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Docking of Tetra-methyl Zirconium to the Surface of Silica: A Well-Defined Pre-Catalyst for Conversion of CO₂ to Cyclic CarbonatesReceived 00th January 20xx,
Accepted 00th January 20xxWalid AL Maksoud,^{ab} Aya Saidi,^{ab} Manoj K. Samantaray,^{*a} Edy Abou-Hamad,^c Albert Poater,^e
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The metal complex (Zr(CH₃)₄(THF)₂) has been fully synthesized, characterized and grafted onto partially dehydroxylated silica to give two surface species [(≡Si–O–)Zr(CH₃)₃(THF)₂] (minor) and [(≡Si–O–)₂Zr(CH₃)₂(THF)₂] (major) which have been characterized by SS NMR, IR, elemental analysis. These supported pre-catalysts exhibit the best conversion of CO₂ to cyclic carbonates, as compared to the previously reported SOMC catalysts.

Transition metal alkyls are catalysts for numerous reactions,^{1–3} but because the metal-alkyl σ-bonds are weak⁴ the likelihood of decomposition of these compounds by facile β-hydride elimination is high.⁴ To hinder such a decomposition, we anchored several homoleptic metal-methyl complexes to various metal oxides, showing that these supported catalysts are effective for improved alkane metathesis.^{5–9} An advantage of the anchored complexes is that some can be readily transformed into reactive organometallic fragments that are active for various organic transformations. For example, silica-supported [(≡Si–O–)W(CH₃)₅] when heated is converted to a carbyne species which is useful for cyclo-trimerization of alkynes in addition to being active for alkyne and cycloalkane metathesis.⁵ Further, treatment of [(≡Si–O–)W(CH₃)₅] with hydrogen at various temperatures leads to a carbene hydride that is also an efficient catalyst for alkane metathesis.¹⁰ Homoleptic supported Ta-methyl complexes [(≡Si–O–)Ta(CH₃)₄] are also active for this reaction.⁶

We recently observed that supported catalysts made from ZrCl₄ on silica are active for the conversion of CO₂ to carbonates.¹¹ We envisioned a step beyond these with zirconium-methyl species on

silica that would be more active than the former for the conversion of CO₂ to cyclic carbonates. As it is widely known, industrial emission levels of carbon dioxide are increasing exponentially which is dramatically affecting both human health and environment (e.g. air pollution, climate change, ecosystem damage). Thus, more research and efficient strategies should be emerged and implemented to reduce these emissions. One well-established approach is to convert CO₂ and epoxides in the presence of a catalyst/pre-catalyst and a nucleophile (i.e. TBAB) into value-added cyclic carbonates; these products could be used as building blocks in various chemical synthesis reactions in industries as well as organic green solvents.^{12, 13} In particular, propylene carbonate, formed from the corresponding propylene oxide, is used as an intermediate for many applications such as in the methanol production, fuel additives, electrolyte batteries, CO₂ storage. etc.^{14, 15}

Herein, for the first time, we disclose synthesis and well-characterization of homogeneous (THF)₂Zr(CH₃)₄ complex and its silica-supported counterpart along with catalytic properties in the conversion of CO₂ to cyclic carbonates.

The synthesis of the supported pre-catalyst required the first preparation of pure (THF)₂Zr(Me)₄ (Me = Methyl; THF = tetrahydrofuran). Zr(Me)₄ was first reported in 1966 by Berthold and Groh,¹⁶ who investigated its decomposition and claimed to have synthesized an ethereal bound Zr(CH₃)₄, although supporting NMR data were lacking.¹⁶ In 1989, Morse et al. reported the alkylation of MCl₄(dippe) (M = Zr or Hf) by MgMe₂ to form M(Me)₄(dippe).¹⁷ In 2012 Nishida et al.¹⁸ prepared an ethereal solution of Zr(CH₃)₄ *in-situ* and used it for the ketone to alcohol reduction.

Zr(CH₃)₄ was synthesized by the reaction of ZrCl₄ and MeLi in THF. In a typical reaction, a mixture of 120 mg of ZrCl₄ with 25 mL of THF in one arm of a double Schlenk line was cooled to –80 °C, and an excess (70 mg) of ¹³C-enriched *MeLi, with 5 mL of THF was added to the other arm and maintained at 0 °C. Then the THF solution of ZrCl₄ was allowed to gently mix with the *MeLi solution for 5 min at –80 °C.

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Scheme 1: Synthesis of (THF)₂Zr(CH₃)₄, **1**

During the reaction, the color of the mixture changed from transparent to red-brown. Thereafter, the temperature of the reaction was held between -10 and 0 °C for 3h. After the completion of the reaction, the mixture was filtered and dried at -10 °C under vacuum. An aliquot of oil was taken and characterized by ^{13}C and ^1H NMR spectroscopy, demonstrating the chemistry shown in Scheme 1 for the synthesis of (THF)₂Zr(CH₃)₄ (**1**).

Figure 1: NMR characterization of **1** was carried out using THF- d^8 as a solvent. (A) represents ^1H NMR; (B) ^{13}C NMR; (C) HSQC; and (D) ^{35}Cl NMR spectra of the resultant $\text{Zr}(\text{CH}_3)_4(\text{THF})_2$

Liquid-state NMR spectra (^1H , ^{13}C , HSQC) of the sample were recorded with THF- d^8 as the solvent (Figure 1). In the ^1H NMR spectrum, two peaks were observed, at 0.26 and 0.07 ppm, consistent with our having used 100% enriched $^*\text{MeLi}$ (carbon-proton coupling results in the splitting of the ^1H signal). Peaks observed at 3.6 and 1.8 ppm are assigned to THF coordinated to Zr, the single resonance in the ^{13}C NMR spectrum at 41 ppm is assigned to $\text{Zr}-\text{CH}_3$ and those at 25.9 and 67.9 ppm to Zr-bonded THF. These latter assignments were confirmed by the results of HSQC experiments. Further, we did ^{35}Cl NMR spectroscopy, finding results that confirm that no $\text{Zr}-\text{Cl}$ bonds remained in our sample after the synthesis (these are typically observed at approximately 300 ppm;¹⁹ the resonance at -44.6 ppm arose from the excess soluble LiCl in the sample). These data, taken together, confirm the clean synthesis of (THF)₂Zr(CH₃)₄.

During the synthesis, it became evident that **1** is not stable at room temperature; thus, it was challenging to use as a pre-catalyst for

further experimentation. Consequently, realizing that mounting on oxide supports stabilizes metal methyl complexes^{5, 6}, we were motivated to use **1** as a precursor of a grafted complex to test it for catalysis. We chose silica from Degussa[®] and treated it at 700 °C under vacuum prior to use and applied grafting methods like those reported for WMe_6 ⁵ and TaMe_5 ⁶ on silica that had been previously dehydroxylated at 700 °C (SiO_{2-700}).

The results summarized below show that we obtained supported species $[(\equiv\text{Si}-\text{O})\text{Zr}(\text{CH}_3)_3(\text{THF})_2]$ and $[(\equiv\text{Si}-\text{O})_2\text{Zr}(\text{CH}_3)_2(\text{THF})_2]$. We characterized them by microanalysis, solid-state NMR, and IR. These supported species were found to be catalyst precursors for the conversion of CO_2 to cyclic carbonate.

The grafting of **1** was carried out by stirring it with SiO_{2-700} , with the number of molecules of **1** being in excess with respect to the number of reactive silanols on the support (ca. 0.3 mmol of $-\text{OH}$ groups/g)²⁰; the anchoring reaction took place at -10 °C for 3h as the sample was blanketed with argon. After several washing cycles with THF and drying under vacuum (10^{-5} mbar), the anchored complex **2** was obtained as a light brown powder composed of a mixture of $[(\equiv\text{Si}-\text{O})\text{Zr}(\text{CH}_3)_3(\text{THF})_2]$ and $[(\equiv\text{Si}-\text{O})_2\text{Zr}(\text{CH}_3)_2(\text{THF})_2]$ (Scheme 2).

Scheme 2: Grafting of (THF)₂Zr(CH₃)₄ onto silica dehydroxylated at 700 °C

An IR spectrum of **2** shows that the anchoring of **1** led to a decrease in intensity of the 3742 cm^{-1} band characterizing isolated silanols on the silica, indicating that these groups reacted with **1**. Concomitantly, new bands were observed in the range of 2900 – 2850 cm^{-1} and at 1450 cm^{-1} , which are assigned, respectively, to $\nu(\text{C}-\text{H})$ and $\delta(\text{C}-\text{H})$ vibrations of methyl groups and THF ligands bonded to Zr (ESI Figure S1).

