On the use of solid-state $^{45}$Sc NMR for structural investigations on molecular and silica-supported scandium amide catalysts.

T. Vancompernolle, a X. Trivelli, b L. Delevoye, a F. Pourpoint*, a and R. M. Gauvin*, a

a Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.
b Univ. Lille, CNRS, UMR 8576 (UGSF), Unité de Glycobiologie Structurale et Fonctionnelle, F-59000 Lille, France.

Supporting Information

Table of contents

General considerations.................................................................................................................. S2
Synthesis of Sc[NSiMe$_3$)$_2$]$_3$ (1).............................................................................................. S2
Synthesis of Sc[NSiMe$_3$)$_2$]$_3$(OPPh)$_3$ (2).............................................................................. S2
Grafting of (1) onto SiO$_2$-700 (1-SiO$_2$-700)............................................................................. S2
General procedure for grafting (1) or (2) onto SiO$_2$-700 to form (1-SiO$_2$-700) or (2-SiO$_2$-700)............................................................................................................................ S2
Alkyne dimerization procedure................................................................................................. S3
Figure S1. DRIFT of a) SiO$_2$-700, b) 1-SiO$_2$-700, and c) 2-SiO$_2$-700........................................ S4
Figure S2. GC trace from dimerization of 1-hexyne with 1........................................................................ S4
Table S1. Scandium-catalysed 1-hexyne dimerization........................................................................ S5
Figure S3. $^1$H NMR spectrum of 7-methyleneundec-5-yne............................................................ S5
Figure S4. $^1$H MAS NMR spectrum of a) 1-SiO$_2$-700, b) 2-SiO$_2$-700........................................ S6
Figure S5. $^{31}$P CPMAS NMR spectrum of a) 2, b) 2-SiO$_2$-700................................................ S6
Figure S6. $^{13}$C CPMAS NMR spectrum of 1-SiO$_2$-700................................................................. S7
Figure S7. $^{13}$C CPMAS NMR spectrum of 2-SiO$_2$-700............................................................... S7
Figure S8. $^{45}$Sc NMR spectrum of 2 recorded at 18.4T...................................................................... S8
Figure S9. $^{45}$Sc NMR spectrum of 2 recorded at 9.4T............................................................... S9
Figure S10. $^{45}$Sc NMR spectrum of 2 recorded at 9.4T under static conditions............................... S10
Figure S11. $^{45}$Sc NMR spectrum of 1 recorded at 9.4T under static conditions............................... S11
Figure S12. $^{45}$Sc NMR spectrum of 1 recorded at 9.4 T and 18.8 T under static conditions............. S12
References........................................................................................................................................ S12
General considerations

Experiments were carried out under an argon atmosphere in an M-Braun glovebox or by using Schlenk techniques. Solvents and reagents were dried by using conventional reagents and stored in the glovebox over 3A molecular sieves. Aerosil 380 silica (Degussa, specific area 380 m² g⁻¹), prior to heat treatment) was subjected to heating under secondary vacuum (10⁻⁶ mbar) for 15 h at 500 °C, followed by 4 h at 700 °C, and stored in a glovebox for limited time. Liquid-state NMR spectroscopic analyses were run at 7 T (300 MHz for ¹H, 161.19 MHz for ³¹P) using a Bruker AVANCE-II console equipped with a 4 mm probe spinning at 10 kHz or (ii) at 18.8 T (800 MHz) using a Bruker AVANCE-III console equipped with a 3.2 mm probe spinning at 20 kHz or used under static conditions. Chemical shifts for ¹H, ⁴⁵Sc, ³¹P are given with respect to adamantane, Sc(NO₃)₃, 3H₂O and H₃PO₄ respectively as external references. For the ³¹P CP MAS experiment, the spinning frequency was 10 kHz, the recycle delay was 5 s, and 11264 scans were collected with a pulse lasting 5 μs. ¹D ⁴⁵Sc static spectra were recorded using a Hahn echo experiment with a QCPMG detection (Quadrupolar Carr-Purcell Meiboom-Gill) using a train of refocusing pulses of echoes. The Hahn echo experiment used rf pulses lasting 0.80 μs and 1.60 μs for the 90° and the 180° pulses respectively and a rf amplitude of 45 kHz. The delay between the two pulses is 5 ms. A total of 22 echoes was recorded in the CPMG experiment. A 4 ms hyperbolic secant (HS) inversion pulse was used initially in order to enhance the polarization of ⁴⁵Sc central transition. The optimal HS enhancement was obtained with an rf field of 12 kHz and an offset frequency of 180 kHz. A SPINAL-64 (small phase incremental alternation with 64-steps) proton decoupling of 78 kHz was used during the acquisition. The recycle delay was 1 s, the number of scans was 1024 and the experiments lasted for 17 minutes for samples 1 and 2. The recycle delay was 0.5 s, the number of scans was 614400 and the experiments lasted for 3 days and 12 hours for samples 1-SiO₂₋₇₀₀ and 2-SiO₂₋₇₀₀. ¹D ⁴⁵Sc MAS spectrum of 2 was recorded using Hahn echo experiment with rf pulses lasting 1.4 μs and 2.80 μs for the 90° and the 180° pulses respectively and a rf amplitude of 45 kHz. The delay between the two pulses is rotor synchronized to 0.5 ms (one rotor period). The recycle delay was 1 s, the number of scans was 1024 and the experiment lasted for 17 minutes. The chemical shift parameters are defined according to the

Haeberlen notation: \[ \delta_{iso} = \frac{1}{3} (\delta_{XX} + \delta_{YY} + \delta_{ZZ}) \] and \[ \Delta_{CSA} = \delta_{ZZ} - \delta_{iso} \]. Where \( \delta_{iso} \) denotes the isotropic chemical shift; \( \delta_{XX} \), \( \delta_{YY} \), and \( \delta_{ZZ} \) are the principal components of the Chemical Shift Anisotropy (CSA) tensor ordered as \( |\delta_{YY} - \delta_{iso}| \leq |\delta_{XX} - \delta_{iso}| \leq |\delta_{ZZ} - \delta_{iso}| \); and \( \Delta_{CSA} \) is the anisotropic chemical shift. Simulation of the spectra were performed using TOPSPIN Bruker® software.

