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# Silica-grafted lanthanum benzyl species: synthesis, characterization and catalytic applications.

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**ABSTRACT:** We describe here the grafting of a lanthanum trisbenzyl derivative onto dehydroxylated silica, which affords a mixture of  $[(\equiv\text{SiO})_2\text{La}(\text{CH}_2\text{Ph})(\text{THF})_n]$  and  $[(\equiv\text{SiO})\text{La}(\text{CH}_2\text{Ph})_2(\text{THF})_m]$  surface sites, in respective proportions of 80 and 20%, as evidenced from mass balance analyses, IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  1D and 2D solid state NMR spectroscopy. Significant transfer of alkyl groups from lanthanum to the surface was demonstrated. The grafting mechanism was also probed by DFT calculations, which confirm that benzyl group transfer from the lanthanum to the surface (via Si-O-Si cleavage) occurs readily. This material proved to be active in alkyne dimerization, and in ethylene, styrene and  $\epsilon$ -caprolactone homopolymerization.

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## INTRODUCTION

Rare-earth metals have attracted constant attention in catalysis thanks to their remarkable properties, mostly owing to their high Lewis acidity.<sup>1</sup> Impressive early examples of lanthanide alkyls' reactivity include C-H activation chemistry or extremely efficient ethylene polymerization.<sup>2</sup> However, this high reactivity (and thus, high sensitivity) of rare-earth alkyl derivatives has hampered their widespread use, which was partly addressed as high yield syntheses of  $\text{LnR}_3$  species (occasionally as Lewis base adducts) were proposed for such starting materials.<sup>3</sup> Among the reported solvated trisalkyl species, the benzyl derivatives have been described by the Hessen-Bouwkamp group, who reported a simple and efficient access route to the THF adducts of these derivatives.<sup>4</sup> These are available to a wide range of metals and are thermally stable (contrary to neosilyl derivatives). Furthermore, contrary to the bis(trimethylsilyl)methyl derivatives, these compounds retain a high reactivity towards protic reagents.

On the other hand, heterogenization of molecular complexes onto inorganic supports is of high interest in the view of their use in industrially-relevant processes (mostly related to polymerization), or to generate site-isolated highly reactive organometallic species. One of the most efficient methods to meet this goal is the use of surface organometallic chemistry, which allows the precise synthesis of supported species.<sup>5</sup> In this context, following the pioneering work from Anwander,<sup>6</sup> we have developed well-defined

silica-grafted amide and borohydride rare-earth metals derivatives.<sup>7</sup> These display interesting properties, affording for instance systems with enhanced selectivity in specific polymerization reactions.<sup>7a,c</sup>

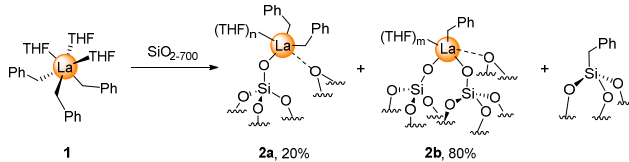
There are very few reported examples of immobilization of lanthanide alkyl derivatives onto inorganic supports, namely grafting of  $[\text{Lu}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  onto dehydroxylated silica,<sup>8</sup> or formation of scandium methyl complexes by metalation of silica-supported scandium amides.<sup>9</sup> No catalytic application of these materials was described. In related approaches, lanthanide alkyl aluminates have been immobilized onto mesostructured supports by Anwander and applied in diene polymerization.<sup>10</sup>

In this contribution, we describe the study of the reaction of  $[\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$  (**1**) with silica dehydroxylated at 700°C, along with theoretical investigations on the grafting pathway, and the performances of this material in four types of catalytic reactions, namely alkyne dimerization, polymerization of styrene, polymerization of ethylene and ring opening polymerization of  $\epsilon$ -caprolactone.

## RESULTS AND DISCUSSION

Our initial goal was the design of well-defined lanthanum alkyl surface sites bearing a single surface-to-metal bond (**2a**, Scheme 1), which would leave two reactive alkyl moieties, starting from  $[\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$  (**1**). This would offer the possibility for further generation of cationic monosiloxy monoalkyl species using

cationizing agents, a step toward enhanced reactivity.<sup>11</sup> To achieve this, we have selected highly dehydroxylated silica, namely Aerosil 380 silica from Evonik, treated under vacuum at 700°C. This support features a specific surface of 350 m<sup>2</sup>.g<sup>-1</sup>. This treatment affords silica bearing only non-interacting silanol groups on its surface, as evidenced by infrared spectroscopy (Figure 1a), and grafting of inorganics and organometallics on such a support typically generates monosiloxide surface species.<sup>5</sup>



Scheme 1. Grafting of  $[\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$  (**1**) on  $\text{SiO}_{2-700}$ .

Reaction of **1** with  $\text{SiO}_{2-700}$  in THF affords a deep orange material (**2**). Elemental analysis indicates La and C loading of 5.48 and 9.58 w%, respectively. The La loading corresponds to 0.39 mmol.g<sup>-1</sup> of material. The corresponding C/La ratio is 20.2. Infrared spectroscopy reveals full consumption of the silanols, as shown by the lack of SiOH signal on the DRIFT spectrum of **2**, notably of the 3747 cm<sup>-1</sup>  $\nu(\text{O-H})$  band (Fig. 1b). We also observe new signals at 3061-3027 and 2983-2885 cm<sup>-1</sup>, accounting respectively for  $\nu(\text{sp}^2 \text{C-H})$  and  $\nu(\text{sp}^3 \text{C-H})$ . In addition, bands at 1588 cm<sup>-1</sup> (characteristic for C=C aromatic-ring-stretching vibrations) and 1494 cm<sup>-1</sup> ( $\delta(\text{C-H})$  vibration of the methylene groups) are also present.

