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Synthesis and grafting of CAN-derived tetravalent cerium alkoxide silylamide precursors onto mesoporous silica MCM-41†

Alan R. Crozier,[a] Christoph Schädle,[b] Cäcilia Maichle-Mössmer,[b] Karl W. Törnroos[a] and Reiner Anwander*[b]

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The heteroleptic tetravalent cerium complex $[Ce(O\textit{i}Pr)_3\{N(SiMe_3)_2\}]_2$ was synthesised by treating ceric ammonium nitrate (CAN) sequentially with sodium isopropoxide and lithium bis(trimethylsilyl)amide in THF. The trivalent ate complex $[Ce(O\textit{i}Pr)_2\{N(SiMe_3)_2\}_2][Li(thf)_2]$ was also isolated from these reaction mixtures. A transsilylamination reaction of $[Ce(O\textit{i}Pr)_3\{N(SiMe_3)_2\}]_2$ with tetramethyldisilazane produced a considerable amount of homoleptic $Ce[N(SiHMe_2)_2]_4$. The polymeric complex $[Li_2Ce_2(O\textit{i}Pr)_{10}(1,4\text{-dioxane})]_n$ was isolated as an additional ligand redistribution product. When tetravalent complexes $Ce[N(SiHMe_2)_2]_4$, $Ce[N(SiMe_3)_2]_3Cl$ and Cp_3CeCl were allowed to react with samples of periodic mesoporous silica MCM-41, Ce(IV) hybrid materials were produced. All hybrid materials were characterised *via* N_2 physisorption, elemental analysis and DRIFT spectroscopy.

Introduction

Tetravalent cerium compounds such as ceric ammonium sulphate or nitrate (CAN) are well-known single-electron oxidants for many organic transformations.[1] Cerium is a unique member of the rare-earth metals in its ability to exist in a high-valent state in solution. The Ce^{4+} ion is isoelectronic to xenon with a closed-shell $4f^0$ configuration, yet pathways to generate tetravalent cerium complexes remain challenging. Recent research areas of tetravalent cerium complexes include (MO)CVD and ALD,[2] polymerisation reactions (ring-opening of lactide),[3] electrochemistry,[4] oxo and peroxo complexes,[5] NHC complexes[6] and cationic species.[7] Soluble and reactive (pseudo)organometallic complexes are desirable in the study of silica-based surface organometallic chemistry. When targeting a Ce(IV) grafted silica, chemical precursors must contain at least one readily hydrolysable Ce–X bond, assuming the surface of a dehydrated silica has a pK_a value of 5–7.[8] With this in mind, three complex categories appear synthetically suitable as grafting precursors – organometallics, (silyl)amides, and alkoxides.[8] Examples of tetravalent alkoxides dominate the literature due to the oxophilic nature of the cerium metal centre.[2–4,9] While the number of Ce(IV) (silyl)amide complexes has increased in the past 15 years, developments have been hampered by the choice of an oxidant[6,10] or intractable reaction pathways.[11] Organometallic complexes are even fewer, with the oxidation state of cerocene and its derivatives still under investigation,[12] the range of complexes are limited to *N*-heterocyclic carbene (NHC)[6,13] and η^5-cyclopentadienyl ligands.[10d,14] It is of interest to note that when approaching an $(\equiv SiO)_xCe^{IV}(NR_2)_y$ $(x + y = 4)$ surface species, such mixed alkoxo(siloxo)/amido ligand sets provide a stabilising environment for tetravalent cerium (Chart 1).[6,15]

In this report, the synthesis of the mixed alkoxide/silylamide complex $[Ce(O\textit{i}Pr)_3\{N(SiMe_3)_2\}_2]_2$ from ceric ammonium nitrate is illustrated and its use for an alternative synthesis of the homoleptic silylamide complex $Ce[N(SiHMe_2)_2]_4$.[16] Moreover, three Ce(IV) hybrid materials have been produced through the grafting of tetravalent precursors $Ce[N(SiHMe_2)_2]_4$, $Ce[N(SiMe_3)_2]_3Cl$ and Cp_3CeCl onto periodic mesoporous silica MCM-41 and the surface species are discussed.

Results and discussion

Cerium silylamide synthesis

The choice of ceric ammonium nitrate (CAN) as a starting material for the generation of soluble Ce(IV) precursors has several advantages – (i) the desired oxidation state is already

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[a] *Department of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway*

[b] *Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: reiner.anwander@uni-tuebingen.de; Fax: +49 7071 292436*

† Electronic supplementary information (ESI) available: Experimental data, powder X-ray diffraction pattern, pore size distribution and transmission electron microscopy image of parent MCM-41 silica, DRIFT spectra of all materials in the region 400–4000 cm^{-1}. CCDC 915627, 915628 and 915629. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33005b

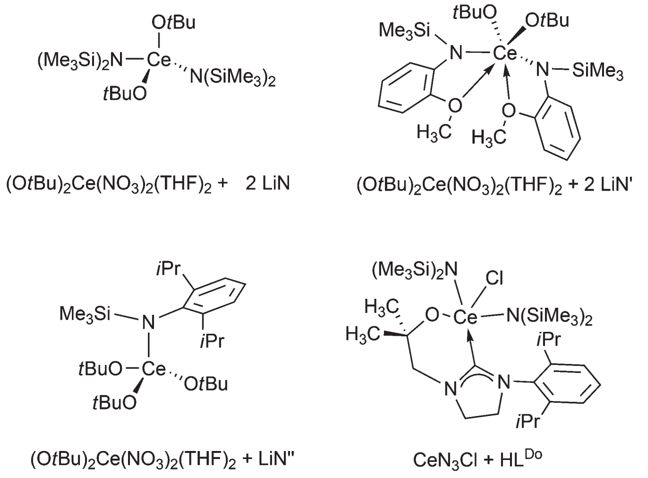
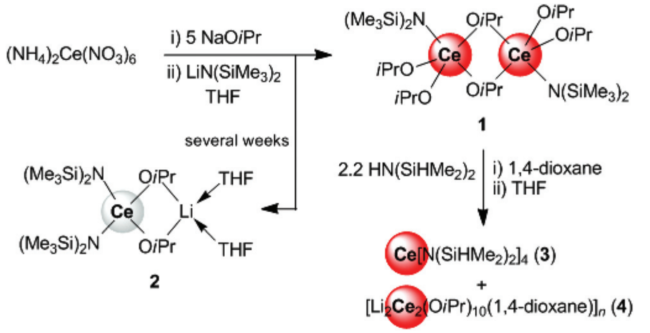