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 of 4 cm⁻¹). Elemental analyses were conducted at London Metropolitan University (CHN) and at LASIR, University of Lille (Ln). For alkyne dimerization, reaction mixtures were analysed using a Shimadzu GC2010 chromatograph fitted with a CP-Sil 5CB 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.

Synthesis of Sc[N(SiMe₃)₃]₃ (1)

In a Schlenk tube a solution of ScCl₃ (120 mg, 0.8 mmol) in THF (20 mL) was stirred for 2 days then LiHMDS (412 mg, 2.4 mmol) in solution in THF (10 mL) was slowly added. The mixture was stirred further for 3 days then the solvent is removed under vacuum for 3 h at 100°C. The solid extracted with pentane and the washing fractions were filtered over celite. Volatiles were evacuated. Sublimation
under high vacuum (10⁻⁵ bar) afforded white crystals in 54 % yield (210 mg). Analytical data are identical to literature values.

**Synthesis of Sc[N(SiMe₃)₂]₃(OPPh₃) (2)**

In glovebox, a Schlenk tube was filled with 1 (75 mg, 0.143 mmol) and freshly sublimed triphenylphosphine (44 mg, 0.157 mmol), dissolved in 5 mL of toluene. After 3 h of stirring at room temperature, the solution was filtered over Celite and washed 3 times with pentane. Crystallization from pentane afforded 2 as white solid (109 mg, 95% yield). ¹H NMR (300 MHz, C₆D₆): δ 7.7 (m, 6H, PPh₃), 7.0 (m, 9H, PPh₃), 0.52 (s, 54H, N(Si(CH₃)₃). ³¹P{¹H} NMR (121.5 MHz, C₆D₆) δ 39.8 (s, OPPh₃). δ(⁴⁵Sc) 360 ppm (C₆D₆, 300 K, FWHM: 4500 Hz).

**General procedure for grafting (1) or (2) onto SiO₂-700 to form (1-SiO₂-700) or (2-SiO₂-700)**

In a glovebox, a double-Schlenk vessel was loaded with the tri or tetra-coordinated scandium precursor (0.3 mmol) dissolved in 20 ml of pentane in one compartment and with SiO₂-700 (1 g) suspended in 20 mL of pentane in the other compartment. The colourless 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. The resulting material (1-SiO₂-700) or (2-SiO₂-700) was then dried under secondary vacuum (10⁻⁶ mbar) at 80°C for 5 h. Elemental analysis (w%): 1: Sc 1.04, C 3.35, H 0.77, N 0.69, 2: Sc: 0.67, C 6.29, H 0.50, N 0.58.

**Alkyne dimerization procedure**

In the glove box, a glass reactor is filled with the catalyst (0.05 mmol), 3 ml of toluene and terminal alkyne (5 mmol, 100 mol eq. per Sc). The reaction mixture is heated at 100 °C. After the desired time, the reaction is quenched by exposure to air. The supernatant is analysed by GC using n-decane (10 mg) as a standard (added after quenching).
Figure S1. DRIFT of a) SiO$_2$-700, b) 1-SiO$_2$-700, and c) 2-SiO$_2$-700

Figure S2. GC trace from dimerization of 1-hexyne with 1
Table S1. Scandium-catalysed 1-hexyne dimerization

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</table>

Conditions: Sc (0.05 mmol), 100 eq 1-hexyne, 3 ml toluene, 4h, 100°C

Figure S3. ¹H NMR spectrum (300 MHz) of 7-methyleneundec-5-yne (C₇D₈)

* Solvent residue
Figure S4. $^1$H MAS NMR spectra (400 MHz) of a) 1-SiO$_2$-700, b) 2-SiO$_2$-700

Figure S5. $^{31}$P NMR spectrum (161.9 MHz) of a) 2 (C$_6$D$_6$, 300 K), b) 2-SiO$_2$-700 (CPMAS)
Figure S6. $^{13}$C CPMAS NMR spectrum (100.6 MHz) of $^1$-SiO$_2$-700

Figure S7. $^{13}$C CPMAS NMR spectrum (100.6 MHz) of $^2$-SiO$_2$-700
Figure S8. $^{45}$Sc NMR spectrum of 2 recorded using a Hahn echo experiment at 18.8 T and a spinning speed of 20 kHz. The simulations (red dashed line spectrum) lead to the NMR parameters given in Table 1.
Figure S9. $^{45}$Sc NMR spectrum of 2 recorded using a QCPMG experiment at 9.4T and a spinning speed of 20 kHz. The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1.
Figure S10. $^{45}\text{Sc}$ NMR spectrum of 2 recorded using a QCPMG experiment at 9.4T under static conditions. The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1.
Figure S11.$^{45}$Sc NMR spectrum of 1 recorded using a QCPMG experiment at 9.4T under static conditions (a). The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1 (b).
Figure S12. $^{45}$Sc NMR spectrum of 1 recorded using a QCPMG experiment at 9.4 (a) and at 18.8 T (b) under static conditions. The simulations (red dashed line spectra) use the NMR parameters obtained by best-fit simulation of the spectrum at 18.8 T, considering no CSA contribution.

References:


