Supported cationic complexes: selective preparation and characterization of the well-defined electrophilic metallocenium cation [≡SiO–B(C₆F₅)₃]⁻[Cp*ZrMe₂(Et₂NPh)]⁺ supported on silica

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The reaction of Cp*ZrMe₃, **1**, with the heterogeneous activator [≡SiO–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺, **2**, has been investigated to generate, by an irreversible process of methane elimination, the well-defined cationic silica-supported metallocenium species [≡SiO–B(C₆F₅)₃]⁻[Cp*ZrMe₂(NEt₂Ph)]⁺, **3**, as an active olefin polymerisation catalyst.

Most of well-defined surface organometallic complexes are linked to oxide surfaces through covalent bonds.[1] In this case the surface plays the role of a strongly coordinated ligand to which the metal is linked through one, two or three σ or π bond(s) *via* the oxygen atom(s). We are exploring the possibility of getting "floating cations" in which the surface will be a non-coordinating anion. For this purpose, we have recently described the selective synthesis of the well-defined heterogeneous activator [≡SiO–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺, **2**.[2] We wish to report here that the reaction of **2** with Cp*ZrMe₃, **1**, irreversibly affords the fully characterized surface species [≡SiO–B(C₆F₅)₃]⁻[Cp*ZrMe₂(NEt₂Ph)]⁺, **3**, in which the surface is really a non-coordinating anion, Scheme 1.†

Typically, the preparation of **3** was achieved by stirring for 1 h at 25 °C a mixture of 1.50 g of **2** (0.31 mmol of surface anilinium) with 102 mg of **1** (0.38 mmol) in pentane, and led to the evolution of 0.36 mmol of methane as the only gaseous product detected. This corresponds to 1.1 ± 0.1 methane formed per initial available surface fragments [≡SiO–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺. The resulting pale yellow surface organometallic species **3**, obtained after washing the excess of **1** and drying under high vacuum at 25 °C, contains 1.77 wt% of Zr (0.64 Zr nm⁻²). This elemental analysis is in agreement with the grafting of one Zr per initial surface fragment [≡SiO–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺ available on **2**.[2] These numbers are further confirmed by the hydrolysis of **3** at 25 °C which produces 1.7 ± 0.2 equiv. of methane per Zr. No pentamethylcyclopentadiene is detected in the impregnation filtrates or in pentane extracts. Therefore, the surface complex **3** is a zirconium complex monografted to the modified silica surface **2** and surrounded by two methyl and one pentamethylcyclopentadienyl ligands.

Infrared studies confirm that Cp*ZrMe₃ reacts primarily with the surface anilinium cation as shown by the disappearance of the *v*(N–H) vibration at 3232 cm⁻¹ initially present in the spectrum of **2**,[2] Fig. 1b–c. Activation of neutral metallocenes *via* irreversible protonolysis reaction with ammonium cations has been reported for molecular analogues.[3,4b] Simultaneously, new bands characteristic of alkyl groups appear at 2983, 2957 and 2740 cm⁻¹. Moreover, IR spectra of surface complex **3_D**, obtained by reaction of Cp*Zr(CD₃)₃, **1_D**, with **2**, exhibit bands at 2199, 2133, 2091, 2038 cm⁻¹ ascribed to Zr–CD₃ fragments,
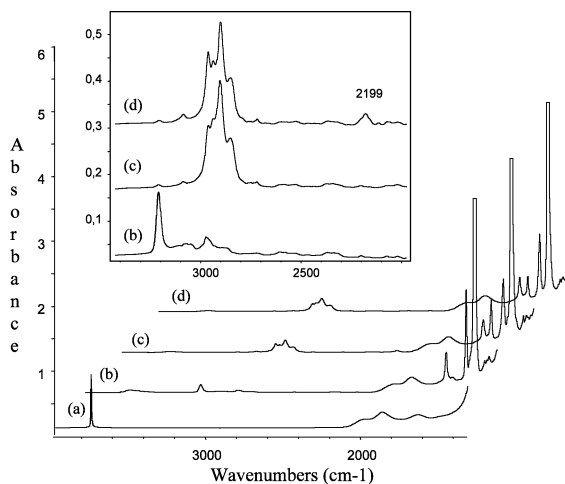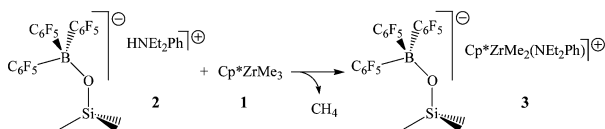
Fig. 1 IR spectra of (a) SiO₂₋₍₈₀₀₎; (b) [≡SiO₈₀₀–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺, **2**; (c) Cp*ZrMe₃/**2**, **3**; (d) Cp*Zr(CD₃)₃/**2**, **3_D**.

which unambiguously attests to the subsistence of surface Zr–Me groups on **3** after the grafting step,[5] Fig. 1d.

