

# Reactions of zirconium amide amidinates with dioxygen. Observation of an unusual peroxy intermediate in the formation of oxo compounds

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## Supplementary information

### Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere with the use of either a glovebox or standard Schlenk techniques. All glassware was flamed dried under vacuum. Solvents were purified by distillation from potassium benzophenone. NMR solvents were dried and stored over 5 Å molecular sieves. O<sub>2</sub> (Airgas) was purified by passing it through a P<sub>2</sub>O<sub>5</sub> column. Deionized H<sub>2</sub>O was degassed and stored in a Schlenk flask. High purity H<sub>2</sub>O<sub>2</sub> was prepared from 30% aqueous H<sub>2</sub>O<sub>2</sub> solution (Fischer Scientific, reagent grade) and its purification is discussed below. Na<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> were bought from Fischer Scientific and used without further purification. N,N'-Diisopropylcarbodiimide, LiNMe<sub>2</sub> and MeLi (1.6 M in Et<sub>2</sub>O) were purchased from Acros and used without further purification. ZrCl<sub>4</sub> (Strem) was sublimed

at 170 °C before use. Li[MeC(N<sup>i</sup>Pr)<sub>2</sub>] was prepared by the reaction of N,N'-diisopropylcarbodiimide with MeLi by an approach similar to that of Hessen et al.<sup>S1</sup> Zr(NMe<sub>2</sub>)<sub>4</sub> and Zr(NEt<sub>2</sub>)<sub>4</sub> were prepared according to literature.<sup>S2</sup> <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on an AMX-400 FT or Varian VNMRS-500 spectrometer. Solid-state NMR spectrum was recorded on a Solid-State Varian INOVA 400 MHz spectrometer equipped with a Chemagnetics 5 mm CPMAS probe and referenced to adamantane. Elemental analyses were conducted by Complete Analysis Laboratories, Inc., Parsippany, NJ.

Mass spectra were recorded on a JEOL AccuTOF™ DART Mass Spectrometer (<http://www.jeolusa.com/PRODUCTS/AnalyticalInstruments/MassSpectrometers/AccuTOF%E2%84%A2DART%C2%AE/AccuTOF%E2%84%A2DART%E2%84%A2Technology/tabid/449/Default.aspx> accessed on May 23, 2014) using He as the carrier gas. The analyte reacted with the protonated water, produced from reacting water with the excited-state helium metastable, to form a protonated molecule before being analyzed by the mass spectrometer. To record IR spectra, solid samples were grounded with KBr, which had been dried at 100 °C and under vacuum, and then pressed into pellets. IR spectra were recorded on a Varian 4100 Excalibur. Thermal gravimetric analysis was recorded on a Q-50 TGA.

*Caution: Extreme care should be taken in using hydrogen peroxide in the reactions. A shield should be used for protection.*

### **Synthesis of <sup>i</sup>PrN(H)C(Me)=N<sup>i</sup>Pr**

<sup>i</sup>PrN(H)C(Me)=N<sup>i</sup>Pr has been prepared by two different groups; Oshima and

Miller. They have reported  $^1\text{H}$  NMR spectra of  $^i\text{PrN}(\text{H})\text{C}(\text{Me})=\text{N}^i\text{Pr}$  in  $\text{CDCl}_3$ <sup>S3a</sup> and  $\text{CD}_3\text{CN}$ <sup>S3b</sup>, respectively. We are reporting its  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra at 208 K in toluene- $d_8$  and in benzene- $d_6$  at 23 °C.