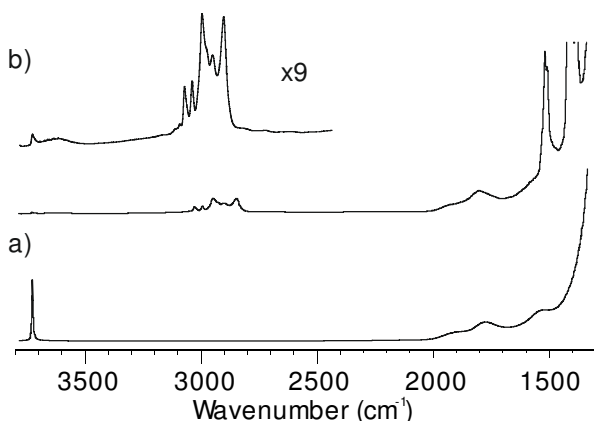


Figure 1. DRIFT of a)  $\text{SiO}_{2-700}$ , b)  $[\text{La}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$  over  $\text{SiO}_{2-700}$  (**2**).

Solid state NMR was used to get further insight into the structure of **2**. <sup>1</sup>H MAS NMR features broad signals even at high magnetic field (18.8 T) (Figure 2a). Thus, signals at 7.1, 3.7 and 1.6 ppm are observed, accounting respectively for aromatic C-H groups, OCH<sub>2</sub> from lanthanum-bound THF and both La-CH<sub>2</sub> and OCH<sub>2</sub>CH<sub>2</sub> protons.<sup>4</sup> The overlap of the signals in the 2.5-1 ppm region prevents precise assignment, however, the intensity of the considered signal compared to that of OCH<sub>2</sub> is fully in line with the presence of overlapping La-CH<sub>2</sub> and OCH<sub>2</sub>CH<sub>2</sub> protons signals. Noteworthy, the width of the signals is reminiscent of that of the group 4 benzyl derivatives (Ti, Zr) on the same support.<sup>12</sup> In this case, this was assigned to occurrence of  $\eta^7$  and/or  $\eta^8$  coordination mode of the benzyl ligand.<sup>13</sup> To further probe the structure of the supported species, we resorted to bidimensional <sup>1</sup>H-<sup>1</sup>H NMR experiment, namely DQ-SQ MAS NMR, which relies on dipolar interactions, and thus that gives information on spatial proximities<sup>14</sup> (Figure 2b). Each signal in the <sup>1</sup>H spectrum gives rise to an on-diagonal correlation, in line with the presence of CH<sub>2</sub> moieties (from LaCH<sub>2</sub> and THF) or with neighboring protons with similar chemical shift

(aromatic C-H protons). Two off-diagonal signals are observed: The first one (tagged as interaction A on Figure 2) associates aromatic CHs at 7.1 ppm and protons at 1.6 ppm, which would be best assigned to interaction within the benzylic fragments, namely between methylenic and aromatic protons of LaCH<sub>2</sub>Ph. A second set of less intense cross-peaks (tagged as interaction B on Figure 2) associates the OCH<sub>2</sub> to the  $\eta^7$  OCH<sub>2</sub>CH<sub>2</sub> protons from THF (at respectively 3.7 and 1.6 ppm). The <sup>13</sup>C CP MAS NMR of **2** features 3 major sets of signals at 128, 69 and 24 ppm, characteristic for aromatic, OCH<sub>2</sub> and OCH<sub>2</sub>CH<sub>2</sub> carbons (Figure 3a). A shoulder at 62 ppm on the 69 ppm peak is assigned to the LaCH<sub>2</sub> group.<sup>3, 15</sup> These assignments were confirmed by a 2D <sup>1</sup>H-<sup>13</sup>C CP HETCOR MAS NMR spectrum (Figure 3b). Indeed, the aromatic moieties gives rise to a <sup>1</sup>H signal at 7.1 ppm and <sup>13</sup>C signals at 128-120 ppm, while the THF OCH<sub>2</sub> feature <sup>1</sup>H and <sup>13</sup>C peaks at 3.6 and 69 ppm, respectively. Accordingly, the THF OCH<sub>2</sub>CH<sub>2</sub> groups give rise to a correlation associating signals at 1.5 (<sup>1</sup>H) and 24 ppm (<sup>13</sup>C). A further long range correlation involves the OCH<sub>2</sub>CH<sub>2</sub> protons and the OCH<sub>2</sub> carbons. However, no <sup>1</sup>H-<sup>13</sup>C correlation was observed for the LaCH<sub>2</sub> moiety under our conditions. Benzyl ligands are known to be involved in dynamic processes, with a rich coordination behavior, from  $\eta^7$  to  $\eta^8$  coordination on electrophilic metal centers.<sup>4, 13</sup> This could prevent efficient dipolar coupling to take place and thus hinder observation of heteronuclear interactions.