Chart 1 Mixed silylamide/alkoxide Ce(IV) complexes, structurally authenticated by X-ray crystallography along with the synthesis protocols (N = $N(SiMe_3)_2$; N′ = $N(SiMe_3)(C_6H_4OMe\text{-}2)$; N′′ = $N(SiMe_3)(C_6H_3iPr_2\text{-}2,6)$).



Scheme 1 Reaction pathway to complexes **1–4**.

achieved, (ii) the reactions of CAN with many alkali metal (pseudo)organometallics have been described,[2,9h,14b,17,18] however, if organometallic reactants such as NaCp are used reduction occurs,[17] (iii) the separation of by-products is uncomplicated as both ammonia and insoluble nitrate salts are formed, (iv) other than an initial dehydration step, it is possible to use CAN in an 'off the shelf' manner unlike many metal chlorides which require donor solvation. When CAN was reacted with 5 equivalents of NaO*i*Pr in THF a white precipitate and bubbles of gas were observed (Scheme 1). Removing the volatiles *via* vacuum and performing a toluene extraction gave a yellow-orange solution, which after removing the volatiles once more yielded a sticky yellow-orange solid presumably $[Ce(OiPr)_3(NO_3)(thf)_2]$. Without further characterisation this solid was redissolved in THF and to this one equivalent of $LiN(SiMe_3)_2$ was added. A further white precipitate and a colour change from orange-yellow to red were observed. Filtering and drying under vacuum gave a red solid.

^1H NMR spectroscopy in C_6D_6 of this residue gave sharp peaks at 0.5 ppm (singlet; Si*Me*$_3$), 1.2 ppm (doublet; OCH*Me*$_2$) and at 4.8 ppm (septet; OC*H*Me$_2$), and broader peaks at 0.4 ppm (singlet; Si*Me*$_3$), 1.3 ppm (doublet; OCH*Me*$_2$) and 5.1 ppm (septet; OC*H*Me$_2$), indicating the presence of two species – one diamagnetic and one paramagnetic (see ESI†). Redissolving this solid in hexane and cooling to −35 °C afforded red crystals in 40% yield. An X-ray diffraction experiment was undertaken and the molecular structure of **1** is shown in Fig. 1.

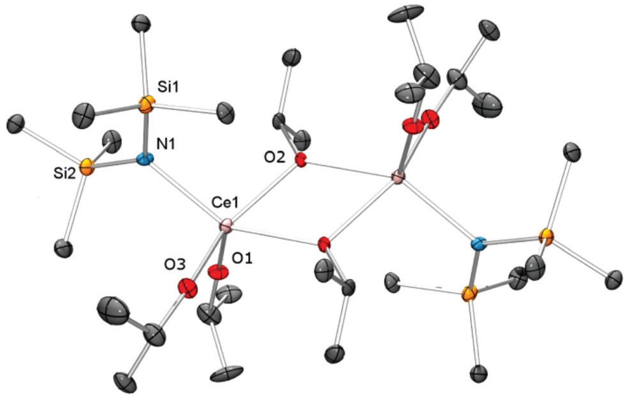


Fig. 1 Molecular structure of $[Ce(OiPr)_3\{N(SiMe_3)_2\}]_2$ **1** (ellipsoids set to 50%). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°). Ce1–O1 2.058(5), Ce1–O2 2.325(5), Ce1–O3 2.061(5), Ce1–N1 2.289(6), Ce⋯Ce 3.892(7); O3–Ce–O1 95.7(2), O3–Ce–N1 101.5(2), O2–Ce1–O2′ 67.9(2), Ce1–N1–Si1 112.9(3), Ce1–N1–Si2 122.3(3).

Complex **1** is a tetravalent dinuclear isopropoxide/hexamethyl silylamide complex with the cerium atoms adopting a geometry intermediate to square pyramidal and trigonal bipyramidal. Each cerium atom is bridged by an alkoxide ligand forming a four-membered ring with cerium–oxygen distances of 2.369(5) and 2.325(5) Å and angles of 67.9(2) and 112.0(2)° at the cerium and oxygen atoms, respectively. The terminal alkoxide Ce–O (avg. 2.059 Å) and bridging alkoxide (avg. 2.347 Å) bond lengths compare well with other Ce(IV) alkoxide complexes, such as mixed-valent $[Ce_3(OtBu)_{10}NO_3]$ (terminal: 2.062(4)–2.069(4) Å; μ_2: 2.261(4)–2.519(4) Å),[15,19] 5-coordinate $[Ce(OCMe_2iPr)_4]$ (terminal: avg. 2.085; μ_2: 2.291(2)–2.468(3) Å),[9i] 7-coordinate $[Ce_2(OiPr)_6(OC_2H_4NMeC_2H_4NMe_2)_2]$ (terminal: 2.122(4)–2.137(5) Å; μ_2: 2.328((4) and 2.411(4) Å)[9e] and 4-coordinate $[Ce\{N(SiMe_3)_2\}_2(OtBu)_2]$ (2.052(6) Å).[15] The Ce–N distance of 2.289(6) Å was found to be considerably longer than in the 5-coordinate complex $[Ce\{N(CH_2CH_2NSiMe_2tBu)_3\}I]$ (2.202 Å)[10a] as well as in the 4-coordinate complexes $[Ce\{N(SiMe_3)_2\}_2(OtBu)_2]$ (2.260(7) Å),[15] $[Ce\{N(SiMe_3)_2\}_3X]$ (X = Cl, Br; avg. 2.218 Å)[10b,c] and $[Ce(NCy_2)_4]$ (Cy = cyclohexyl; 2.247 Å),[11a] however, shorter than in the amidinate complex $[Ce\{p\text{-}MeOC_6H_4C(NSiMe_3)_2\}_3Cl]$ (avg. 2.432 Å).[10d]

