth elements.‡ Approach A is based on a two step reaction sequence, comprising an initial grafting of silylamide complexes[5] and a subsequent surface ligand exchange.[6] Our approach B presented here utilizes tailor-made heteroleptic molecular precursors exhibiting reactive docking positions (a silylamide moiety) and a strongly chelating ancillary ligand which disfavours protonolysis and counteracts oligomerization reactions. Both of the procedures exploit a novel heterogeneously performed silylamine elimination,[5] featuring a mild surface reaction, the formation of a thermodynamically stable lanthanide siloxide bond, and the absence of any insoluble side products. The concomitant surface silylation (due to the released silylamine) affects the hydrophobicity and the presence of the dimethylsilyl moiety is an excellent spectroscopic probe to monitor the surface reaction.[7] Furthermore, a "face-to-wall" arrangement (sterically blocked ≡Si–O–Ln site) might favour the approach of substrate molecules *via* a chiral ancillary ligand, a desired feature in ligand-enhanced enantioselective catalysis.[8]



Scheme 1 Generation of tailor-made lanthanide surface species (R = $SiHMe_2$).

Results and discussion

Synthesis and characterization of the hybrid materials

High-quality MCM-41 materials **1** (d_p = 2.7 nm) and **2** (d_p = 3.8 nm) were synthesized according to modified literature procedures (for characterization see Table 1).[2] The number of reactive silanol groups was determined by tetramethyldisilazane silylation, affording materials **1a** (1.42 $SiHMe_2$ nm^{-2}) and **2a** (1.44 $SiHMe_2$ nm^{-2}).[7] Two heteroleptic, *n*-hexane-soluble yttrium complexes **3** and **4** with *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)ethane-1,2-diamine (H_2L^1)[9] and *trans*-1,2-bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexane (H_2L^2) ligands[10] were employed for the grafting procedure.

Reaction of 1.3 mmol ("excess") of these complexes with 1 g of MCM-41 material **1** produced the hybrid materials **1c** and **1d**. Their IR spectra revealed the disappearance of the sharp peak at 3695 cm^{-1} indicative of isolated silanol groups.[11] In addition, characteristic vibrations of the salen (1618, 1551, 1536 cm^{-1}) and sulfonamide ligand (1601, 1564 cm^{-1}) appeared. Through *in situ* silylation of the released silylamine a considerable amount of [MCM-41]$SiHMe_2$ surface sites is

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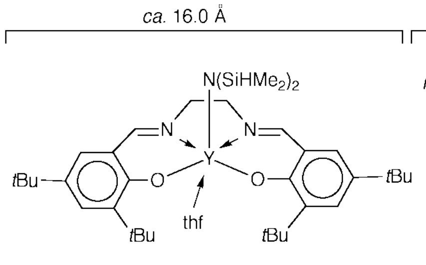
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3611/

‡ Recently, polymer-immobilized and -included $Sc(OTf)_3$ (OTf = triflate = O_3SCF_3) was employed for catalytic carbon–carbon bond-forming reactions.[4]



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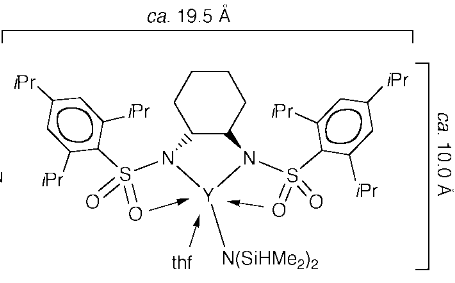

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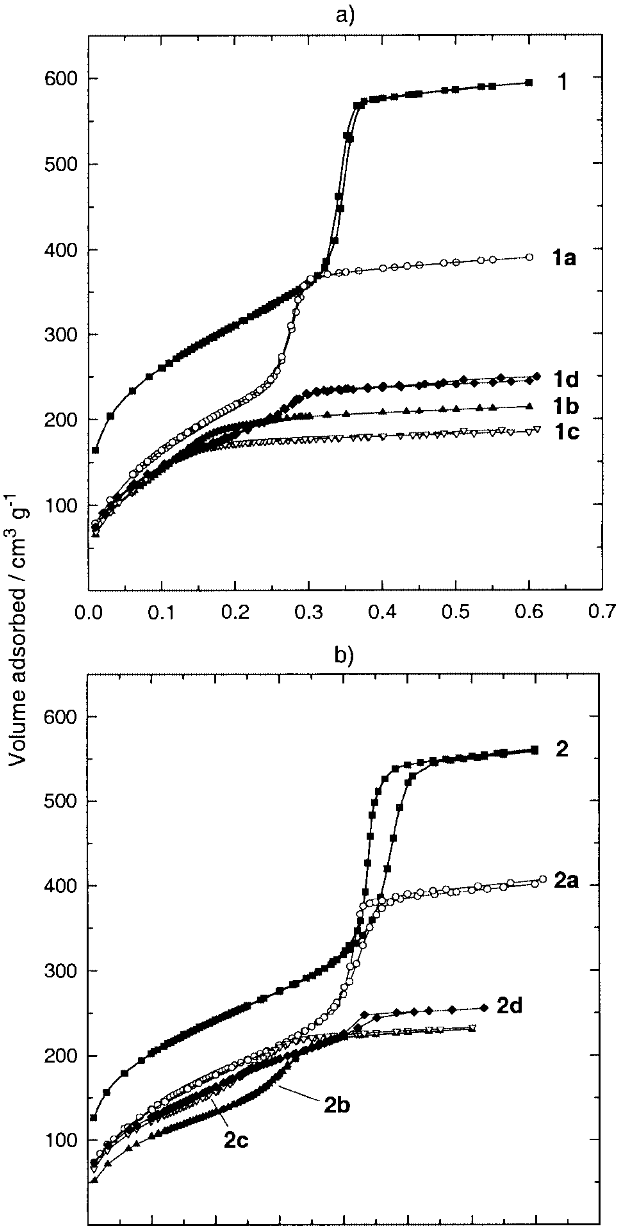

Fig. 1 Nitrogen adsorption/desorption isotherms at 77.4 K (*cf.* Table 1): (a) **1** (■; 10^{-3} Torr, 4 h, 280 °C); **1a** (○; **1** + HN(SiHMe$_2$)$_2$; 10^{-3} Torr, 3 h, 250 °C); **1b** (▲; **1** + [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$]; 10^{-3} Torr, >5 h, r.t.); **1c** (▽; **1** + **3**; 10^{-3} Torr, >5 h, r.t.); **1d** (◆; **1** + **4**; 10^{-3} Torr, >5 h, r.t.); (b) **2** (■; 10^{-3} Torr, 4 h, 280 °C); **2a** (○; **2** + HN(SiHMe$_2$)$_2$; 10^{-3} Torr, 3 h, 250 °C); **2b** (▲; **2** + [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$]; 10^{-3} Torr, >5 h, r.t.); **2c** (▽; **2** + **3**; 10^{-3} Torr, >5 h, r.t.); **2d** (◆; **2** + **4**; 10^{-3} Torr, >5 h, r.t.).

produced as indicated by the appearance of the Si–H stretching vibration at 2151 cm^{-1}.[5]

The surface reaction could be further corroborated by nitrogen physisorption measurements (Fig. 1a, Table 1). In the case of material **1c** the host-characteristic type-IV isotherm is replaced by a type-I isotherm indicative of a microporous solid having a relatively small external surface.[12a] According to the BJH method,[12b] material **1c** with the larger salen ligand exhibits a mesopore volume which is significantly lower than that of the [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$]-grafted material **1b**.[5] Interestingly, the sulfonamide-derived hybrid material **1d** produces an isotherm which still resembles the type IV. According to the BJH pore size distribution, a maximum at 2.2 nm assignable to exclusively silylated mesopores is present in addition to microporous areas. Possible explanations for this peculiar immobilization behaviour might be (i) that the lower-rate silylation reaction more effectively competes for the silanol groups due to a diffusion-controlled process involving the bulkier sulfonamide complex **4** ("diffusion-controlled grafting") or (ii) a markedly changed reactivity of the salen *vs.* the disulfonamide metal complex as revealed by the pronounced tendency of the latter to dimerize.[10]

As the BJH method produces reliable values only for d_p > 2.0 nm, complexes **3** and **4** were also grafted onto the pore-enlarged MCM-41 material **2**. As expected the resulting hybrid materials **2c** and **2d** reveal the consumption of all of the surface silanol groups and a pronounced silylation. A uniform pore filling is proposed for **2c** by the appearance of the adsorption/desorption isotherm (Fig. 1b). Although the pore diameter ($\Delta d_p = 1.3$ nm) and pore volume ($\Delta V_p = 0.40$ cm^3 g^{-1}) are markedly decreased (Table 1), the isotherm of material **2c** is still of type IV. Similar to material **1d**, immobilization of the bulkier disulfonamide complex **4** on material **2** yielded a material which exhibits two maxima according to the BJH pore size distribution: pore areas of composition [MCM-41]Y(L^2) (2.2 nm, broad) and [MCM-41]SiHMe$_2$ (3.5), respectively. The high pore loading of materials **2c** and **2d** is also revealed by yttrium and carbon elemental analysis (Table 1). Examination of the residual hexane solutions by ^{1}H NMR spectroscopy showed the absence of both metal-bonded silylamide moieties and "free" chelating ligand, pointing out the occurrence of surface-mediated ligand redistribution reactions.

Synthesis and characterization of model complexes: X-ray analysis of [YL^1(OSiPh$_3$)(thf)(CH$_3$CN)]

To probe the stability of the yttrium–salen and –disulfonamide moieties towards silanolysis, complexes **3** and **4** were treated with an excess of HOSiPh$_3$, eqn. (1).§ The ^{1}H NMR experiments

$$[(L)Y\{N(SiHMe_2)_2\}(thf)] + HOSiPh_3 \xrightarrow[-HN(SiHMe_2)_2]{\text{toluene, r.t.}} [YL(OSiPh_3)(thf)] \quad (1)$$

$$\mathbf{5}\ (L = L^1)$$
$$\mathbf{6}\ (L = L^2)$$

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§ Triphenylsilanol is commonly used as a model compound for isolated surface silanol sites [pK_a(DMSO) = 16.57; ν(SiO–H) 3677 cm^{-1}].[13]

Table 1 Analytical data, pore volume and effective mean pore diameter of MCM-41 materials

Material[a]	wt% Y[b]	wt% C	V_p[c]/cm^3 g^{-1}	d_p[d]/nm
1 MCM-41	—	—	0.85	2.7
1a [MCM-41]SiHMe$_2$	—	6.5	0.58	2.1
1b [MCM-41]Y[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$[e]	7.6	12.0	0.28	(1.7)
1c [MCM-41]YL^1(thf)	—	20.4	0.09	<1.5
1d [MCM-41]YL^2(thf)	—	21.8	0.27	<1.5, 2.2
2 MCM-41	—	—	0.96	3.8
2a [MCM-41]SiHMe$_2$	—	5.3	0.55	2.9
2b [MCM-41]Y[N(SiHMe$_2$)$_2$]$_x$(thf)$_y$[e]	6.6	11.9	0.38	2.7
2c [MCM-41]Y(L^1)(thf)	3.2	17.4	0.42	2.5
2d [MCM-41]Y(L^2)(thf)	3.1	17.3	0.45	2.2, 3.5

[a] Pretreatment temperature: 280 °C, 4 h, 10^{-3} Torr for **1** and **2**; 250 °C, 3 h, 10^{-3} Torr for **1a** and **2a**; 25 °C, 5 h, 10^{-3} Torr for **1b**, **1c**, **1d**, **2b**, **2c** and **2d**. [b] Y by ICP analysis. [c] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [d] Pore diameter according to the maximum/maxima of the BJH pore size distribution (d_p < 2.0 nm have to be viewed critically). [e] 1.1 mmol [Y{N(SiHMe$_2$)$_3$}$_3$(thf)$_2$] per 1 g of dehydrated MCM-41.[5]

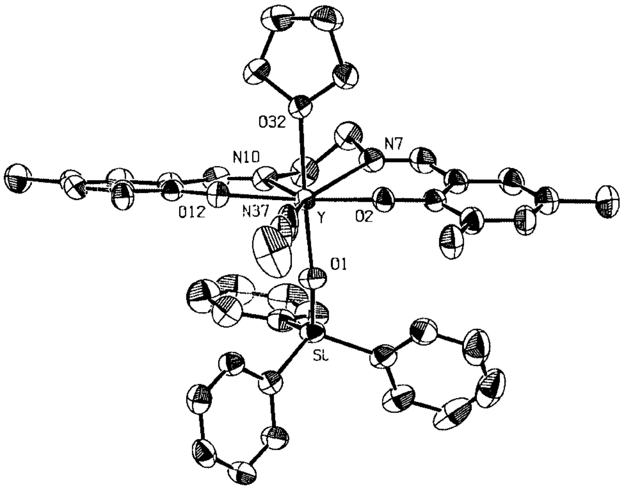


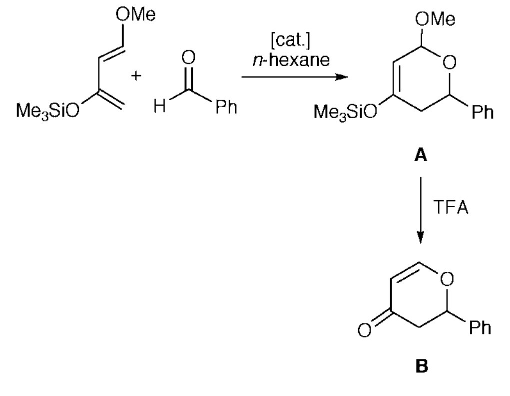
Fig. 2 A PLATON[14] plot of the molecular structure of complex **5**. Thermal ellipsoids are drawn at the 50% probability level. The Bu^t methyl groups and non-refined hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y–O(1) 2.094(2), Y–O(2) 2.216(2), Y–O(12) 2.213(2), Y–O(32) 2.401(3), Y–N(7) 2.486(3), Y–N(10) 2.464(3) and Y–N(37) 2.558(3); O(1)–Y–O(2) 94.18(9), O(1)–Y–O(12) 100.88(9), O(1)–Y–N(7) 96.2(1), O(1)–Y–N(10) 86.88(9), O(1)–Y–N(37) 95.9(1), O(2)–Y–O(32) 85.57(9), O(12)–Y–O(32) 82.10(9), O(32)–Y–N(7) 78.9(1), O(32)–Y–N(10) 90.12(9), O(32)–Y–N(37) 88.9(1), O(1)–Y–O(32) 174.93(8), O(2)–Y–N(7) 72.42(9), O(2)–Y–N(37) 72.98(9), O(12)–Y–N(10) 72.95(8), O(12)–Y–N(37) 73.25(9), N(7)–Y–N(10) 68.49(9) and Y–O(1)–Si 166.3(2).

in C_6D_6 reveal both silylamide/siloxide ligand exchange and the stability of the yttrium salen and disulfonamide fragments under the prevailing conditions. Only prolonged treatment (>10 d) of complex **4** with HOSiPh$_3$ results in ligand redistribution and formation of [Y(OSiPh$_3$)$_3$(thf)$_3$]. The siloxide complexes **5** and **6** were isolated and fully characterized and can be regarded as model compounds of the predominant metal surface species of the hybrid materials **1c**/**2c** and **1d**/**2d**, respectively. For example, the ν(C=N) vibration of both complex **5** and hybrid materials **1c**/**2c** is located at 1618 cm^{-1} ("free" H$_2$L^1: 1626 cm^{-1}).

The molecular structure of the acetonitrile adduct of the yttrium siloxide complex **5** is shown in Fig. 2. The yttrium centre is 7-co-ordinated in a slightly distorted pentagonal bipyramidal fashion. The salen and the acetonitrile ligands are located in the equatorial plane, while the siloxide and the thf ligand occupy the apical positions. For comparison, 5-co-ordinated aluminium complexes of composition [Al("salen")(OSiPh$_3$)] adopt a square pyramidal and trigonal bipyramidal co-ordination geometry, respectively, depending on the type of the salen ligand.[15] Complex **5** is a rare example of a mononuclear rare earth Schiff base complex which is soluble in non-aqueous solvents.[9,16] The bond lengths of the yttrium salen fragment are comparable to those of the 6-co-ordinated synthetic precursor **3**, taking into account the increased co-ordination number. The bonding features of the Y–OSiPh$_3$ moiety are similar to those found in [Y(OSiPh$_3$)$_3$(thf)$_3$] [Y–O, average 2.13 Å; Y–O–Si, average 171°].[17] A remarkable co-ordinative flexibility of the salen ligand is documented by its significantly bent (**3**: aryl/aryl 74°) and almost flat co-ordination mode (**5**: aryl/aryl 19°). This co-ordinative flexibility seems to be highly desirable during the grafting reaction onto the bent walls of the MCM-41 material. The lateral extension of the salen and disulfonamide ligands and the final pore diameters of 2.5 (**2c**) and 2.2 nm (**2d**) suggest an orientation of the bulky ligands parallel to the internal walls.

Preliminary catalytic investigations

The catalytic activities of the hybrid materials **1c** and **1d** as well as the siloxide model compounds **5** and **6** were tested in the hetero Diels–Alder cyclization of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky's diene) and benzaldehyde (Scheme 2).[18,19] Recently, we reported this transformation to be a useful reaction for evaluating the catalytic behaviour of grafted Lewis acidic metal centres in [MCM-41]M(fod)$_x$(thf)$_y$ (M = Al or Ln; fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate).[6b]



Scheme 2 The Danishefsky hetero Diels–Alder transformation as a catalytic test reaction.

In a standard procedure, 1 equivalent of Danishefsky's diene was treated with 1.1 equivalent of benzaldehyde at 40 °C using a catalyst amount of 2 mol% (metal content relative to the diene) suspended in *n*-hexane (**1c**,**d**) or dissolved in toluene (**5**, **6**). As a first cycloadduct product **A** is obtained which can be converted into dihydropyrone **B** after acidic work-up with trifluoroacetic acid. The results of the catalytic experiments are depicted in Fig. 3.

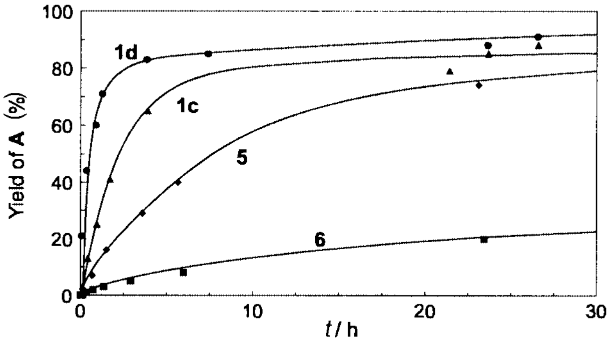


Fig. 3 Catalytic activities of the hybrid materials **1c**, **1d** and the siloxide model derivatives **5** and **6**. Yields were determined by GC analysis (error *ca.* 5%).

Again, the moderate Lewis acidity of the lanthanide(III) cations and the mild reaction conditions cause the transformation to stop at product **A** without further conversion into **B** as has been observed with other Lewis acid catalysts, *e.g.* BF_3.[20] Interestingly, the immobilized yttrium species **1c** and **1d** exhibit a strikingly higher activity compared to their molecular model complexes **5** and **6**, respectively. This effect is particularly pronounced for the sulfonamide derivatives. While the grafted species results in yields of **A** of >80% after 5 h, which is comparable to those of [MCM-41]Y(fod)$_x$(thf)$_y$ reported recently,[6b] the heteroleptic sulfonamide siloxide complex **6** gives only 11% **A** after 10 h. This can be explained by the preferred formation of dinuclear species of **6** in non-polar solvents *via* strongly co-ordinating bridging sulfonyl groups which efficiently compete with substrate co-ordination. Apparently, this steric oversaturation is reduced upon surface grafting. This is also indicated by the BJH pore size distributions calculated from the nitrogen physisorption experiments which indicate “mononuclear surface species”. As reported earlier, surface grafting can cause deoligomerization of higher agglomerized soluble species and thus generate geometrically distorted metal centres with accessible co-ordination sites and increased Lewis acidity.[21] An interesting feature of the model complexes **5** and **6** is their reversed diastereoselectivity (average ≈ 40% *exo* in **A**) compared to that of the commonly used [Ln(fod)$_3$] complexes (average ≈ 40% *endo* in **A**).

Concluding remarks

We have reported the immobilization of tailor-made heteroleptic rare earth complexes on MCM-41 materials. Utilization of strongly co-ordinating ancillary ligands and a heterogeneously performed silylamine elimination facilitate both the feasibility and monitoring of these surface reactions. Our results further emphasize that the use of high-quality MCM-41 materials and the application of nitrogen physisorption measurements are crucial for a proper interpretation of such immobilization reactions, in particular when bulky metal complexes[22] are employed. Thus, striking evidence for an unprecedented diffusion-controlled grafting sequence was obtained. Preliminary catalytic examinations reveal promising activity of the novel hybrid materials in hetero Diels–Alder reactions. The synthesis and grafting of corresponding chiral complexes is presently under investigation.

Experimental

General

All of the manipulations were performed under rigorous exclusion of air and moisture in an argon-filled glove-box. Solvent pretreatment and physicochemical characterization were performed as described previously.[5] The MCM-41 materials **1** and **2**,[2] silylated materials **1a** and **2a**,[7] [Y{N-(SiHMe$_2$)$_2$}$_3$(thf)$_2$]-grafted materials **1b** and **2b**,[5] as well as compounds **3**[9] and **4**[10] were synthesized according to published procedures.

Preparations

General procedure for hybrid materials 1c, 1d, 2c and 2d. The heteroleptic yttrium complex (**3**, **4**), dissolved in 10 cm^3 of *n*-hexane, was added to a suspension of dehydrated MCM-41 material (**1**, **2**) in 10 cm^3 of *n*-hexane within <1 min. The reaction mixture was allowed to stir for 20 h at ambient temperature and then separated *via* centrifugation. The residue was washed several times with *n*-hexane (20 cm^3). The *n*-hexane fractions were collected and the solvent was evaporated to determine unchanged complex. The resulting hybrid materials were dried *in vacuo* for at least 5 h: **1c**, from **3** (0.165 g, 0.211 mmol) and **1** (0.205 g), 0.047 g residue in hexane (Found: C, 20.4; H, 3.5; N, 1.6%), $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2151 (H–SiMe$_2$), 1618 (C=N), 1551 and 1531 (C=C); **1d**, from **4** (0.241 g, 0.257 mmol) and **1** (0.200 g), 0.101 g residue in hexane (Found: C, 21.8; H, 3.7; N, 1.6%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2151 (H–SiMe$_2$), 1601 and 1564 (C=C); **2c**, from **3** (0.358 g, 0.457 mmol) and **2** (0.609 g), 0.068 g residue in hexane (Found: C, 17.4; H, 2.6; N, 1.7; Y, 3.2%), IR spectrum comparable to that of **1c**; **2d**, from **4** (0.480 g, 0.511 mmol) and **2** (0.603 g), 0.196 g residue in hexane (Found: C, 17.3; H, 2.7; N, 1.5; Y, 3.1%), IR comparable to that of **1d**.

[*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)ethane-1,2-diaminato)](triphenylsilanolato)yttrium(III) 5. Triphenylsilanol (0.207 g, 0.75 mmol) was added to complex **3** (0.588 g, 0.75 mmol) dissolved in 15 cm^3 of toluene. The clear yellow solution was stirred for 12 h at ambient temperature and then the volatiles were removed *in vacuo*. The residue was recrystallized from 10 cm^3 of *n*-hexane at −50 °C to obtain 0.461 g (66%) of **5**. Yellow crystals of the acetonitrile adduct–solvate **5**(CH$_3$CN)·CH$_3$CN suitable for an X-ray diffraction study could be grown by diffusion of acetonitrile into a saturated solution of **5** in *n*-hexane (Found: C, 68.4; H, 7.5; N, 2.9. $C_{54}H_{69}N_2O_4SiY$ requires C, 69.96; H, 7.50; N, 3.02%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 3065m, 3042m, 1628s, 1618s, 1550m, 1536m, 1413m, 1320m, 1308s, 1274m, 1257s, 1200m, 1168m, 1106s, 1059m, 1031m, 1000s, 989vs, 930w, 911m, 876m, 837m, 810w, 789w, 745m, 704s, 640w, 514s, 431w and 417w. δ_H (400 MHz, C_6D_6, 25 °C) 7.83 [d, $^3J = 5.1$, 6 H, Si(C$_6$H$_5$)$_3$], 7.74 (d, $^4J = 2.5$, 2 H, CH$_{arom}$), 7.69 (s, 2 H, CH=N), 7.17 [m, 12 H, Si(C$_6$H$_5$)$_3$], 7.07 (d, $^4J = 2.5$ Hz, 2 H, CH$_{arom}$), 3.83 (m, 4 H, thf), 3.23 [br s, 4 H, N(CH$_2$)$_2$N], 1.68 [s, 18 H, C(CH$_3$)$_3$], 1.43 [s, 18 H, C(CH$_3$)$_3$] and 1.10 (m, 4 H, thf). $\delta_C\{^1H\}$ (100 MHz, C_6D_6, 25 °C, assignments according to 135° DEPT spectra and increment calculations) 169.5 (CH=N), 164.3 (C-2), 141.0 [Si(C$_6$H$_5$)$_3$], 139.3 (C$_{arom}$), 136.5 (C$_{arom}$), 135.6 [Si(C$_6$H$_5$)$_3$], 129.7 (CH$_{arom}$), 129.4 (CH$_{arom}$), 128.8 [Si(C$_6$H$_5$)$_3$], 127.7 [Si(C$_6$H$_5$)$_3$], 122.5 (C-1), 69.9 (thf), 59.5 [N(CH$_2$)$_2$N], 35.7 [*C*(CH$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 31.8 [C(*C*H$_3$)$_3$], 30.0 [C(*C*H$_3$)$_3$] and 25.1 (thf); $\delta_{Si}\{^1H\}$ (79 MHz, C_6D_6, 25 °C) −22.4.

[*trans*-1,2-Bis(2,4,6-triisopropylbenzenesulfonamido)cyclohexanato-*N*,*N*′](triphenylsilanolato)yttrium(III) 6. Triphenylsilanol (0.138 g, 0.50 mmol) was added to a solution of sulfonamide complex **4** (0.469 g, 0.50 mmol) in 10 cm^3 of toluene. The clear solution was stirred for 12 h at ambient temperature. Afterwards, the volatiles were removed *in vacuo*, producing **6** (0.486 g) in almost quantitative yield. Recrystallization from hot toluene yielded the solvated complex **6**·C$_6$H$_5$CH$_3$ (Found: C, 66.4; H, 7.2; N, 2.6. $C_{54}H_{71}N_2O_5S_2SiY\cdot C_6H_5CH_3$ requires C, 66.52; H, 7.23; N, 2.54%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 3065m, 3042m, 1598m, 1564w, 1427s, 1330w, 1316w, 1289w, 1258 [s, ν(S=O)], 1244m, 1220s, 1204m, 1176m, 1151m, 1135s, 1112s, 1073w, 1063 [m, ν(S=O)], 1042m, 1003s, 968vs, 916m, 890m, 843w, 803m, 778w, 740m, 706vs, 675s, 657m, 633w, 604m, 592w, 561w, 557m, 526w, 516s, 508m and 426w. δ_H (400 MHz, [D$_8$]thf, 25 °C) 7.7–6.9 (br m, 24 H, -C$_6$*H*$_2$*i*Pr$_3$,

$\mathrm{Si(C_6H_5)_3}$ and $\mathrm{C_6}H_5\mathrm{CH_3}$), 4.50 [sept, $^3J = 6.7$, 4 H, o-CH($\mathrm{CH_3}$)$_2$], 3.49 [m, 2 H, $\mathrm{CH_\alpha NY}$-], 2.88 [sept, $^3J = 7.0$, 2 H, p-CH($\mathrm{CH_3}$)$_2$], 2.30 (s, 3H, $\mathrm{C_6H_5C}H_3$), 1.96 (m, 2H, $\mathrm{CH}H_\beta$), 1.61 (m, 2H, $\mathrm{C}H\mathrm{H_\beta}$), 1.40 (m, 4 H, $\mathrm{CH_{2,\gamma}}$), 1.24 [d, $^3J = 6.7$, 24 H, o-CH(CH_3)$_2$] and 1.20 [d, $^3J = 7.0$ Hz, 12 H, p-CH(CH_3)$_2$]. $\delta_\mathrm{C}\{^1\mathrm{H}\}$ (100 MHz, [$\mathrm{D_8}$]thf, 25 °C, assignments according to 135° DEPT spectra and increment calculations) 151.3 (C-4), 149.0 (C-2,6), 142.4 (C-1), 138.4 [$\mathrm{Si(C_6H_5)_3}$], 136.4 ($C_6\mathrm{H_5CH_3}$), 136.1 [$\mathrm{Si(C_6H_5)_3}$], 129.6 [$\mathrm{Si(C_6H_5)_3}$], 128.9 ($C_6\mathrm{H_5CH_3}$), 128.7 ($C_6\mathrm{H_5CH_3}$), 127.7 [$\mathrm{Si(C_6H_5)_3}$], 126.0 ($C_6\mathrm{H_5CH_3}$), 124.5 (C-3,5), 64.2 ($C\mathrm{H_\alpha NY}$) 35.1 [p-CH($\mathrm{CH_3}$)$_2$], 35.0 ($\mathrm{CH_{2,\beta}}$), 30.5 [o-CH-($\mathrm{CH_3}$)$_2$], 25.8 [o-CH(CH$_3$)$_2$], 25.7 ($\mathrm{CH_{2,\gamma}}$), 24.0 [p-CH(CH$_3$)$_2$] and 21.5 ($\mathrm{C_6H_5}C\mathrm{H_3}$). $\delta_\mathrm{Si}\{^1\mathrm{H}\}$ (79 MHz, [$\mathrm{D_8}$]thf, 25 °C) −21.6.