<sup>29</sup>Si CP MAS NMR (Figure 4) features an intense signal characteristic for T<sub>3</sub> groups ( $\equiv\text{SiCH}_2\text{Ph}$ ) at -66 ppm,<sup>16</sup> along with the signal from the Q-type ( $\text{SiO}_4$ ) sites at -103 ppm. This indicates that significant benzyl group transfer onto the silica support occurred, as observed during the grafting of electrophilic metal complexes on (very) highly dehydroxylated silica supports.<sup>17</sup>

This prompted us to assess the stoichiometry of the grafting reaction and the precise structure of the surface organometallic centers in **2**, most noteworthy through mass balance analysis. The lanthanum loading (5.48 w%, 0.39 mmol.g<sup>-1</sup>) is higher than what would be expected from a grafting mode involving only protonolysis of **1** by silanols, which would afford 0.27 mmol(La).g<sup>-1</sup>. Thus, other reaction pathways must be operative, such as grafting by siloxane opening, forming  $\equiv\text{SiO-La}$  and  $\equiv\text{SiCH}_2\text{Ph}$  sites. When comparing the expected and observed lanthanum loading (0.27 and 0.39 mmol.g<sup>-1</sup>, respectively), this shows that about 70% of grafting proceeds with protonolysis as the first step, and that about 30% results from initial nucleophilic cleavage of (strained) Si-O-Si fragments.

We reacted **2** with excess (5 eq) *n*-butanol in C<sub>6</sub>D<sub>6</sub>, and we quantified by <sup>1</sup>H NMR the released organic compounds (THF and toluene), using ferrocene as an internal standard. The toluene and THF detected after alcoholysis of **2** amount to 0.47 and 0.51 mmol.g<sup>-1</sup> respectively (resulting from average of 4 different runs). Thus, the average number of benzyl ligand moiety per lanthanum center is 1.2, which is significantly different from the ratio of 2.0 expected from species **2a**. On the same line, the average number of THF molecules per lanthanum center is 1.3 (if considering that excess butanol fully displaces THF from grafted centers). Thus, the average formulation for the surface species is  $[(\equiv\text{SiO})_{1.8}\text{La}(\text{CH}_2\text{Ph})_{1.2}(\text{THF})_{1.3}]$ . This means that grafted species consists of 20%  $[(\equiv\text{SiO})\text{La}(\text{CH}_2\text{Ph})_2(\text{THF})_n]$  (**2a**) and 80%  $[(\equiv\text{SiO})_2\text{La}(\text{CH}_2\text{Ph})(\text{THF})_m]$  (**2b**), namely that alkyl transfer plays a significant role in the surface chemistry of **1** on  $\text{SiO}_{2-700}$  (Scheme 1). If one considers that THF is fully released upon alcohol addition, the residual C content (accounting for silica-transferred benzyl groups) after removing the benzyl and THF contribution (13.6 C/La) is 6.6 C/La. This corresponds to 0.9 equivalent of  $[\equiv\text{SiCH}_2\text{Ph}]$  per surface La center.<sup>18</sup> This significant amount of alkyl transfer is in sharp contrast with the surface chemistry of

[Lu{CH(SiMe<sub>2</sub>)<sub>2</sub>}<sub>3</sub>] on silica,<sup>8</sup> where grafting proceeds only via protonolysis of the Lu-C by silanols, most probably due to the bulk of the alkyl moieties which could hinder attack of siloxane bridges.