The trivalent ate complex **2** was isolated as colourless crystals in low yield from solutions of **1** when left for periods of over two weeks at −35 °C. The complex could also be achieved by using an excess of LiO*i*Pr in the reaction mixture. The molecular structure of **2** is shown in Fig. 2 with both cerium and lithium metal centres in a distorted tetrahedral geometry. The cerium atom is four-coordinate with two terminal hexamethyl silylamido ligands and two isopropoxy ligands bridging to a lithium atom with two coordinated THF molecules. The central four-membered ring has average Ce–O and Li–O bond lengths of 2.252 and 1.957 Å and bond angles of 78.2 and 93.1°, respectively. The Ce–N bond length (avg. 2.408(3) Å) lies well within the range of other relevant trivalent cerium amide complexes $[Ce\{N(SiMe_3)_2\}_4][Na(thf)_4(OEt_2)]$ (2.440 Å),[20] $[Ce\{(N(SiMe_3)C(C_6H_4tBu\text{-}4))_2CH\}\{N(SiMe_3)_2\}_2]$ (2.453 Å),[21] being considerably longer than in homoleptic 3-coordinate $[Ce\{N(SiMe_3)_2\}_3]$ (2.320 Å)[22] and $[Ce(TMP)_3]$ (2.323 Å).[23] While **2** can be considered an undesirable by-product with **1**, it is not without interest as trivalent cerium alkoxide/(silyl)amide ate complexes appear uncommon. Only one other complex $[Ce\{N(SitBuMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)\}_2(\mu\text{-}OtBu)_2Na(tmeda)]$ was reported.[24] Other amido-containing ate complexes such as $[Ce[NCy_2]_4Li(thf)]$[11a] and $[Ce\{(\mu\text{-}N(H)(CH_2tBu)\}_2C_6H_4\text{-}1,2)\text{-}Na_3(OEt_2)]$[25] share similar cerium alkali metal separation distances with **2** (Ce⋯Li = 3.089(6), 3.077(5) and 3.442(3) Å, respectively).

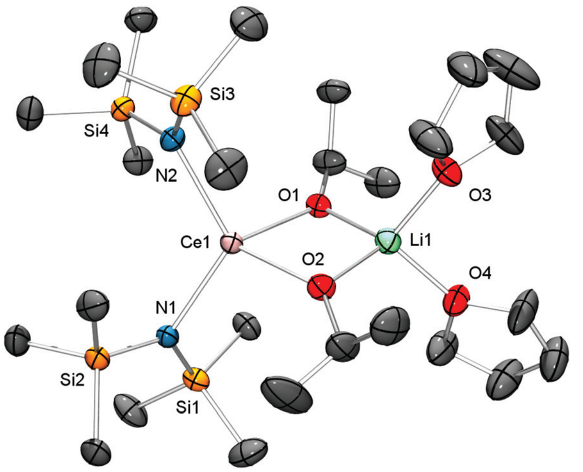


Fig. 2 Molecular structure of $[Ce(OiPr)_2\{N(SiMe_3)_2\}_2][Li(thf)_2]$ **2** (ellipsoids set to 30%). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°). Ce1–N1 2.408(3), Ce1–N2 2.408(3), Ce1–O1 2.253(2), Ce1–O2 2.250(2), Li1–O1 1.962(7), Li1–O2 1.953(8), Li1–O3, 1.962(7), Li1–O4 1.970(8), Ce1⋯Li1 3.089(6); O1–Ce1–O2 78.22(9), Ce1–N1–Si1 121.0(1), Ce1–N1–Si2 114.3(1), Ce1–N2–Si3 119.9(1), Ce1–N2–Si4 113.8(1).

When a *trans*(silyl)amination reaction with a slight excess of $HN(SiHMe_2)_2$ was attempted on **1** in hexane, only an oily red product was obtained after removing the volatiles. The FTIR data for this oil showed evidence of amido ligand exchange with the characteristic Si–H peak close to 2000 cm^{-1}. Redissolving this oil in hexane and adding 2 equivalents of 1,4-dioxane caused an immediate colourless precipitate to form. After filtering this precipitate and removing the volatiles from the filtrate a red solid was isolated. The Schlenk 1,4-dioxane disproportionation/precipitation method[26,27] seems to apply also in the case of Ce(IV), presumably co-producing insoluble polymeric alkoxides. The FTIR spectrum for this red solid also showed a peak at 2000 cm^{-1} indicating the retention of the tetramethyl silylamido ligand. ^1H NMR spectroscopy showed a doublet at δ 0.34 and a septet at δ 6.01 with a ratio of 6 : 1 as expected for the $N(SiHMe_2)_2$ ligand. Performing a recrystallisation on this red solid from a cooled hexane solution produced red single crystals. An X-ray structure analysis confirmed the formation of $Ce[N(SiHMe_2)_2]_4$ (**3**) which was previously synthesised *via* an oxidation/redistribution sequence employing $Ce[N(SiHMe_2)_2](thf)_2$ and chlorinating reagents such as Ph_3CCl.[16] When stored for longer times colourless crystals of $[Li_2Ce_2(OiPr)_{10}(1,4\text{-dioxane})]_n$ (**4**) were isolated and characterised by X-ray crystallography. The solid-state structure of **4** (Fig. 3) shows a tetravalent polymeric isopropoxide ate complex consisting of two 6-coordinate anionic cerium entities