Analysis of the gas-phase products formed during the hydrolysis of **2** at 150 °C showed that the reaction produced 2.6 equivalents of methane, suggesting that a mixture of a monopodal (theory: 3) and bipodal (theory: 2) zirconium methyl species had been formed on the silica surface.

^1H magic-angle spinning (MAS) solid-state NMR spectrum of **2** includes two broad signals, at 3.5 and 1.4 ppm, which were found to be auto-correlated in a double quantum (DQ) and Triple quantum (TQ) experiments at 20 kHz MAS, as shown in Figures 2A, 2B and 2C respectively. The ^{13}C CP/MAS NMR spectrum includes four resonances, at 67, 58, 23 ppm, and -5 ppm (Figure 2D). Those at 67, 58, and 23 ppm were correlated with proton resonances at 3.5, 1.5, and 1.4 ppm, as indicated in the 2D ^1H – ^{13}C HETCOR NMR spectrum

recorded with a contact time of 0.2 ms (Figure 2E). By comparing these chemical shifts with those observed in the solution NMR spectrum of **1**, we inferred that the resonances at 67 and 23 ppm correspond to the THF coordinated to Zr, and that at 58 ppm corresponds to methyl bound to Zr. The Zr-CH₃ peak in the grafted species is shifted slightly downfield relative to its homogeneous counterpart; this shift is understandable as at least one of the CH₃ groups on the precursor was replaced by a support surface O atom. Apart from the signals corresponding to Zr-CH₃ and Zr-THF in the spectra of the supported species, we also observed a signal at -5 ppm, which is well known to be evidence for a ≡Si-Me. The formation of such a surface species is known to result from a transfer of Me from Zr-Me to an adjacent Si-O-Si, leading to the formation of a bipodal species, as indicated by the above-mentioned gas analysis data.

Figure 2: (A) One-dimensional (1D) ¹H MAS solid-state NMR spectrum of **2** acquired at 600 MHz (14.1 T) with a 22 kHz MAS frequency, a repetition delay of 5 s, and 8 scans. (B) Two-dimensional (2D) ¹H-¹H double-quantum (DQ)/single-quantum (SQ) and spectra of **2** (acquired with 32 scans per *t*₁ increment, 5 s repetition delay, 32 individual *t*₁ increments). (C) Two-dimensional (2D) ¹H-¹H Triple quantum (TQ)/single-quantum (SQ) and spectra of **2** (acquired with 32 scans per *t*₁ increment, 5 s repetition delay, 32 individual *t*₁ increments). (D) ¹³C CP/MAS NMR spectrum of **2** (acquired at 9.4 T with a 10 kHz MAS frequency, 5000 scans, a 4 s repetition delay, and a 2 ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation. (E) 2D ¹H-¹³C CP/MAS dipolar HETCOR spectrum of **2** (acquired at 9.4 T with a 10 kHz MAS frequency, 4000 scans per *t*₁ increment, a 4 s repetition delay, 64 individual *t*₁ increments and a 0.2 ms contact time). For all spectra depicted here, -CH₃ was 55% ¹³C labeled.

Additionally, to understand the peak at 58, whether it corresponds to Zr-CH₃ or not we introduced O₂/air in our sample for a short time (About 20 minutes). As expected the peak at 58 slightly shifted to 59 and a new peak evolves at 50 ppm due to insertion of O₂ in Zr-CH₃ to form Zr-O-CH₃, which again proved that, indeed the peak at 58 ppm is due to Zr-CH₃ (ESI Figure S2). Further, DFT calculations^{21, 22} were conducted to clarify the silica supported complex **2**. At first, the simplicity of the homogeneous complex **1** (calculated NMR value

0.09 ppm) confirmed a near agreement with the experimental ¹H NMR peaks at 0.18 ppm. Secondly, DFT calculations on silica models monopodal (models 1 and 2, see ESI) and bipodal (model 3) were carried out to check if there is a NMR chemical shift due to the methyls bonded to the metal center. However, the shift is equivalent to only 0.5-1 ppm in average for the monopodal as well as bi-podal models which is in close agreement with the experimental data (1.5 ppm for Zr-CH₃) (see Figure 2 and Table S1 ESI). Thus the experimental peaks at 3.5 and 1.4 ppm are assigned to be THF bound to Zr center. Additionally, calculations were carried out to understand the peak at -5 ppm which is formed due to the methyl migration from Zr-CH₃ to nearby silicon atom. Our calculation showed that it comes around -2 ppm which is also closely agreement with the experimental data (-5 ppm).