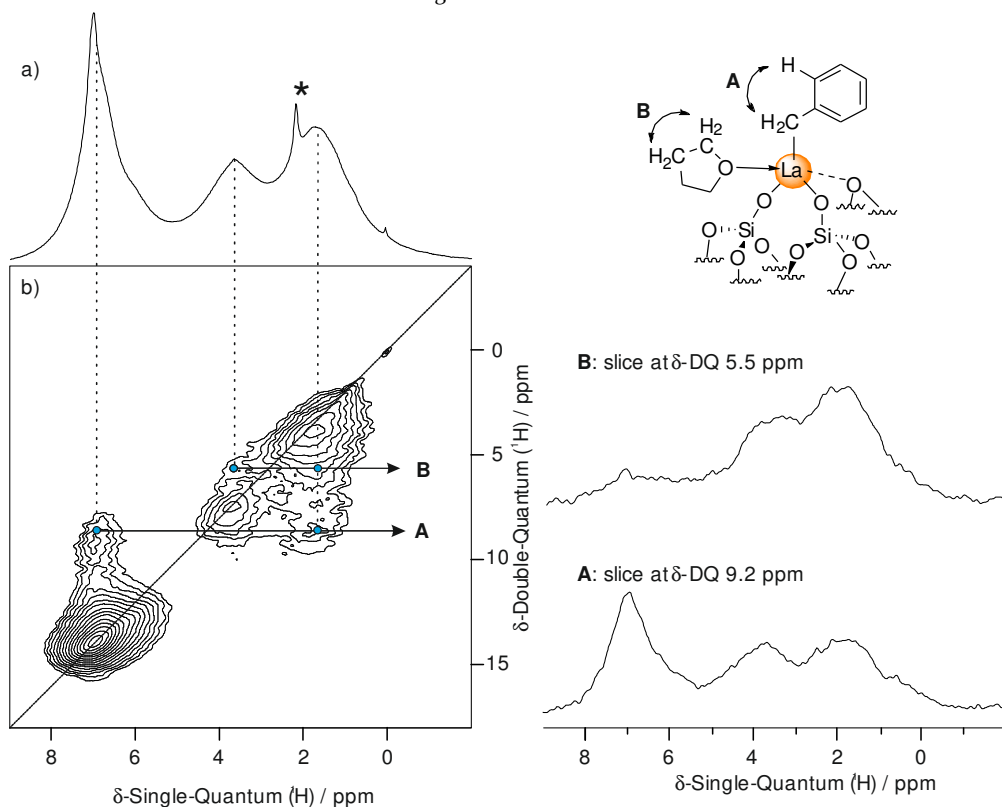


Figure 2. <sup>1</sup>H (a) and <sup>1</sup>H-<sup>1</sup>H DQ-SQ (b) MAS NMR spectra of **2** (18.8 T, spinning speed 20 kHz).

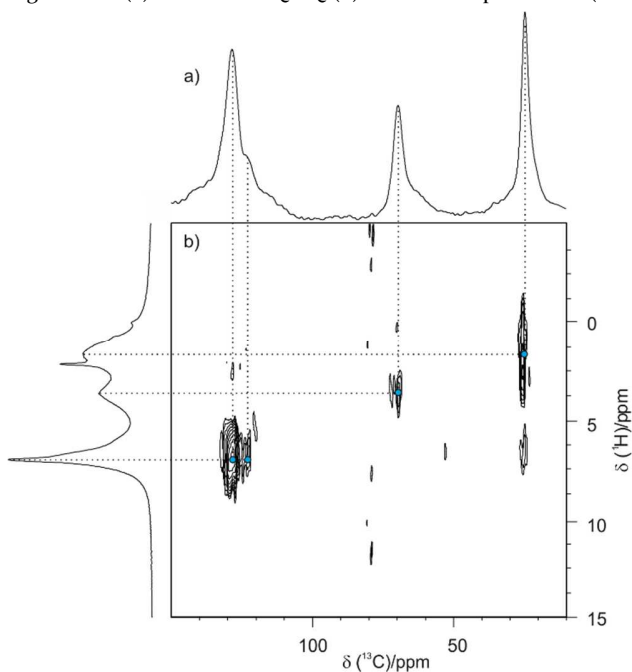


Figure 3. <sup>13</sup>C (a) and <sup>1</sup>H-<sup>13</sup>C HETCOR (b) CP MAS NMR spectra of **2** (<sup>13</sup>C: 100.6 MHz, <sup>1</sup>H: 400 MHz, spinning speed 14 kHz)

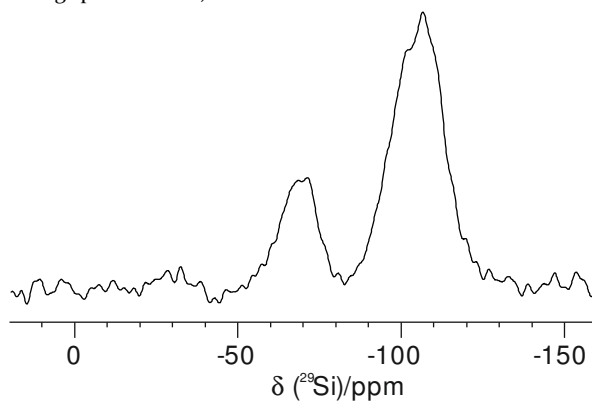


Figure 4. <sup>29</sup>Si CP MAS NMR spectrum of **2** (79.5 MHz, spinning speed 6 kHz)

To confirm and further refine the understanding of the formation of **2a** and **2b**, DFT calculations has been carried out at the DFT-B<sub>3</sub>PW<sub>91</sub> level of theory. Thus, the grafting reaction of **1** onto a silica surface treated at 700°C has been studied using a poly-oligosilsesquioxane derivative-type surface model (called **c** model), successfully used to study both the grafting reaction of several d/f metal complexes<sup>19</sup> and their catalytic activity.<sup>20</sup> The Gibbs free-energy profile for the grafting reaction leading to **2a** is given in Figure 5.

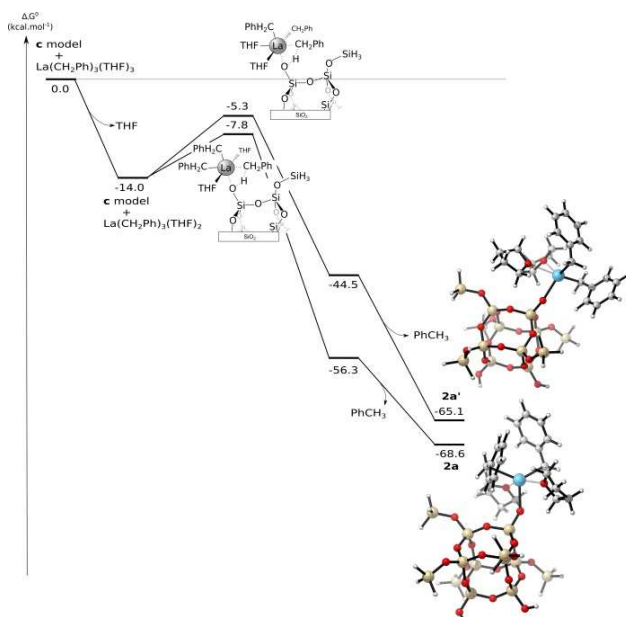


Figure 5. Calculated Gibbs free-energy profile (in kcal/mol) for the grafting reaction of **1** onto the **c** model.

