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Synthesis, characterisation and grafting onto silica of alkoxide–triflate lanthanum complexes. Molecular structure of $La(OC_6H_3\text{-}2,6\text{-}Me_2)_2(\eta^1\text{-}O_3SCF_3)$(tetraglyme)

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Abstract

Reactions between lanthanum triflate adducts $La(OTf)_3(LL^x)$ ($OTf = O_3SCF_3$; LL^1 = triglyme, LL^2 = tetraglyme] and 2 equiv. of LiOAr ($Ar = C_6H_3\text{-}2,6\text{-}Me_2$) in THF lead to $La(OTf)(OC_6H_3\text{-}2,6\text{-}Me_2)_2(LL^x)$ [LL^1 = triglyme (**1**); LL^2 = tetraglyme (**2**)] derivatives. They were characterised by elemental analysis, FT IR and NMR (^1H, ^{13}C, ^{19}F). The adduct with tetraglyme (**2**) was also characterised by single crystal X-ray diffraction. The metal is octacoordinated, surrounded by anionic monodentate ligands including the triflate and a pentadentate glyme. The La–O bond distances spread over the range 2.225(3)–2.692(3) Å with the ranking La–O(Ar) < La–O(Tf) < La–O(tetraglyme). The grafting of **1** onto silica led to an hybrid material, characterised by elemental analysis, FT IR, ^{13}C CP-MAS NMR and XPS. It was used as hydroxymethylation catalyst of silyl enol ether in mild conditions.

Keywords: Lanthanum; X-ray structures; Alkoxides; Triflate; Grafting

1. Introduction

Lanthanide derivatives have been used as catalysts in a variety of organic reactions [1]. Trifluoromethanesulfonates (triflates) are water-tolerant Lewis acids and lanthanide triflates are versatile catalysts for C–C bond-forming reactions and can induce cationic polymerisation reactions [2]. On the other hand, lanthanide alkoxides and aryloxides have proven to be good polymerisation catalysts by ring-opening reactions [3]. By contrast to early transition metals for instance, derivatives whose coordination sphere incorporates alkoxide (or aryloxide) and triflate ligands namely $Ln(OR)_{3-x}(O_3SCF_3)_x$ species remain scarce for rare earth metals. The only examples are the $[\{Ln(O_3SCF_3)(pyridine)_x(terpyridine)_y\}_2H_2L]$ [Ln = Sm, $x = 4$, $y = 0$; Ln = Yb, $x = 1$, $y = 1$] complexes based on *t*-Bu-calix [6]arene (H_6L) [5]. Although those compounds could be structurally characterised, they underwent degradation during storage in the solid state, even under inert atmosphere, and no reactivity or catalytic behaviour was reported for them. This combination of ligands could be of interest since lanthanide triflate and aryloxide have been widely used in organic synthesis as acid [6] and base [7] catalysts, respectively.

We describe herein the synthesis and characterisation of two bisaryloxotriflate lanthanum based on more simple ligands namely 2,6-dimethylphenoxide and stabilised as adducts with glymes. Single crystal X-ray diffraction established the monomeric character of the

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tetraglyme adduct. Heterogenisation was achieved by anchoring onto silica. The resulting hybrid material was tested in acid and base catalytic reactions.

2. Experimental

All experiments were carried out under argon with Schlenk-type glassware on a dual manifold Schlenk line. All solvents were pre-dried over sodium wire. Hydrocarbons (pentane, hexane and toluene) and THF were distilled from sodium benzophenone ketyl, and stored over molecular sieves and/or sodium mirror. Deuterated THF-d_8 was distilled and degassed prior to use. 2,6-dimethylphenol (Aldrich) was freshly distilled under vacuum. All other reagents [L-lactide, HCHO, 1-(trimethylsilyloxy)cyclohexene] (Aldrich) were used as received. $La(OTf)_3(LL^x)$ compounds ($OTf = O_3SCF_3$; LL^1 = triglyme; LL^2 = tetraglyme) were prepared as reported [8]. Silica 200 aerosil (200 m^2 g^{-1}) was annealed at 500 °C for 15 h and cooled down in vacuo. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 300 MHz spectrometer at 295 K unless otherwise stated, and were referenced internally to residual solvent resonances. $CFCl_3$ was used as reference for ^{19}F NMR data. ^{13}C CP-MAS NMR spectra were recorded on a Bruker 400 MHz spectrometer at 295 K. FT IR spectra were obtained as Nujol mulls with a Perkin–Elmer Paragon 500 spectrometer. Elemental analyses were obtained from the Centre de Microanalyses du CNRS. XPS experiments were performed with an ESCALAB 200R (VG Scientific) spectrometer using the monochromated Kα Al radiation as excitation source.