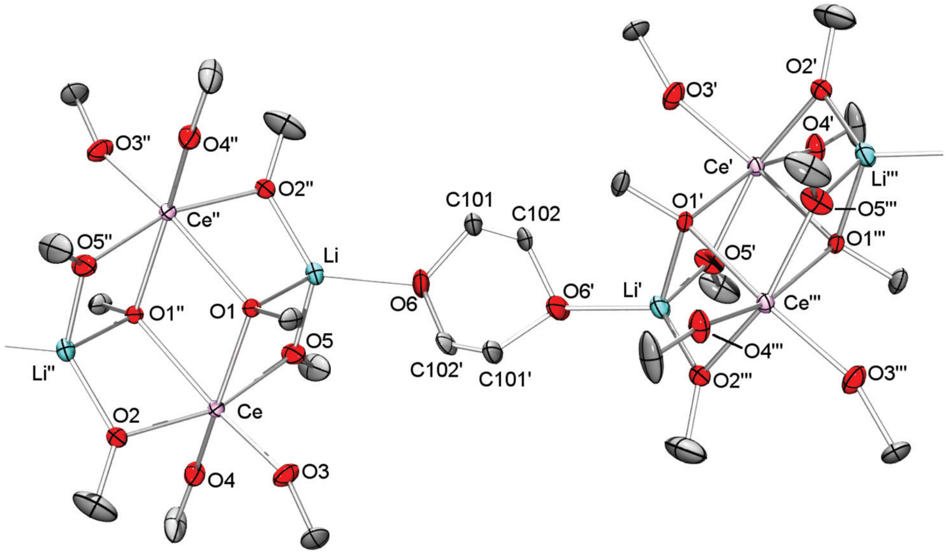


Fig. 3 Molecular structure of $[Li_2Ce_2(OiPr)_{10}(1,4\text{-dioxane})]_n$ (**4**) (ellipsoids set to 30%). All hydrogen atoms and peripheral methyl groups as well as the disorder of the dioxane molecule have been omitted for clarity. Selected interatomic distances (Å) and angles (°). Ce–O1 2.440(4), Ce–O2 2.257(4), Ce–O3 2.095(4), Ce–O4 2.080(4), Ce–O5 2.234(4), Li–O1 2.098(12), Li–O5 1.899(12), Li–O6 2.066(11), Li⋯Li''#1 5.117(4); Ce–O1–Li 91.0(3), Ce–Li–O6 119.2(4), O1–Ce–O3 90.93(15). #1 = $-x + 1/2, -y + 1/2, -z + 1/2$.

charge-balanced with two 4-coordinate lithium cations. A disordered 1,4-dioxane molecule bridges between two lithium atoms accomplishing a polymeric chain structure. The cerium centres adopt a distorted octahedral arrangement with O–Ce–O isopropoxy bond angles ranging from 71.2(2) to 102.3(2)°. There are three different types of isopropoxy ligands per cerium: two terminal, two μ_2-bridging (to lithium), two μ_3-bridging (to lithium and the other cerium). As a consequence, distinct 4-membered metal–oxygen rings are featured in this structure. The Ce–O1–Li–O5 ring shows Ce–O and Li–O bond lengths of avg. 2.327 and 1.999 Å and bond angles of 75.44 and 90.9°, respectively. The two terminal Ce–O distances average 2.087 Å corresponding to the terminal Ce–OR alkoxy groups in $[Ce_2(O\mathit{i}Pr)_8(HO\mathit{i}Pr)_2]_n$.[9d] The 1,4-dioxane molecule bridges a Li···Li distance of 6.82(2) Å. Only one structurally authenticated trivalent example of a 1,4-dioxane-bridged cerium compound is known ($[Ce(\eta^3\text{-}C_3H_5)_3(1,4\text{-dioxane})]_n$)[28] and further examples have also been reported for La,[29,30] Sm,[30,31] Nd,[30,32] Pr,[30] and Y.[31]

Hybrid materials

While CAN-derived hybrid materials (support: silica,[33] perfluorinated resin-sulphonic acid (Nafion),[34] alumina[35] or charcoal[36]) have been successfully employed for oxidative organic transformations, to our knowledge surface organocerium(IV) chemistry (SOCe(IV)C) has not been tackled so far. There are, however, reports on combining Ce(IV) complexes with silica using methods such as incipient wetness,[37] sol–gel[33d] and CVD.[33e] The most relevant work from Bell *et al.* has exploited the alkoxide complexes $[Ce(O\mathit{i}Pr)_4]$ and $[Ce(O\mathit{t}Bu)_4]$ for grafting onto periodic mesoporous silica (PMS) MCM-41 and SBA-15 in order to synthesise CeO_2 nanoparticles.[33f] While nanoparticles were produced, the latter report describes incomplete grafting with surface SiOH groups remaining after the first alkoxide treatment and requiring a subsequent grafting step to achieve higher loadings. We anticipated that the heterogeneously performed silylamide route, previously proved for rare-earth metals (Ln(III),[38] Ln(II)[39]), main group (Mg(II), Ba(II),[40] Al(III)[41]) and 3d transition metals (Ti(IV),[42] Fe(II)/(III),[43] Zn(II)[44]) might as well apply for Ce(IV) silylamides. Using precursors exhibiting higher proligand pK_a values such as metal silylamides (≈ 25) should ensure complete surface silanol consumption and higher initial loadings. Particularly, the strongly reducing hybrid materials $Sm(II)(NR_2)_2$@PMS revealed a stabilising effect for ketyl radicals *via* pore confinement.[38] Moreover, surface attachment *via* the formation of Ce–O(siloxide)-bonds (electron-withdrawing effect of the silica matrix) might not only stabilise the +IV oxidation state, but also counteract ligand redistribution. Accordingly, this approach was tested by using complexes **3**, $Ce[N(SiMe_3)_2]_3Cl$ and Cp_3CeCl as three candidates for grafting precursors in the production of Ce(IV) hybrid silicas.