The reaction sequence starts by the loss of one THF molecule leading to a complex in which the lanthanum center exhibits a distorted trigonal bipyramidal environment with two THF molecules in axial positions and the three benzyl ligands on the equatorial plane. From an energy point of view, the formation of this complex is exergonic by  $-14.0$  kcal.mol $^{-1}$  with respect to the entrance channel. The reaction continues by the grafting of this intermediate onto the silica surface through a protonolysis of a La – C bond by a surface silanol, leading to two possible mono-grafted  $\equiv\text{Si-O-La}(\text{THF})_2(\text{CH}_2\text{Ph})_2$  isomers with benzyl and THF ligands in a *cis* (**2a'**) or *trans* (**2a**) configuration with the concomitant formation of a free toluene molecule. The formation of these two isomers is, in both cases, computed to be exergonic, by  $-65.1$  kcal.mol $^{-1}$  for the *cis* isomer and by  $-68.6$  kcal.mol $^{-1}$  for the *trans* configuration, and kinetically accessible (highest barrier of  $8.7$  kcal.mol $^{-1}$ ). It is interesting to note that in both isomers the two benzyl groups are  $\eta^2$  coordinated to the metal center. Thus, these complexes are stabilized by the formation of an interaction between the *ipso*-carbon atom and the metal center, *i. e.*, by a donation from the  $\text{CH}_2 - \text{C}_{\text{ipso}}$  bond to an empty d orbital of lanthanum as indicated by the second-order perturbation natural bond order (NBO) analysis. We can therefore conclude that, according to the slightly stability difference between both isomers and the small activation needed to their formation, these two isomers can coexist onto the silica surface. DFT calculation also used to consolidate the above-proposed spectroscopic assignment (Table 1). Good agreement was observed between both calculated and experimental  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR chemical shifts. The spectral signatures of both isomers are very close evidencing that they cannot be distinguished by NMR which argues for the coexistence of the two complexes onto the silica surface. It is also noteworthy that, from **2a** and **2a'**, the loss or addition of a THF molecule is an endergonic process, by around  $11.0$  kcal.mol $^{-1}$ , that presumably would not occur.

Table 1. Experimental and calculated NMR data for silica-supported lanthanum benzyl complexes

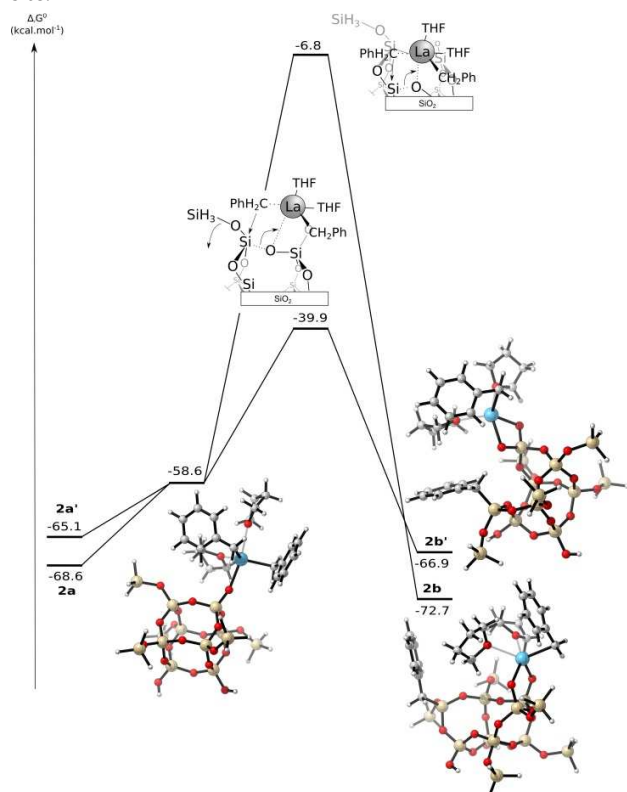
	$^1\text{H}$ NMR (ppm)					
	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph		OC H <sub>2</sub>	OCH <sub>2</sub> CH <sub>2</sub>	
		H <sub>ortho</sub>	H <sub>meta</sub>	H <sub>para</sub>		
<b>2</b> (exp.)	1.6		7.1		3.7	1.6
<b>2a</b>	2.0	6.5	7.1	6.4	3.9	1.8
<b>2a'</b>	1.8	6.7	7.3	6.4	3.9	1.8
<b>2b</b>	2.2	6.8	7.1	6.4	3.6	1.7
<b>2b'</b>	2.1	6.8	7.1	6.2	3.7	1.7
CH <sub>2</sub> Ph (Transf)	2.7	7.6	7.3	7.2	-	-

	$^{13}\text{C}$ NMR (ppm)						
	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph			OCH <sub>2</sub>	OCH <sub>2</sub> CH <sub>2</sub>	
		C <sub>ipso</sub>	C <sub>ortho</sub>	C <sub>meta</sub>	C <sub>para</sub>		
<b>2</b> (exp.)	62	-		128		69	24
<b>2a</b>	55.9	144.1	118.4	127.6	113.5	70.2	28.8
<b>2a'</b>	56.3	146.3	117.8	128.7	112.9	70.2	28.8
<b>2b</b>	59.9	145.5	118.7	127.2	114.1	70.2	28.6
<b>2b'</b>	56.7	149.2	116.6	129.2	112.5	68.9	28.4
CH <sub>2</sub> Ph (Transf)	24.9	134.7	126.2	124.1	120.1	-	-