2.1. Synthesis of $La(OTf)(OAr)_2(LL^x)$ [$Ar = C_6H_3$-2,6-Me_2, LL^1 = triglyme (1), LL^2 = tetraglyme (2)]

About 0.378 g (2.94 mmol) of LiOAr in 10 ml of THF were added to 1.12 g (1.47 mmol) of a suspension of $La(OTf)_3(LL^1)$ in 20 ml of THF. The resulting yellow solution was stirred for 20 h. After removing the volatiles in vacuo, several crops of **1** (0.9 g, 87%) were isolated. The last crops were contamined by LiOTf. *Anal.* Calc. for $C_{25}H_{36}O_9F_3SLa$: C, 42.4; H, 5.1. Found: C, 41.9; H, 4.9%. FT IR (cm^{-1}, Nujol): 1589s (νC=C); 1466vs, 1424vs, 1378m, 1346w, 1314m, 1283vs, 1238s, 1198w, 1153w, 1098s, 1078vs, 1050s, 1008m, 974w, 924m, 912w, 852vs, 820w; 776m, 746vs, 694s; 564w, 521s, 488w (νLa–O). ^1H NMR (ppm, THF-d_8): 6.68 [d, $J = 7.35$ Hz, 4H, CH(Ar)], 6.16 [t, $J = 7.35$ Hz, 2H, CH(Ar)], 3.53–3.48 [br, m, 12H, OCH_2], 3.32 [s, 6H, OMe], 2.16 [br, $\Delta\nu_{1/2} = 6$ Hz, 12H, Me(Ar)]. $^{13}C\{^1H\}$ NMR (ppm, THF-d_8): 127.9 [br, $\Delta\nu_{1/2} = 26$ Hz], 125.0 [br, $\Delta\nu_{1/2} = 44$ Hz], 120.9 [q, $J_{C-F} = 319$ Hz], 116.5; 72.2, 70.6, 58.4 [OCH_2]; 25.8 [Me–Ar]. ^{19}F NMR (ppm, THF-d_8): −78.61 [CF_3].

The same procedure applied to 2.15 g (2.68 mmol) of $La(OTf)_3(LL^2)$ and 0.688 g (5.37 mmol) of LiOAr led to 0.96 g (77%) of **2**. *Anal.* Calc. for $C_{27}H_{40}O_{10}F_3SLa$: C, 43.1; H, 5.3. Found: C, 42.8; H, 5.1%. FT IR (cm^{-1}, Nujol): 1588s (νC=C), 1495m, 1463vs, 1423vs, 1377m, 1348w, 1312vs, 1289s, 1276vs, 1237vs, 1222vs, 1165s, 1120w, 1086vs, 1072vs, 1054s, 1031vs, 1014m, 947m, 932w, 913w, 853vs, 766s; 754m, 745vs, 696vs, 636vs; 579w, 570w, 525m, 511w, 486w, 469w (νLa–O). ^1H NMR (ppm, THF-d_8): 6.70 [d, $J = 7.35$ Hz, 4H, CH(Ar)], 6.23 [t, $J = 7.35$ Hz, 2H, CH(Ar)], 4.00–3.78 [m, 16H, OCH_2], 3.38 [s, 6H, OMe], 2.17 [s, 12H, Me(Ar)]. $^{13}C\{^1H\}$ NMR (ppm, THF-d_8): 136.0, 123.6, 126.1, 119.0 [q, $J_{C-F} = 319$ Hz], 113.3; 68.8, 58.8 [OCH_2]; 19.04 [CH_3–Ar]. ^{19}F NMR (ppm, THF-d_8): −78.56 [CF_3].

Compound **1** and **2** were soluble in ethers, CH_2Cl_2 and slightly soluble in toluene. They were hygroscopic and were hydrolysed after 24 h of exposure to air.