X-Ray crystallography

Crystal data for complex 5. $\mathrm{C_{56}H_{72}N_3O_4SiY}$, $M_\mathrm{r} = 968.17$, triclinic, space group $P\bar{1}$, $a = 11.1378(2)$, $b = 16.8069(5)$, $c = 18.0549(5)$ Å, $\alpha = 108.218(1)$, $\beta = 102.675(2)$, $\gamma = 106.052(2)°$, $V = 2906.8(1)$ Å^3, $Z = 2$, $D_\mathrm{c} = 1.106$ cm^{-3}, $F(000) = 1028$, μ(Mo-Kα) = 1.07 mm^{-1}, $\lambda = 0.71073$ Å, $T = 193(2)$ K.

The 18260 reflections measured on a Nonius Mach3 diffractometer equipped with a Kappa CCD area detector[23] yielded 11174 unique reflections ($2\theta_\mathrm{max} = 52.74°$, $R_\mathrm{int} = 0.027$). Preliminary positions of heavy atoms were found by direct methods,[24] while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least squares refinement.[25] The atoms of two disordered *t*Bu groups *para* to the oxygen were refined with isotropic thermal displacement factors, all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, included in the structure factor calculation but not refined. A highly disordered solvent molecule, probably acetonitrile, was dealt with by the Calc Squeeze option, implemented in the program PLATON,[14] leaving a void of 198 Å^3 in the asymmetric unit ($x = 0.401$, $y = 0.828$, $z = 0.698$). The final refinement on F^2 converged at $wR2 = 0.1433$ on all data, conventional $R1 = 0.0522$ on F values of 9633 reflections having $F_\mathrm{o}^2 > 2\sigma(F_\mathrm{o}^2)$, goodness of fit = 1.018 for all F^2 values and 583 refined parameters. Largest difference peak and hole (e Å^{-3}): 0.70, −0.70.

CCDC reference number 186/1642.

See http://www.rsc.org/suppdata/dt/1999/3611/ for crystallographic files in .cif format.

Catalytic experiments

All catalytic runs were carried out in a glove-box as follows: the catalyst (complex **1c**, 0.093 g; **1d**, 0.115 g; **5**, 0.034 g; **6**, 0.043 g 0.04 mmol; 2 mol%) was suspended in 3 cm^3 of *n*-hexane or dissolved in 3 cm^3 of toluene, and *n*-dodecane (0.128 g, 0.75 mmol) added as an inert internal standard. A freshly prepared solution of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (0.345 g, 2 mmol) and benzaldehyde (0.234 mg, 2.2 mmol) in 2 cm^3 of *n*-hexane or 2 cm^3 of toluene was immediately added. The mixture was left to stir at 40 °C and samples of 0.1 cm^3 were withdrawn at regular intervals, centrifuged in the case of the supported catalysts, and analyzed by GC (HP 5890 series II FID equipped with a 12.5 m × 0.33 mm 100% polysiloxane column).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) and Degussa AG for financial support. H. W. G. thanks the Fonds der Chemischen Industrie for a fellowship (with participation of the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie). Generous support from Professor W. A. Herrmann is gratefully acknowledged.

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Paper 9/03096D