Next, we focused on the mechanism leading to the formation of a bi-grafted complex (**2b**) through the transfer of a benzyl group to the silica surface. The Gibbs free-energy profile for the alkyl transfer is given in Figure 6. The formation of the bi-grafted complexes takes place through a concerted mechanism in which the transfer of the benzyl group from lanthanum to a neighboring silicon atom is concomitant to the activation of a Si–O bond and the formation of a La–O bond. Starting from **2a** and **2a'**, two different bi-grafted complexes can be obtained, depending if the silicon to which the alkyl group is transferred is linked by a siloxane bridge or not to the silanol group on which the lanthanide complex is grafted. In all the cases, the reaction starts by an endergonic isomerization of **2a** and **2a'**, by  $10.0$  and  $6.5$  kcal.mol $^{-1}$  respectively, leading to an isomer exhibiting a trigonal-bipyramidal geometry around the metal center, with the oxygen atom of the silanol group and one THF ligand in axial positions and the two benzyl groups and the second THF ligand on the equatorial plane. From this intermediate, the benzyl transfer to a silicon atom linked by a siloxane bridge to the silanol group on which the lanthanide complex is grafted leads to the formation of a bi-grafted complex on the same silanol group (**2b'**). The alkyl transfer reaction proceeds with an accessible energy barrier of  $28.7$  kcal.mol $^{-1}$  with respect to **2a** and  $25.2$  kcal.mol $^{-1}$  with respect to **2a'**. From a thermodynamic point of view, the formation of **2b'** is found to be an athermic process

with respect to **2a** and **2a'**, which is in agreement with the coexistence of both mono and bi-grafted complexes onto the silica surface as experimentally observed. In this case, the Si – O and La – C bond breaking is counterbalanced by the formation of a strong La – O bond and Si – C bond. However, this complex is destabilized by the ring constraint of the grafting mode which explains the athermicity of this reaction. On the other hand, the transfer of a benzyl group to a silicon atom not linked by a siloxane bridge to the silanol group on which the lanthanide complex leads to the formation of a bi-grafted complex on two vicinal silanol group (**2b**). The alkyl transfer reaction takes place via a highly costly process with an activation barrier calculated to be 61.8 kcal.mol<sup>-1</sup> with respect to **2a** and 58.3 kcal.mol<sup>-1</sup> with respect to **2a'**. Thus, even if in this case the formation of **2b** is found to be exergonic by 4.1 kcal.mol<sup>-1</sup> with respect to **2a** and by 7.6 kcal.mol<sup>-1</sup> with respect to **2a'**, this reaction would not occur. Thus, the benzyl transfer can only be carried out on silicon atoms close to the initial grafting site.

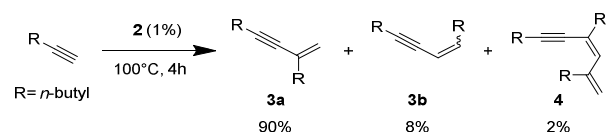


**Figure 6.** Calculated Gibbs free-energy profile (in kcal/mol) for the alkyl transfer mechanism leading to **2b** and **2b'**.

With this material at hand, we proceeded to probe its performances in catalytic reactions performed by rare-earth molecular species, namely alkyne dimerization, along with ethylene, styrene and  $\epsilon$ -caprolactone homo-polymerization.

Alkyne dimerization catalyzed by rare-earth metal derivatives was first described by the Teuben group,<sup>21</sup> originally with bis-pentamethylcyclopentadienyl systems. It proceeds by reaction between metal-C bond and acidic C-H from the substrate, followed by alkyne insertion into the La-C bond and protonolysis by the C-H from a further substrate molecule. This reaction thus forms a C-C bond to generate an enyne moiety from two terminal alkyne substrates (Scheme 2). It can afford either branched, head-to-tail (**3a**) or linear, head-to-head (**3b**) dimers. Trimers (**4**) can also be produced. We have previously reported that grafted amides can catalyze this reaction.<sup>7b,22</sup> Thus, in the presence of **2** (1% catalytic

loading) after 4 hours at 100°C, 1-hexyne is converted into a mixture of dimers with 40% conversion. The major species is the head-to-tail isomer **3a** (90%), while the tail-to-tail **3b** species accounts for 8% (Scheme 2). Only traces (2%) of trimer **4** were detected. Conversion was not improved with a longer reaction time (15 h).



**Scheme 2.** Dimerization of 1-hexyne catalyzed by **2**.

The presence of lanthanum-carbon bonds within **2** also opens up the possibility to use it as an ethylene polymerization catalyst, as, in contrast with group 4 catalysts, rare-earth species do not necessarily require activators to achieve ethylene polymerization.<sup>23</sup> Indeed, under mild reaction conditions (90°C, 1.5 bar), **2** affords polyethylene, though with modest activity (1.9 kg<sub>PE</sub>.mol<sub>La</sub><sup>-1</sup>.bar<sup>-1</sup>.h<sup>-1</sup> after 1h). This is within the same range as that of silica-supported lanthanum silylamides activated by tris(isobutyl) aluminum.<sup>22,24</sup> Use of 1eq. per La of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as cationizing agent does not improve reactivity (activity of 1.0 kg<sub>PE</sub>.mol<sub>La</sub><sup>-1</sup>.bar<sup>-1</sup>.h<sup>-1</sup> after 1h). This can be related to the fact that, as we have shown above, 80% of the lanthanum centers bear a single alkyl group (**2b**): Alkyl abstraction would lead to a catalytically inert system. Thus, only the 20% of bis alkyl species (**2a**) could react and afford a cationic alkyl entity able to polymerize ethylene.