2.2. X-ray crystal structure determination for $La(OTf)(OC_6H_3$-2,6-$Me_2)_2$(tetraglyme), C_7H_8

Suitable crystals of **2** were obtained by recristallisation in toluene:THF [20:1] and were mounted on a CAD4 Enraf–Nonius diffractometer. Accurate cell dimensions and orientation matrix were obtained by

Table 1
Crystallographic data of $La(OAr)_2(OTf)$(tetraglyme) (**2**)

Formula	$C_{34}H_{48}F_3O_{10}SLa$
Formula weight	844.7
a (Å)	8.978(3)
b (Å)	11.128(2)
c (Å)	19.014(3)
α (°)	94.99(1)
β (°)	93.42(2)
γ (°)	91.85(2)
V ($Å^3$)	1887.6(7)
Z	2
Crystal system	triclinic
Space group	$P\bar{1}$
Linear absorption coefficient μ (cm^{-1})	12.5
Density ρ ($g\ cm^{-3}$)	1.49
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
θ Range for data collection (°)	2–25
Temperature of measurement (K)	180
Octants collected	0, 10; −13, 13; −22, 22
Number of data collected	7089
Number of unique data collected	6622 ($R_{int} = 0.02$)
Number of unique data used for refinement	5139 $(F_o)^2 > 3\sigma(F_o)^2$
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0339
$R_w^* = [\Sigma\ w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\ w\lvert F_o\rvert^2]^{1/2}$	0.0412
S	1.16
Extinction parameter	none
Number of variables	641

*, $w = w'[1-((\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma\ rA_rT_r(X)$ with three coefficients 3.12, −1.06 and 2.22 for a Chebyshev Series, for which X is F_c/F_c (max).

least-squares refinement of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Table 1. The data were corrected for Lorentz and polarisation effects. Computations were performed by using the PC version of CRYSTALS [9]. Scattering factors and corrections for anomalous dispersion were taken from ref [10]. The structure was solved by Fo–Patterson techniques and Fourier analysis and refined by full-matrix least-squares with anisotropic displacement parameters for all non hydrogen atoms. Hydrogen atoms were located on a difference Fourier map; their coordinates and an overall isotropic displacement parameter were refined. The SO_3CF_3 anion is disordered. Refinement of the used model (the S atom, one of the three O atoms and the CF_3 group were disordered over two positions [S(1) and S(11) for sulfur] led to a satisfactory solution with a 0.69:0.31 occupancy ratio.

2.3. *Procedure for grafting onto silica*

About 0.21 g (0.3 mmol) of **1** dissolved in 30 cm^3 of THF ([1] = 0.1 M l^{-1}) were added to a suspension of pre-treated silica (1.76 g) in 20 cm^3 of THF. The reaction mixture was stirred for 4 days at ambient temperature and then separated by filtration. The solid **3** was washed several times with THF (20 cm^3) and petroleum ether (20 cm^3). The THF fractions were collected and the solvent was removed in vacuo to check for unloaded and/or by-product compounds. **3** was dried in vacuo for 8 h. FT IR (cm^{-1}, Nujol): 3398 (νO–H); 1407vs, 1369w, 1349s, 1329vs, 1194vs, 1052s, 987w, 903sh, 872s, 760m, 733w; 670 w (νLa–OTf); 481m (νLa–OR) cm^{-1} *Anal*. Calc. for $C_{25}H_{33}O_{207}F_3SLaSi_{100}$: C, 3.62; H, 0.38; La, 2.01. Found: C, 3.48; H, 0.89; La, 1.81%.

2.4. *Procedure for L-lactide polymerisation reactions*

In a typical reaction, a mixture of **3** and L-lactide in CH_2Cl_2 (or toluene) was stirred 24 h at 20 °C (or under reflux). After filtration, precipitation of a white solid occurred by addition of hexanes. In some experiments a small amount of benzylic alcohol (20 µl) was added. The product was analysed by ^1H NMR and Size Exclusion Chromatography (SEC).

2.5. *Procedures for hydroxymethylation reactions of silyl enol ether*

2.5.1. *Procedure a*

A mixture of silyl enol ether (65 µl, 0.3 mmol) and 1 cm^3 of aqueous commercial formaldehyde solution in 2 cm^3 of THF was added to a suspension of **3** (0.23 g, 0.03mmol) (THF:H_2O = 2:1, 6 cm^3) at room temperature (r.t.).