Periodic mesoporous silica MCM-41 was chosen as the support material due to its hexagonal (*P6mm*) pore arrangement with uniform 1-D channels and relatively narrow pore size distribution.[45,46] The MCM-41 material used in this study has the following characteristics: a_s = 1040 m^2 g^{-1}, d_p = 3.3 nm and $SiOH_{population}$ = 2.9 mmol g^{-1}.[47]

When solutions of Ce(IV) precursors **3**, $Ce[N(SiMe_3)_2]_3Cl$ and Cp_3CeCl were added to suspended samples of the parent material MCM-41, peach $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**), brown $Ce[N(SiMe_3)_2]_3Cl$@MCM-41 (**6**) and dark grey Cp_3CeCl@MCM-41 (**7**) hybrid materials were obtained, respectively (Fig. 4).

The DRIFT spectra of the hybrid materials **5** and **6** showed complete consumption of the surface silanol groups with the absence of a peak at 3747 cm^{-1} found in the parent material (Fig. 5). The ν(C–H) band between 3043 and 2824 cm^{-1} indicates the presence of the methyl groups from the silylamido ligands. The use of the tetramethyl silylamido ligand and its usefulness as a spectroscopic probe can be seen in the spectrum of material **5**. The ν(Si–H) peak centred at 2116 cm^{-1} differs from its precursor with an increase of 100 cm^{-1}. The reaction of the cyclopentadienyl complex Cp_3CeCl with the silica support did not lead to complete consumption of the silanols. Material **7** shows a residual peak at 3747 cm^{-1} but

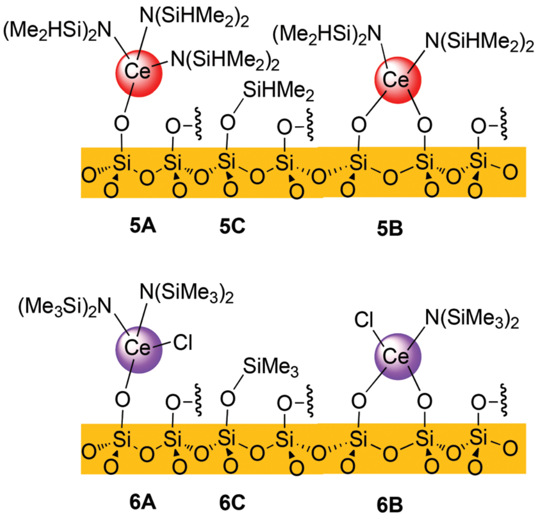


Fig. 4 Proposed surface species for $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**) and $Ce[N(SiMe_3)_2]_3Cl$ (**6**).

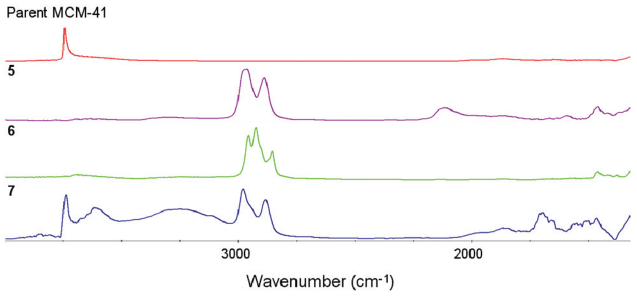


Fig. 5 IR spectra (DRIFT) of the parent material MCM-41, $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**), $Ce[N(SiMe_3)_2]_3Cl$ (**6**) and $CeCp_3Cl$@MCM-41 (**7**) in the range 1300–4000 cm^{-1}.

Table 1 Analytical data of parent and Ce(IV)-grafted MCM-41 materials

Sample	a_s [a]	d_p [b]	V_p [c]	C[d]	N[d]
Parent MCM-41	1040	3.3	1.11	—	—
$HN(SiHMe_2)_2$@MCM-41	725	2.7	0.71	5.97	—
$Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**)	472	2.3	0.44	14.13	0.79
$Ce[N(SiMe_3)_2]_3Cl$@MCM-41 (**6**)	375	2.2	0.36	11.20	0.90
$CeCp_3Cl$@MCM-41 (**7**)	712	2.7	0.77	13.34	—

[a] Specific BET surface area [m^2 g^{-1}]. [b] Pore diameter [nm]. [c] Pore volume determined at the relative pressure P/P_o = 0.996 [cm^3 g^{-1}]; all samples were pretreated at 250 °C (parent material) and 25 °C (hybrid materials) *in vacuo* until the pressure was <10^{-3} Torr. [d] Expressed in wt%.

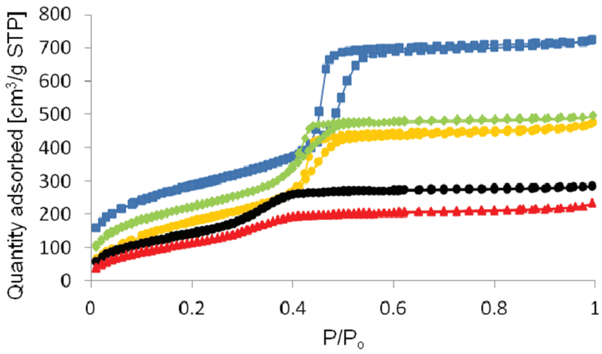


Fig. 6 Nitrogen adsorption–desorption isotherms of MCM-41 parent material (blue squares), $HN(SiHMe_2)_2$@MCM-41 (green diamonds) $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**, black circles) $Ce[N(SiMe_3)_2]_3Cl$@MCM-41(**6**, red triangles), and Cp_3CeCl@MCM-41 (**7**, orange circles).

also two broad bands between 3600 and 3100 cm^{-1} indicating significant interaction of the complex Cp_3CeCl with the silica surface.

The carbon loadings of materials **5** and **6** are high (14 and 11 wt%) compared to that of **7** (13 wt%) (Table 1), when taking into consideration the carbon contents of the Ce(IV) precursors (**3**: 28.71; $Ce[N(SiMe_3)_2]_3Cl$: 32.92; Cp_3CeCl: 48.58%). The nitrogen content of **5** is lower than **6** indicating an overall higher podality, meaning a comparatively higher amount of species $(\equiv SiO)_2Ce^{IV}[N(SiR_3)_2]_2$ (**5B** > **6B**). Furthermore, competitive surface silylation is a well-documented feature of silylamide functionalised silica.[38a,40,42–44,47] These differences are also reflected in the nitrogen physisorption data as for material $Ce[N(SiMe_3)_2]_3Cl$@MCM-41 (**6**) bearing the bulkier silylamido ligand the decreases in pore volume and pore diameter are more pronounced than in the case of $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**) (Fig. 6). Organocerium(IV) hybrid material Cp_3CeCl@MCM-41 (**7**) maintains a higher surface area, pore diameter and pore volume as expected for an incompletely grafted material (712 m^2 g^{-1}, 2.7 nm and 0.77 cm^3 g^{-1}, respectively).

When an excess of 1,1,4,4-tetramethyldisilylazane was added to material **7** complete SiOH consumption was achieved, affording $HN(SiHMe_2)_2$@Cp_3CeCl@MCM-41 (**7a**, not shown). This was evidenced by the disappearance of the SiOH peak and a new peak appearing at 2152 cm^{-1} assigned as ν(Si–H). While the reaction of metal silylamides with a silica surface and more specifically, the surface silylation side-reaction is well understood, less so is the reaction of metal cyclopentadienyl derivatives and the accompanying side-reactions.[48] Grafting of Cp_3CeCl can occur in two ways, firstly *via* the loss of a $[C_5H_5]^-$ fragment from the complex forming free cyclopentadiene or *via* the loss of the chloro ligand atom forming HCl. While the former reaction would involve protonolysis at a sterically highly encumbered Ce(IV) centre, the latter would preferentially take place in the presence of a base like triethylamine. Not surprisingly, an attempted chlorine analysis of hybrid material **7** out rules any surface reaction *via* the Ce(IV)–Cl bond. Further, the mild reaction conditions (ambient temperature) might also suggest surface interaction of complexes Cp_3CeCl *via* Ce–Cl···HOSi≡ and Cp···HOSi≡ hydrogen bonds. A more detailed investigation of **7**-type materials is currently pursued.

While silylamides generate silylamines of the form $HN(SiR_x)_2$ upon grafting, which can react further with the surface, the cyclopentadienyl fragments released are unable to react further with the silica surface. It is noteworthy that sterically encumbered metal silylamide complexes such as **3** do not necessarily have to react *via* the metal–nitrogen bond but also *via* peripheral Si–N silazane moieties.[43] This lack of additional side-reactions may also be responsible for the incomplete consumption of the surface silanols. Furthermore, cerium–silica species containing Cp ligands may sterically inhibit access to another SiOH site adjacent and so force an additional incoming precursor to interact with a less crowded SiOH site. This can also be rationalised upon the addition of $HN(SiHMe_2)_2$ (**7a**) which is small enough to access such unreacted SiOH sites while the larger Cp_3CeCl is unable to.

Conclusions

A CAN-based salt metathesis protocol gives access to heteroleptic silylamide/alkoxide complexes as evidenced for $[Ce(O\mathit{i}Pr)_3\{N(SiMe_3)_2\}]_2$. The reactions of tetravalent cerium involving the tetramethyl silylamido ligand show a marked difference in complexity of ligand redistribution and reduction chemistry. In the case of homoleptic Ce(IV) silylamide complexes the decrease in symmetry and increase in coordinative saturation with Ce(IV)···SiH β-agostic interactions appear to increase the stability compared with the hexamethyl congeners. The large electron-withdrawing effect of the silica surface can be seen as a very bulky siloxide ligand and the site-isolation of the cerium metal on the surface increases the stability of Ce(IV) complexes that appear unstable in solution. Undesirable phenomena such as decomposition, ligand scrambling and bimolecular deactivation are avoided *via* the stabilising effect of the silica surface. The absence of side reactions associated with incomplete grafting with Cp_3CeCl@PMS may be considered advantageous as the material produced is not as hydrophobic with SiOH species contributing to the polar nature of the surface.

Experimental

General considerations

The synthesis of all cerium-containing compounds and hybrid materials was performed in an argon-filled glovebox (MBraun MB150B-G; <1 ppm O_2, <1 ppm H_2O). Hexane, toluene and THF were dried and degassed using Grubbs columns (MBraun SPS800, solvent purification system) and stored in a glovebox. C_6D_6 was obtained from Deutero GmbH, degassed, dried over sodium metal and filtered. 1,1,3,3-Tetramethyldisilazane and ceric ammonium nitrate (CAN) were purchased from ABCR (97%; 98% purity). Sodium isopropoxide was synthesised from sodium metal and anhydrous isopropanol (Sigma-Aldrich, 99.5% purity). Lithium bis(trimethylsilyl)-amide was synthesised from *n*-butyllithium (Sigma 2.5 M in hexanes) and 1,1,1,3,3,3-hexamethyldisilazane. Tetraethyl orthosilicate (98% purity) was purchased from Fluka, CTMABr (98% purity), 1,4-dioxane (99%) and tetramethylammonium hydroxide (25 wt% in H_2O) were bought from Sigma-Aldrich and $C_{16\text{-}3\text{-}1}$ was synthesised according to the literature procedure.[49] All chemicals were used as bought except CAN which was heated under vacuum for 5 h at 60 °C then stored in a glovebox. MCM-41 was synthesised in bulk using previous descriptions (*cf.*, ESI†).[45] As-synthesised MCM-41 was calcined (450 °C, 24 h) in air and dehydrated (270 °C, 10^{-5} Torr). Parent material MCM-41 was characterised by FTIR spectroscopy, powder X-ray diffraction, N_2-physisorption at 77.4 K, transmission electron microscopy (see ESI†) and stored in a glovebox. The SiOH population of the parent material was determined by the carbon content of a sample reacted with an excess of 1,1,3,3-tetramethyldisilazane in hexane.[50] $Ce[N(SiMe_3)_2]_3Cl$[10b] and Cp_3CeCl[10d] were prepared according to previous reports. IR spectra were recorded on a NICOLET 6700 FTIR spectrometer using a DRIFT chamber with KBr/sample mixtures. ^1H NMR spectra were recorded in C_6D_6 solutions on a Bruker-ADVANCE-DMX400 (5 mm BB, ^1H: 400.13 Hz), ^1H shifts are referenced to the internal solvent and reported in parts per million relative to TMS. CHN elemental analyses were performed on an Elementar Vario MICRO cube. N_2 physisorption was carried out on either an ASAP 2010 or ASAP 2020 volumetric adsorption apparatus (Micromeritics) at 77.4 K [$a_m(N_2, 77\ K) = 0.162\ nm^2$]. All samples underwent an outgassing step of 3 h, 10^{-3} Torr and at ambient temperature before measurement began. The specific surface areas of the samples were obtained using the BET method.[51] Pore size distributions were determined *via* the Barrett–Joyner–Halenda (BJH) method using the Kelvin equation to calculate the mean pore diameter.[52] Powder X-ray diffraction patterns were obtained using a Bruker D8 ADVANCE instrument in the step/scan mode (step width = 0.00825; accumulation time = 2 s per step; range (2θ) = 0.50–10.00°) using monochromatic $CuK_{\alpha 1}$ (λ = 1.540562 Å).

Synthesis of cerium complexes

$[Ce(O\textit{i}Pr)_3\{N(SiMe_3)_2\}]_2$ (1). In a two-step procedure, CAN (1.000 g, 1.824 mmol) was stirred in THF (10 ml) for 30 min at ambient temperature, to which a THF slurry of NaO*i*Pr (0.748 g, 9.120 mmol) was added. An orange suspension was formed along with gas bubbles and a white precipitate. The volatiles were removed *via* vacuum and a toluene (15 ml) extraction was performed followed by centrifugation. Removing the toluene *via* vacuum gave a red-orange oily solid (presumably $Ce(NO_3)(O\textit{i}Pr)_3(thf)_x$). Redissolving this solid in THF (10 ml) and addition of $LiN(SiMe_3)_2$ (0.1281 g, 0.766 mmol) in THF (5 ml) gave a deep red solution with further precipitation of a white solid. Removal of the volatiles produced a red/brown oily solid, a component of which could be extracted into hexane producing a deep red solution. Concentration and cooling of the solution led to the formation of red crystals suitable for X-ray diffraction (yield 40%). IR (DRIFT): ν_{max} = 2960 (vs), 2894 (m,sh), 2864 (m,sh), 2618 (w), 1585 (w,br), 1463 (m), 1454 (m), 1379 (m), 1360 (m) 1327 (m), 1329 (m), 1247 (s), 1163 (m), 1130 (s), 1048 (m), 1016 (s,sh), 976 (vs), 917 (m,sh), 870 (s,sh), 845 (vs), 770 (m), 746 (m,sh), 664 (m), 599 (m), 533 (m), 467 (m), 444 (m), 418 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 0.53 (s, 18H, Si*Me*$_3$), 1.22 (d, *J* = 15 Hz, 18H, OC(H)*Me*$_2$), 4.82 (septet, *J* = 15 Hz, 3H, OC(Me$_2$)*H*). Anal. Calc. for $C_{30}H_{78}Ce_2N_2O_6Si_4$: C, 37.71; H, 8.23; N, 2.93. Found: C, 37.91; H, 8.86; N, 2.69%.