Material **2** is also able to polymerize styrene in the absence of activator. Reacting 100 equivalent of monomer per lanthanum center at 80°C affords high molecular weight polystyrene (M<sub>w</sub> 4.1 10<sup>5</sup> g/mol, with a substantial dispersity of 5.7) with isolated yield of 42%. This moderate activity and the lack of mass control indicate poor initiation control of the polymerization process.

Finally,  $\epsilon$ -caprolactone is efficiently polymerized by **2**: A conversion of 89% for 650 equivalents of monomer per lanthanum center is readily achieved at room temperature within 2 hours, affording a white solid upon precipitation in methanol. SEC analysis shows that polymerization is rather controlled (M<sub>w</sub> 1.8 10<sup>5</sup> g.mol<sup>-1</sup>,  $\bar{D}$  = 1.64, Figure S4).

## Conclusion.

We have described here the surface chemistry of a lanthanum tris-benzyl derivative onto dehydroxylated silica. This highly reactive organometallic species reacts not only with silanols, but also with (strained) siloxane moieties, affording as major surface site the bisgrafted surface species, along with [SiCH<sub>2</sub>Ph] groups, as shown by a combination of mass balance analysis and spectroscopic techniques. These elements were confirmed by DFT calculations, in particular showing that siloxane bridge opening occurs readily on a neighboring siloxane site after a first protonolysis step. Furthermore, this material catalyzes a range of reactions, however with modest activity. Further attempts will be aimed at the study of the influence of the nature of the metal center by grafting [Ln(CH<sub>2</sub>Ph<sub>2</sub>)(THF)<sub>n</sub>] complexes on silica. As reactivity is known to depend on the nature of the rare-earth metal (ionic radius, Lewis acidity ...),<sup>24,25</sup> it should allow us drawing relationship with the catalytic performances of the resulting materials.

## EXPERIMENTAL SECTION

**General considerations.** Experiments were carried out under an argon atmosphere in an M-Braun glove-box or by using Schlenk techniques. Solvents and reactants were dried by using conventional reagents and stored in the glove-box over 3Å molecular

sieves. Aerosil 380 silica (Degussa, specific area 380 m<sup>2</sup> g<sup>-1</sup>, prior to heat treatment) was subjected to heating under secondary vacuum (10<sup>-6</sup> mbar) for 15 h at 500 °C, followed by 4 h at 700 °C, and stored in a glovebox. Liquid-state NMR spectroscopic analyses were run on a Bruker Avance 300 spectrometer. Solid-state MAS NMR spectra were recorded on Bruker Avance 400 and 800 spectrometers. Chemical shifts are given with respect to adamantane, glycine and TMS as external references for <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy, respectively. The two-dimensional homonuclear experiment (DQ-MAS) was obtained at a spinning frequency of 20 kHz by using excitation and reconversion pulse blocks of two rotor periods each (200 μs). The 90° pulse length was 2.25 μs, the recycle delay was 30 s, and 16 scans were collected for each slice (128 in total). The <sup>1</sup>H-<sup>13</sup>C CP MAS NMR experiment (HETCOR) was obtained at a spinning frequency of 14 kHz. The 90° pulse length was 4 μs, the recycle delay was 5 s, and 512 scans were collected for the 32 slices. For the CP step, a ramped radio frequency (RF) field centered at 45 kHz was applied on protons, and the contact time was set to 1 ms. The <sup>29</sup>Si CP MAS spectrum was recorded at a spinning frequency of 6 kHz, with a recycling delay of 3 s.

Diffuse reflectance infrared spectra were collected with a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm<sup>-1</sup>). Elemental analyses were conducted in at the Service d'Analyse Élémentaire, LSEO, Université de Bourgogne (CHN) and in the Service Central d'Analyse du CNRS (La).

The weight- and number-average molar masses ( $M_w$  and  $M_n$ ) and dispersities ( $\bar{D} = M_w/M_n$ ) of the polymers were determined by size exclusion chromatography (SEC) in THF at 40 °C (1 mL/min) with a triple detection system, equipped with an Alliance Waters e2695, a multiangle light scattering detector (MALS, Wyatt Technology mini DAWN TREOS), and a refractive index detector (Waters 2414). The SEC system was equipped with three Waters Styragel (HT1, HT3 and HT4) columns. The refractometer was used to determine the molar masses against polystyrene standards with the corrections  $M_n(\text{SEC}) = 0.56 \times M(\text{obs})$  for polycaprolactone.<sup>26</sup> Samples were prepared by dissolving the product (10 mg) in 4 mL of THF. The solutions were then filtered with 0.45 μm filters. For alkyne dimerization, reaction mixtures were analysed using a Shimadzu GC2010 chromatograph fitted with a CP-Sil5CB column (25m × 0.25mm × 0.2 μm), argon as carrier gas, and both injector and detector temperature at 250 °C. Heating program: starting at 50 °C then a ramp of 10 °C/min up to 250°C, hold for 10 min is applied (more details in supplementary information about conversion and selectivity calculations).