Furthermore, to demonstrate the structure of **2**, elemental analysis was carried out, showing that **2** contains 3.9 wt. % Zr and 5.23 wt. % C, corresponding to a C/Zr ratio of 10.2 (± 0.2) and consistent with the formation of a mixture of mono- (theoretical: 11) and bi-podal (theoretical: 10) complexes of zirconium on the surface.

Species **2** was tested for catalysis of CO₂ conversion. Realizing that supported catalysts formed from ZrCl₄ are active for the conversion of CO₂ to cyclic carbonates, we anticipated that **2** might be more active than those.

Scheme 3: Conversion of CO₂ to cyclic carbonates obtained with **2** as a catalyst precursor

In a typical reaction, pre-catalyst **2** (10 mg, 3.3 × 10⁻³ mmol), CO₂ and propylene oxide (PO) (reactants), and TBAB (nucleophile) were introduced into a high-pressure batch reactor (Scheme 3). Three different initial volumes of propylene oxide were employed at NTP; 1 mL (14.34 mmol), 2 mL (28.68 mmol) and 3 mL (43.03 mmol), to these mixtures, 47 mg (0.14 mmol), 94 mg (0.28 mmol) and 141 mg (0.42 mmol) of TBAB were added respectively. Then, 100 psi of CO₂ were introduced in each mixture. The vessel was heated to 60 °C and held for 16 h. Then the mixture was cooled to room temperature, mixed with dichloromethane, and filtered, and the product composition was quantified by gas chromatography. The catalytic performance of **2** was compared with that of the known supported pre-catalyst [(≡Si-O-)ZrCl₃(THF)₂] (Table 1).

Table 1: TON and conversion for the reaction of CO₂ with propylene oxide to give cyclic propylene carbonate in the presence of a pre-catalyst mixture consisting of [(≡Si-O-)Zr(CH₃)₃THF₂] and [(≡Si-O-)Zr(CH₃)₂(THF)₂] or [(≡Si-O-)ZrCl₃(OEt)₂]¹¹ and TBAB at 60 °C for 16h

Catalyst precursor	Propylene oxide to pre-catalyst (mono and bipodal) molar ratio	Conversion of propylene oxide (%)	TON
Complex 2	4361	64	2791

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Complex 2	8722	48.5	4227
Complex 2	13084	28.7	3756
$[(\text{Si}-\text{O}-\text{Zr})(\text{Cl}_3(\text{OEt}_2)_2)]$	4361	37.6	1640
None, but TBAB was present	---	30.4	---

A turnover number (TON) of 4227 with a conversion of 48.5 % to cyclic carbonates were obtained when the ratio of propylene oxide to catalyst is 8722. Thus, **2** is an efficient pre-catalyst by comparison with $[(\text{Si}-\text{O}-\text{Zr})(\text{Cl}_3(\text{THF})_2)]$ (Table 1).

These results provide a basis for a preliminary suggestion of a catalytic cycle (ESI Scheme S1), although we recognize the further work is needed to assess this suggestion.

The suggested cycle comprises coordination of propylene oxide with the Lewis acidic Zr center followed by a nucleophilic attack on the propylene oxide ring followed by CO_2 insertion and then ring closure.

In summary, a THF adduct of a tetramethyl Zr species $[\text{Zr}(\text{CH}_3)_4(\text{THF})_2]$ was synthesized and characterized by ^1H , ^{13}C , HSQC, and ^{35}Cl NMR spectroscopies. This highly unstable species was grafted at low temperature onto partially dehydroxylated silica to give a mixture of $[(\text{Si}-\text{O}-\text{Zr})(\text{CH}_3)_3(\text{THF})_2]$ and $[(\text{Si}-\text{O}-\text{Zr})_2(\text{CH}_3)_2(\text{THF})_2]$, and characterized by solid-state NMR, IR, and complemented by elemental analysis and gas quantification methods besides DFT calculations. The mixture of mono- and bi-podal species on the silica surface served as a precursor to catalyze the conversion of CO_2 to carbonates, outperforming the previously reported $[(\text{Si}-\text{O}-\text{Zr})(\text{Cl}_3(\text{THF})_2)]$.

Conflicts of interest

There are no conflicts to declare.

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