$Ce(O\textit{i}Pr)_2\{N(SiMe_3)_2\}_2Li(thf)_2$ (2). CAN (1.000 g, 1.824 mmol) was slurried in THF (10 ml), to which NaO*i*Pr (0.449 g, 5.472 mmol) was added dropwise. An orange suspension was formed along with gas bubbles and a white precipitate. Volatiles were removed *via* vacuum and a toluene (15 ml) extraction was performed followed by centrifugation. Removing the toluene *via* vacuum gave a red orange oily solid (presumably $Ce(NO_3)_3(O\textit{i}Pr)(thf)_x$). Redissolving this solid in THF (10 ml) and adding of $LiN(SiMe_3)_2$ (0.1070 g, 0.639 mmol) in THF (5 ml) gave a red solution with further precipitation of a white solid. Removal of volatiles produced a red/brown oily solid, a component of which could be extracted into hexane producing a deep red solution. Concentration and cooling of this solution led to the formation of colourless crystals suitable for X-ray diffraction. ^1H NMR (400 MHz, C_6D_6): δ = −3.86 (s), 0.37 (s), 0.43 (s), 1.24 (d, *J* = 15 Hz), 1.46 (s), 4.0 (s), 4.86 (septet, *J* = 15 Hz). Anal. Calc. for $C_{26}H_{66}CeLiN_2Si_4$: C, 42.77; H, 9.11; N, 3.84. Found: C, 41.26; H, 7.47; N, 4.09%.

$Ce[N(SiHMe_2)_2]_4$ (3) and $[Li_2Ce_2(O\textit{i}Pr)_{10}(1,4\text{-dioxane})]_n$ (4). A 10 ml pentane solution of **1** (0.221 g, 0.211 mmol) was added to a 2 ml pentane solution containing a slight excess of tetramethyldisilazane (0.035 g, 0.263 mmol) dropwise under stirring. This dark red solution was allowed to stir for 1 h. The volatiles were removed *via* vacuum leaving a red oil (89% yield). Redispersal in a 1,4-dioxane/pentane or THF solution caused precipitation, whereupon filtration, concentration and cooling to −35 °C produced dark red crystals suitable for X-ray diffraction, analysed as **3**.[16] *N.B.* Colourless crystals were also formed with prolonged storage and found to be $[Li_2Ce_2(O\textit{i}Pr)_{10}(1,4\text{-dioxane})]_n$ (**4**) crystallographically.

Table 2 Crystallographic data for **1**, **2** and **4**

	1	**2**	**4**
Formula	$C_{30}H_{78}Ce_2N_2O_6Si_4$	$C_{26}H_{66}CeLiN_2O_4Si_4$	$C_{34}H_{78}Ce_2Li_2O_{12}$
F_w	803.51	730.23	973.08
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_12_12_1$	$C2/c$
a/Å	15.2304(16)	12.5799(3)	18.9892(5)
b/Å	18.3123(18)	16.2153(3)	16.7465(5)
c/Å	16.960(2)	19.6833(5)	15.0041(4)
α/°	—	—	—
β/°	—	—	101.0900(10)
γ/°	—	—	—
V/Å^3	4730.2(9)	4015.13(16)	4682(2)
Z	4	4	4
$F(000)$	1968	1540	2000
T/K	173(2)	173(2)	100(2)
ρ_{calcd}/g cm^{-3}	1.342	1.208	1.380
μ/mm^{-1}	2.035	1.280	1.968
R_1 ^{a} (obsd)	0.0673	0.0443	0.0486
wR_2 ^{b} (all)	0.1475	0.0771	0.1160
S^c	1.151	1.203	1.340

$^a R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $F_o > 2\delta(F_o)$. $^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $^c S = [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

Hybrid material general procedure

Hybrid materials were produced from an equimolar or excess solution of the cerium complex stirred with the parent silica material in hexane or toluene for 2 h. A series of centrifuge/THF (**5**), hexane (**6**) or toluene (**7**) extractions were performed on the produced material prior to drying under vacuum.

Ce[N(SiHMe$_2$)$_2$]$_4$@MCM-41 (**5**). Peach-coloured hybrid material (472 m^2 g^{-1}). IR (DRIFT): $\nu_{\max}$ = 2983 (m,sh), 2960 (m, sh), 2891 (m), 2114 (m,br), 1462 (m), 1246 (s), 1063 (vs), 899 (m), 834 (m,sh), 807 (m,sh), 670 (w), 601 (m,br), 454 (s) cm^{-1}. C, 14.1; H, 2.4; N, 0.8%.

Ce[N(SiMe$_3$)$_2$]$_3$Cl@MCM-41 (**6**). Brown-coloured hybrid material (375 m^2 g^{-1}). IR (DRIFT): $\nu_{\max}$ = 2960 (m,sh), 2924 (m, sh), 2855 (m), 1459 (w), 1462 (m), 1243 (s), 1070 (vs), 844 (m), 762 (m,sh), 615 (m), 557 (w), 455 (m,sh), 442 (m,sh) cm^{-1}. C, 11.2; H, 2.1; N, 1.7%.

CeCp$_3$Cl@MCM-41 (7). Dark grey-coloured hybrid material (375 m^2 g^{-1}). IR (DRIFT): $\nu_{\max}$ = 3744 (w), 2983 (m,sh), 2855 (m,sh), 1245 (m), 1186 (m), 1140 (m), 1081 (vs), 793 (m,br), 594 (w,br), 453 (s) cm^{-1}. C, 13.3; H, 2.1%.

X-ray crystallography and crystal structure determination of complexes 1, 2 and 4. Crystals were grown by standard techniques from saturated solutions using hexane at −35 °C. Suitable crystals for diffraction experiments were selected in a glovebox and mounted in Paratone-N (Hampton Research) on a fibre. Data collection for **1** and **2** was done on a STOE IPDS 2T, and **4** on a Bruker AXS APEX II instrument using MoK$_\alpha$ radiation (λ = 0.71073 Å). Structure solution and final model refinement was done using Stoe's X-Area,[53] SMART[54] and SAINT,[54] WinGX suite,[55] SHELXS97[56] and SHELXL-97.[56] All plots were generated using the program ORTEP-3.[57] Further details of the refinement and crystallographic data are listed in Table 2, and in the CIF file; CCDC reference numbers are 915627 (**1**), 915628 (**2**) and 915629 (**4**).

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