**Grafting of **1** onto SiO<sub>2-700</sub>.** In a glovebox, a double-Schlenk vessel was loaded with **1** (655 mg, 0.6 mmol) dissolved in 20 mL of THF in one compartment and with SiO<sub>2-700</sub> (1.5 g) suspended in 20 mL of toluene in the other compartment. The orange complex solution was added at room temperature to the support by filtering through the sintered glass separating the two Schlenk tubes, and the reaction mixture was stirred for 15 h. The supernatant liquid was then separated by filtration into the other compartment, from which the solvent was gas-phase transferred by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual molecular precursor. This operation was repeated thrice (resulting in color-less washing fractions). The resulting material (**2**) was then dried under secondary vacuum (10<sup>-6</sup> mbar) at room temperature for 14 h.

**Alkyne dimerization.** In the glove box, a glass reactor is filled with **2** (100 mg, 0.039 mmol La), 3ml of toluene and 1-hexyne (325 mg, 3.9 mmol, 100 mol eq. per La). The reaction mixture is heated at 100°C. After 4 hours, the reaction is quenched by exposure to air. The supernatant is analysed by GC using *n*-decane as a standard (added after quenching). See Figures S1 and S2.

**Polymerization of ethylene.** A solution of TIBA (300 mg) in 18 mL toluene was introduced in a thermostated (90°C) glass reactor

equipped with a powerful mechanical stirrer. The reactor was pressurized on and continuously fed with 1.5 bar ethylene. A suspension of **2** (253 mg containing 5.48% La, 100 μmol) in 2 mL toluene was prepared in the glove box and injected through a septum into the polymerisation reactor. The ethylene consumption was then monitored with a mass flowmeter. The polymerisation was stopped after 2 h by hydrolysis with acidic methanol (100 mL with 1 mL concentrated HCl). The solid material was recovered by filtration, washed with pure methanol, dried and weighed (580 mg). Integration of the mass flowmeter signal indicated consumption of 350 mg of ethylene.

**Polymerization of styrene.** In the glove box, a glass reactor is filled with **2** (128 mg, 0.05 mmol La) and 0.575 ml of toluene. Then freshly distilled styrene (0.52 g, 5 mmol, 100 eq. per La) is added dropwise while the reaction mixture is vigorously stirred. The reaction is heated at 80°C. After 2h, the reaction is quenched with a methanol/water mixture and polystyrene is precipitated from methanol and dried under vacuum, affording to obtain 0.22 g of white polymer (42% yield).

**Ring-opening polymerization of ε-caprolactone.** In the glove box, a glass reactor is filled with **2** (50 mg, 0.02mmol La) and 3 ml of toluene. Then, a freshly distilled ε-caprolactone solution in 2 mL toluene (1.48 g, 13 mmol, 650 eq. per La) is added dropwise while the reaction mixture is vigorously stirred. Exothermicity is observed and formation of a gel occurred within about an hour. After 2 hours, the reaction mixture was exposed to air, and extracted with THF. The poly-ε-caprolactone was precipitated from methanol and dried under vacuum, affording ? to obtain 1.32 g of white polymer (89% isolated yield). <sup>1</sup>H NMR features are consistent with reported data (Figure S3).<sup>27</sup>

**DFT calculations.** All DFT calculations were performed with Gaussian 09.<sup>28</sup> Geometries were fully optimized in gas phase without symmetry constraints, employing the B3PW91 functional<sup>29</sup> and the Stuttgart effective core potential for La and Si<sup>30</sup> augmented with a polarization function ( $\zeta_4 = 0.284$  for Si and  $\zeta_6 = 1.000$  for La). For the other elements (H, C and O), Pople's double- $\zeta$  basis set 6-31G(d,p)<sup>31</sup> was used. Calculations of vibrational frequencies were systematically done in order to characterize the nature of stationary points. Calculating a theoretical chemical shift requires the knowledge of the chemical shielding of a reference, since it is explicitly calculated as  $\delta = (\sigma_{\text{ref}} - \sigma)$ , in ppm, where  $\sigma_{\text{ref}}$  is the isotropic <sup>1</sup>H and <sup>13</sup>C chemical shielding of a molecule of tetramethylsilane (calculated at the same level as the studied systems):  $\sigma_{\text{ref}}(\text{C}) = 196.1148$  ppm,  $\sigma_{\text{ref}}(\text{H}) = 31.6435$  ppm. Among the various theories available to compute chemical shielding tensors, the gauge including atomic orbital (GIAO) method has been adopted for the numerous advantages it presents.<sup>32</sup> The same methodology was used in previous studies involving grafted systems, showing that theoretical results are fairly accurate with respect to experimental values with an error lower than 15% for <sup>29</sup>Si,<sup>19a</sup> 10% for <sup>31</sup>P<sup>33</sup> and <sup>17</sup>O<sup>19b-d</sup> and 5% for <sup>1</sup>H<sup>12</sup> and <sup>13</sup>C<sup>12</sup>. The electron density and partial charge distribution were examined in terms of localized electron-pair bonding units using the NBO program<sup>34</sup> available in Gaussian 09.

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