Solid state CP-MAS ¹³C NMR spectra of **3** give two signals at 9 and 42 ppm attributed to methyl groups bound to Cp* ligand and zirconium atom, respectively, Fig. 2a. The peak at 42 ppm whose intensity strongly increased for the ¹³C isotopically enriched species **3*** (99% labelled), Fig. 2b, is characteristic of a cationic Zr–¹³CH₃ moiety.[6a] This resonance is very close to those reported for the molecular analogues [Cp*ZrMe₂(arene)]⁺[MeB(C₆F₅)₃]⁻ ($\delta = 46$ ppm)[7] or [Cp*ZrMe₂]⁺[CB₁₁H₁₂]⁻ ($\delta = 47$ ppm),[8] and different from those observed for neutral [(≡SiO)ZrCp*Me₂] ($\delta = 39$ ppm)[9] and cationic [(≡SiO)
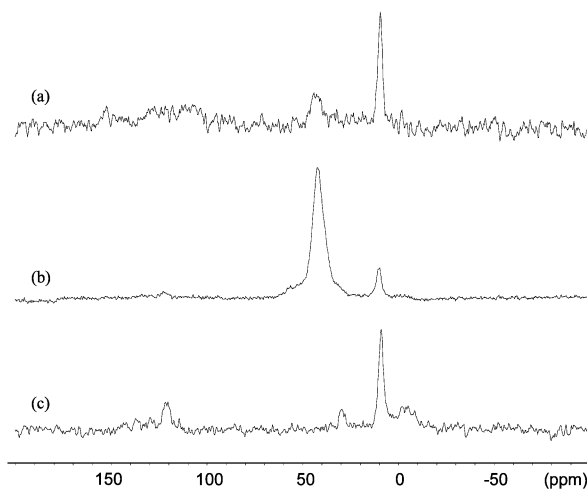
Fig. 2 CP-MAS ¹³C NMR spectra of (a) Cp*ZrMe₃/[≡SiO₈₀₀–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺, **3**; (b) Cp*Zr(¹³CH₃)₃/[≡SiO₈₀₀–B(C₆F₅)₃]⁻[HNEt₂Ph]⁺, **3***; (c) **3*** after hydrolysis.

Scheme 1

ZrCp*Me]+[MeB(C_6F_5)$_3$]− (δ = 55 ppm)[10] grafted complexes.[11] Additionally, the second peak (δ = 9 ppm) present in **3*** can be independently attributed to the Cp* ligand[7] or to the free [($^{13}CH_3$)B(C_6F_5)$_3$]− anion.[6,7,12] ^{1}H-^{13}C HETCOR solid state NMR experiments, Fig. 3, permit the unambiguous assignment of the latter peak to methyl groups of the Cp* ligand. The existence of surface Zr–$^{13}CH_3$ groups is also confirmed after hydrolysis of **3*** leading to the complete disappearance of the resonance at 42 ppm, Fig. 2c. Only peaks representative of the ring carbons (120 ppm) and methyl groups (9 ppm) of the Cp* ligand are still present on **3*** after hydrolysis. The fact that near two equivalents of methane per zirconium are liberated after hydrolysis, combined to the ^{13}C NMR spectra recorded for **3*** after hydrolysis, also supports the presence of a surface [Cp*ZrMe$_2$]+ fragment. Solid state ^{11}B NMR spectra of **3**, Fig. 4, display a strong and sharp resonance at −8 ppm indicating that the surface anion [≡SiO–B(C_6F_5)$_3$]− is still present after reaction of **1** with **2**.[13]

Preliminary catalytic tests indicate that **3** is still active in ethylene polymerisation catalysis at 80 °C (69.4 kg PE per mol Zr h bar). The absence of any additional co-catalyst and the subsistence of the amine on the support (as evidenced by elemental analysis, IR and ^{1}H NMR spectroscopies) should be taken into account when comparing this moderate value with the activities of other conventional heterogeneous catalysts.[14] The fact that the amine remains in the coordination sphere of
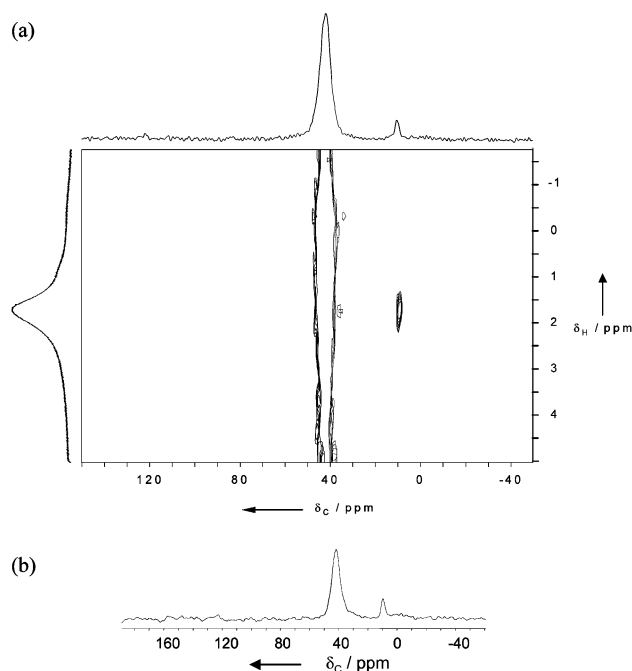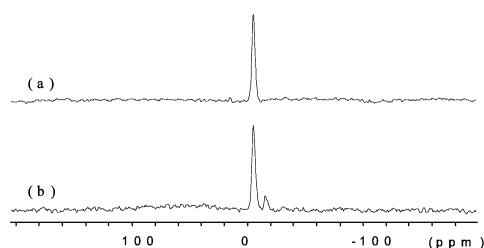
zirconium is not excluded and could be due to an insufficient steric hindrance of the methyl groups. Current research is directed towards elucidating coordinating interactions between the amine and the metal center and extending these studies to more encumbered alkyl precursors.

Notes and references

†   Cp*ZrMe$_3$,[15] **1**, and [≡SiO–B(C_6F_5)$_3$]−[HNEt$_2$Ph]+,[2] **2**, were prepared according to literature procedures.
    3 : In a Schlenk tube, a solution of 102 mg (0.38 mmol, 1.2 equiv.) of **1** in 15 mL of dry pentane was filtered on 1.5 g of **2**. The color of the solid turned to light yellow and the suspension was stirred at ambient temperature for 1 hour. The impregnation solution was then vacuum transferred at 73 K into a large glass flask of known volume (for quantification of the volatile and gaseous products). The pale yellow solid **3** was washed four times with dry pentane (20 mL), dried under high vacuum (10^{-5} Torr) for 1 hour at room temperature, and stored at −20°C under argon. A similar procedure was used on modified silica pellets (30 mg) of **2** for IR experiments. IR (silica pellet): 2983, 2957, 2924, 2873, 1645, 1592, 1517, 1462, 1384, 1366, 1337 cm^{-1}; solid state NMR (298 K): δ_H (300.18 MHz) 6.4 (br, C_6H_5), 1.5 (s, CH$_3$–Cp*), −0.25 (s, Zr–CH$_3$); δ_C (75.47 MHz) 44 (br, Zr–CH$_3$), 9 (s, CH$_3$–Cp*), carbon on ring Cp* not resolved; δ_B (96.31 MHz; referenced to BF$_3$·OEt$_2$ at 0 ppm) −8.4 (s, [≡SiO–B(C_6F_5)$_3$]−).

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Fig. 3 (a) 2D map ^{1}H-^{13}C HETCOR solid state NMR spectrum of **3** (contact time: 1 ms; 2048 scans; repetition delay: 1 s.); (b) trace at 1.8 ppm.

Fig. 4 Solid state ^{11}B NMR spectra of (a) [≡SiO$_{800}$–B(C_6F_5)$_3$]−[HNEt$_2$Ph]+, **2** (1700 scans); (b) Cp*Zr(CH$_3$)$_3$/**2**,**3** (2800 scans).