2.5.2. *Procedure b*

Aqueous formaldehyde solution (0.5 cm^3, 37%) and silyl enol ether (45 µl, 0.2 mmol) in THF (1 cm^3) at r.t. were successively added to a suspension of **3** (0.16 g, 0.02 mmol) in 2 cm^3 of THF.

The medium was stirred for 24 h in both procedures. After filtration, the solvent was removed in vacuo to afford a yellow pasty solid. It was dissolved in CH_2Cl_2 and the solution dried over $MgSO_4$ and analysed by GC–MS.

3. Results and discussion

3.1. *Synthesis*

Treatment of lanthanum trifluoromethanesulfonate adducts $La(OTf)_3(LL^x)$ ($OTf = O_3SCF_3$; LL^1 = triglyme; LL^2 = tetraglyme) with 2 equiv. of $LiOC_6H_3$-2,6-Me_2 in THF gave $La(OTf)(OC_6H_3\text{-}2,6\text{-}Me_2)_2(LL^x)$ derivatives [$x = 1$ (**1**); $x = 2$ (**2**)] in good yields. Intractable ill-defined products were obtained when either equimolar amounts of lithium aryloxide or no glymes were used.

$$La(OTf)_3(LL^x) + 2LiOAr \underset{-2LiOTf}{\overset{THF,\ 20\ °C}{\rightarrow}} \underset{x=1;\ (\mathbf{1})\ 87\%;\ x=2;\ (\mathbf{2})\ 77\%}{La(OTf)(OAr)_2(LL^x)} \quad (1)$$

The new compounds **1**–**2** were colourless, more soluble than the triflate adducts $La(OTf)_3(LL^x)$ in organic media such as ethers, gave satisfactory microanalysis (C, H) and were characterised by NMR (^1H, ^{13}C, ^{19}F). By contrast to the triflate adducts which were air stable, compounds **1** and **2** were hygroscopic, and underwent hydrolysis after 24 h in air. The FT-IR spectra and especially the absorption bands around 850 and 1080 cm^{-1} are indicative of glyme coordination to the lanthanum moiety. The absorption bands assigned to the νSO stretching at 1378 and 1377 cm^{-1} for **1** and **2**, respectively, suggest a monodentate coordination mode of the trifluoromethanesulfonate ligands [11]. The ^1H and ^{13}C NMR spectra in THF-d_8 at room temperature displayed a single set of resonances for the aryloxide and glyme ligands for each complex. The broad pattern of the signals of the OCH_2 groups of the tetraglyme adduct **2** accounts for their interaction with the quadrupolar lanthanum centre. The signals of the triglyme ligand of **1** were, by contrast, sharp and displayed chemical shifts close to those of the free ligand. Ligand exchange between triglyme and THF was also confirmed by the presence of two signals (1.76 and 1.80 ppm) for the OCH_2 groups of the THF-d_8 solvent, although the original complex **1** was totally recovered by evaporation. Another feature of the ^{1}H NMR spectra of **1** was the broadness of the signal at 2.16 ppm attributed to the methyl groups of the aryloxides. Field dependency of its FWHM value ($\Delta\nu_{1/2} = 6$ and 42 Hz for spectrometers resonating at 300 and 500 MHz, respectively) accounts for a restricted dynamic process at the NMR time scale although it was not more investigated.

The molecular and monomeric structure of **2** (Fig. 1) was established by single crystal X-ray diffraction. Selected bond lengths and angles are collected in Table 2. The structure of **2** is based on an octacoordinated lanthanum atom surrounded by monodentate anionic ligands namely two aryloxides and one triflate O_3SCF_3 and the pentadentate tetraglyme. The coordination polyhedron is based on a square antiprisme whose faces are built up on O(1)O(2)O(3)O(7) and O(4)O(5)O(6)O(8). The La–O bond distances spread over the range 2.225(3)–2.692(3) Å. The shortest ones are the La–OAr linkages [2.239(3) Å av.] whereas the La–O(tetraglyme) coordination bonds are, as expected, the longest ones [2.607(3)–2.692(3) Å]. These bond distances are actually longer than those observed for La(OTf)$_3$(tetraglyme)(H$_2$O) [2.547(4)–2.617(4) Å] where the metal is nine-coordinated.[12] The bite angles (60.92° av.) of **2** are also slightly smaller than those observed for the nine-coordinated triflate adduct. The La atom of **2** is displaced by 0.61 Å from the least-squares plane defined by the five oxygen atoms O(3)–O(7) of the glyme.

Table 2
Selected bonds (Å) and angles (°) of La(OAr)$_2$(OTf)(tetraglyme) (**2**)

Bond lengths			
La(1)–O(1)	2.254(3)	La(1)–O(2)	2.225(3)
La(1)–O(3)	2.644(3)	La(1)–O(4)	2.644(3)
La(1)–O(5)	2.683(3)	La(1)–O(6)	2.607(3)
La(1)–O(7)	2.692(3)	La(1)–O(11)	2.526(3)
Bond angles			
O(1)–La(1)–O(2)	111.7(1)	O(1)–La(1)–O(3)	82.7(1)
O(2)–La(1)–O(3)	79.9(1)	O(1)–La(1)–O(4)	77.2(1)
O(2)–La(1)–O(4)	138.6(1)	O(3)–La(1)–O(4)	60.7(1)
O(1)–La(1)–O(5)	95.4(1)	O(2)–La(1)–O(5)	148.6(1)
O(3)–La(1)–O(5)	120.5(1)	O(4)–La(1)–O(5)	60.94(9)
O(1)–La(1)–O(6)	125.3(1)	O(2)–La(1)–O(6)	89.1(1)
O(3)–La(1)–O(6)	151.9(1)	O(4)–La(1)–O(6)	119.5(1)
O(5)–La(1)–O(6)	61.6(1)	O(1)–La(1)–O(7)	74.9(1)
O(2)–La(1)–O(7)	77.8(1)	O(3)–La(1)–O(7)	139.5(1)
O(4)–La(1)–O(7)	141.0(1)	O(5)–La(1)–O(7)	95.2(1)
O(1)–La(1)–O(11)	149.4(1)	O(2)–La(1)–O(11)	86.1(1)
O(3)–La(1)–O(11)	76.0(1)	O(4)–La(1)–O(11)	73.3(1)
O(5)–La(1)–O(11)	77.4(1)	O(6)–La(1)–O(7)	60.44(9)
O(6)–La(1)–O(11)	77.6(1)	O(7)–La(1)–O(11)	134.8(1)
La(1)–O(1)–C(1)	178.1(3)	La(1)–O(2)–C(9)	167.3(3)
La(1)–O(11)–S(1)	149.0(2)	La(1)–O(11)–S(11)	162.7(3)

Coordination of the triflate results in an increase of the corresponding S–O bond [S(1)–O(11) 1.483(3) Å vs. 1.430(4) and 1.39(1) Å] as usually observed. The La–O–C angles associated to the aryloxide ligands are quite large namely 178.1(3)° for La(1)–O(1)–C(1) and 167.3(3)° for La(1)–O(2)–C(9) as usually observed [13].

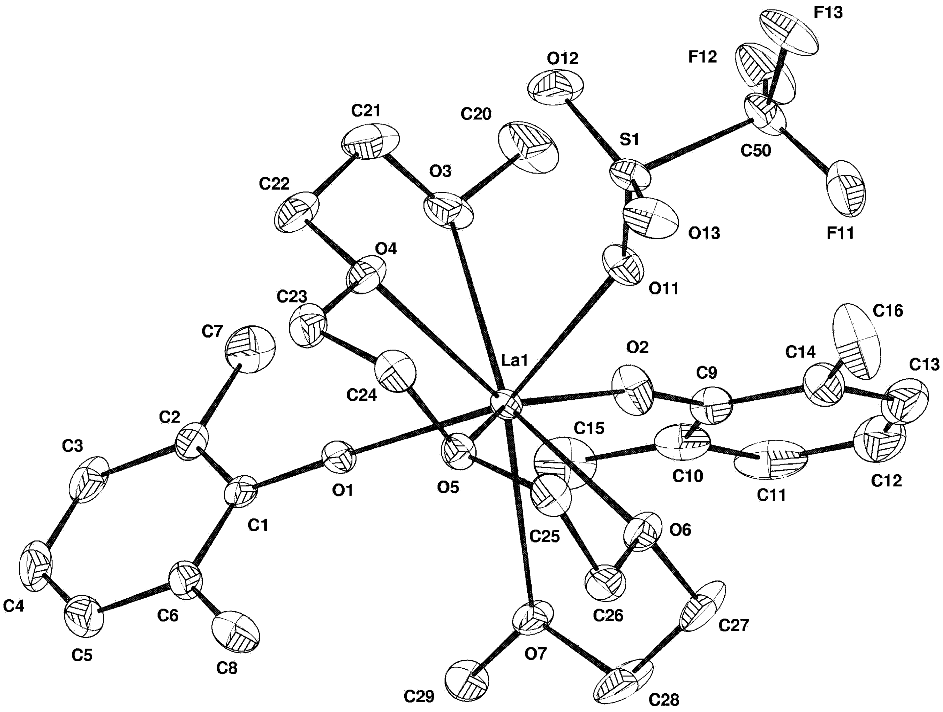
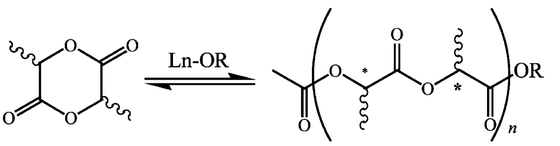


Fig. 1. Molecular structure of La(OAr)$_2$(OTf)(tetraglyme) (**2**) (thermal ellipsoids at 20% probability). For sake of clarity, only one position is represented for the triflate ligand.

3.2. Reactivity

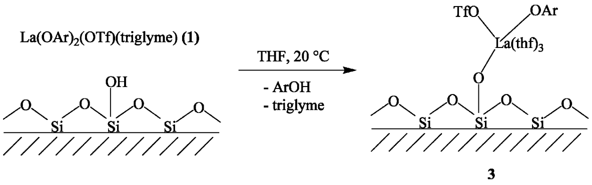
3.2.1. Grafting onto silica

The presence of different ligands on the same metal centre (one trifluoromethanesulfonate and two aryloxide ligands) prompted us to investigate the acidic and basic catalytic properties. Alkoxides and aryloxides of lanthanides have been used as ring-opening polymerisation catalysts especially of lactides (Eq. (2)). [4] Lanthanum derivatives were generally the most efficient initiators, the activity decreasing as the size of the lanthanide increases. However, transesterification reactions favoured by the presence of several alkoxide or aryloxide ligands were also observed to be the highest for lanthanum derivatives, thus resulting in low control of the stereochemistry and microstructure of the polymer [4,14,15].



(2)

In order to develop single-site as well as multifunctional catalysts we considered the possibility to remove one aryloxide by an exchange reaction with silica silanol groups [14,16]. Compound **1** was selected as the less sterically encumbered aryloxotriflate lanthanum derivative and for the lability of its polyether ligand. Hence the reaction between **1** (0.3 mmol) in 30 cm^3 of THF and 1.76 g of pre-treated silica (Si–La = 100) in 20 cm^3 of THF afforded a solid **3** which has been characterised by elemental analysis, FT IR, ^{13}C CP-MAS NMR and XPS (Eq. (3)).



(3)

Its FT IR spectrum indicated the disappearance of the sharp absorption band at 3691 cm^{-1} corresponding to isolated silanol groups [17] whereas, the absorption bands characteristic of non-isolated silanol groups [3398 cm^{-1}], aryloxide [481 ν(La–OR), 760, 872, 1349 cm^{-1}] and triflate ligands [670 ν(La–OTf), 1052, 1194 cm^{-1}] were present. ^{1}H NMR spectra of the THF reaction residues showed the presence of a mixture of HOC_6H_3-2,6-Me_2 and triglyme (1:1) whereas the ^{19}F NMR spectra exhibited trace amounts of triflic acid at -78.9 ppm. No trace of lanthanum could be detected by ICP which means that the metal loading is quantitative. In the ^{13}C MAS NMR spectrum only two peaks merged at 67.40 and 24.74 ppm corresponding to THF ligands.

XPS experiments recorded from 0 to 1200 eV indicated the presence of silicon, oxygen, carbon and lanthanum. The adventitious C 1s signal at 284.5 eV was used as the energy reference to correct for charging. The binding energies of the O 1s, Si 2p, La $3d_{3/2}$ and La $3d_{5/2}$ signals are summarised in Table 3. The signals of S 1s and F 1s were either masked by the silicon one or too small, respectively, to be detected and assigned unequivocally. Comparison to the XPS data of pre-treated SiO_2 200 Aerosil showed that the O 1s and Si 2p peaks of **3** appeared broadened with larger full width at half maximum height (FWHM) values but with same binding energies. The O–Si ratio has a value of 2.08 indicating a slight excess of oxygen at the surface while the Si–La ratio corresponded to 20.00. About 0.3 mmol of complex **1** (1.81×10^{20} atoms of La) and 1.76 g of silica 200 m^2 g^{-1} (352 m^2) give a density of one atom of La per 2 nm^2 of SiO_2. This matches with one atom of La per 20 atoms of silicon and implies that the lanthanum complex is essentially grafted at the silica surface. A $\{La(O_3SCF_3)(OC_6H_3\text{-}2,6\text{-}Me_2)(THF)_3[SiO_2]_{100}\}$ formula is in agreement with all data. The slightly higher proton percentage in elemental analysis was attributed to silanol groups still present and a more realistic formula would thus be $\{La(O_3SCF_3)(OC_6H_3\text{-}2,6\text{-}Me_2)(THF)_3[SiO_{2-x}(OH)_x]_{100}\}$ (**3**). Modelling using the CERIUS^2 sofware [18] has been carried out for **3** as a monolayer of 40 silicon atoms with two grafted-lanthanum complexes. Preliminary results with geometry relaxation applied using the Universal Force Field 1.02 program (UFF) [19], show that the average distance between two lanthanum centres is around 16 Å.

3.2.2. Investigation of catalytic behaviour

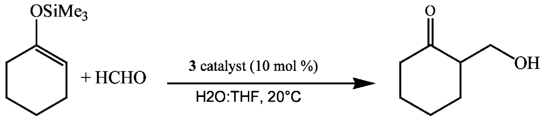
Reactions between the grafted-La species **3** and L-lactide in different conditions namely L-lactide/catalyst ratio of 500 or 1000, at room temperature in CH_2Cl_2 or refluxing toluene gave only the monomer. Addition of small amounts of benzylic alcohol as transfert reagent did not restore activity [20]. These data suggest that coordination of lactide, a necessary step for ring-opening polymerisation by a coordination-insertion mechanism, is disfavoured either for steric reasons or due to the strong coordination of the THF ligands. Ligands with electron withdrawing substituents were actually reported to desactivate the activity of the catalyst in similar polymerisation reactions [4].

The activity as Lewis acid was investigated with the hydroxymethalation of silyl enol ether in the presence of 10 mol% of **3** in aqueous-THF media (Eq. (4)). The yield of the desired aldol was low (ca. 15%) and was influenced by the amount of water. 2,6-dimethylphenol, resulting from hydrolysis of the Ln–OAr bond, was detected amongst unidentified products. No aldol was isolated for a ratio THF:H_2O of 6 (procedure b) instead of 2 (procedure a). Such an observation was explained

Table 3
XPS data (eV) of **3** and of non-grafted silica SiO_2

Compounds (eV)	O1 (s)	FWHM	Si 2p	FWHM	La $3d_{3/2}$	La $3d_{5/2}$
3	532.75	2.41	103.3	2.53	852.5	835.9
SiO_2	532.77	2.27	103.3	2.35		

by the fact that in the presence of small amounts of water, lanthanide triflates are predominantly coordinated with THF this decreasing their activity as Lewis acids [21].



(4)

In conclusion, new bis-aryloxotriflate species were synthesised and characterised. They provide the only second example of lanthanide species having that combination of ligands and the first example of species based on simple OR ligands [5]. Grafting onto silica proceeds in mild conditions and afforded an hybrid material with two potential reactive sites: one aryloxy ligand as Lewis base site and one triflate ligand as Lewis acid site. Preliminary results of the evaluation of this bi-functionnality in lactide polymerisation and Lewis acid-catalysed carbon–carbon coupling reactions, respectively, are reported. By contrast to **1**, no ring-opening polymerisation reaction of lactide was observed in our conditions. However, activation of formaldehyde in water for hydroxymethylation of silyl enol ether could be achieved in mild conditions. The amount of water appeared as a major parameter influencing the yield and should be optimised.

4. Supplementary material

Crystallographic data (tables of coordinates, of thermal parameters, of bond lengths and angles) have been deposited at the Cambridge Crystallographic Data Base Centre. CCDC reference number for **2**: 138851. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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