$\text{Li}[\text{MeC}(\text{N}^i\text{Pr})_2]$  (5.893 g, 39.77 mmol) was dissolved in THF (50 mL) and  $\text{H}_2\text{O}$  (0.80 mL, 0.80 g, 44.42 mmol) was added via syringe. The solution was allowed to stir for 20 min and  $\text{Et}_2\text{O}$  (100 mL) was added.  $\text{Na}_2\text{SO}_4$ , a drying agent, was added to the solution and stirred for 12 h, followed by filtration.  $\text{Et}_2\text{O}$  in the filtrate was removed at 23 °C. The liquid product  $^i\text{PrN}(\text{H})\text{C}(\text{Me})=\text{N}^i\text{Pr}$  was distilled from the liquid residue at 115 °C and ~0.1 Torr. We have found that at room temperature the  $^1\text{H}$  NMR spectrum in benzene- $d_6$  and toluene- $d_8$  showed a dynamic exchange as the peaks were broad. A variable temperature NMR experiment was performed and  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were collected from 203 K to 298 K in 5 K intervals. We had hoped to obtain its rate of exchange and calculate its activation parameters. However, due to peak overlap in the  $^1\text{H}$  NMR these efforts were not successful.

$^1\text{H}$  NMR (benzene- $d_6$ , 400.17 MHz, 23 °C):  $\delta$  3.85 (br, 2H,  $\text{CHMe}_2$ ), 3.01 (br, 1H,  $\text{NH}$ ), 1.36 (s, 3H,  $\text{NC}(\text{Me})\text{N}$ ), 1.13 (d, 12H,  $\text{CHMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 100.62 MHz, 23 °C):  $\delta$  151.58 ( $\text{NC}(\text{Me})\text{N}$ ), 45.29 (br,  $\text{CHMe}_2$ ), 24.22 ( $\text{CHMe}_2$ ), 15.71 ( $\text{NC}(\text{Me})\text{N}$ ).  $^1\text{H}$  NMR (toluene- $d_8$ , 400.17 MHz, 23 °C):  $\delta$  3.74 (br, 1H,  $\text{NH}$ ), 3.33 (br, 2H,  $\text{CHMe}_2$ ), 1.43 (s, 3H,  $\text{NC}(\text{Me})\text{N}$ ), 1.04 (d, 12H,  $\text{CHMe}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 100.62 MHz, 23 °C):  $\delta$  151.55 ( $\text{NC}(\text{Me})\text{N}$ ), 45.18 (br,  $\text{CHMe}_2$ ), 24.18 ( $\text{CHMe}_2$ ), 15.47 ( $\text{NC}(\text{Me})\text{N}$ ).  $^1\text{H}$  NMR (toluene- $d_8$ , 400.17 MHz, -65 °C):  $\delta$  4.71 (br, 1H,  $\text{NH}$ ), 4.28 (m, 1H,  $\text{CHMe}_2$ ), 3.47 (m, 1H,  $\text{CHMe}_2$ ), 1.60 (s, 3H,  $\text{NC}(\text{Me})\text{N}$ ), 1.22 (d, 6H,  $\text{CHMe}_2$ ), 1.11

(d, 6H, CHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 100.62 MHz, -65 °C): δ 152.11 (NC(Me)N), 49.04 (CHMe<sub>2</sub>), 41.10 (CHMe<sub>2</sub>), 25.58 (CHMe<sub>2</sub>), 22.54 (CHMe<sub>2</sub>), 15.79 (NC(Me)N). DART-MS: Calculated *m/z* = 143.15482 [M+H<sup>+</sup>], Found *m/z* = 143.15488 [M+H<sup>+</sup>]; 0.419 ppm difference.

### Synthesis of Zr(NMe<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (1)

Zr(NMe<sub>2</sub>)<sub>4</sub> (1.601 g, 5.984 mmol) was dissolved in pentane (50 mL) and cooled to -30 °C. <sup>*i*</sup>PrN(H)C(Me)=N<sup>*i*</sup>Pr (1.758 g, 12.36 mmol) was dissolved in pentane (50 mL) and added dropwise to the solution of Zr(NMe<sub>2</sub>)<sub>4</sub> (Scheme 2). The solution was stirred for 12 h and volatiles were removed in vacuo affording a yellow solid (2.7640 g, 5.985 mmol, 95.6% yield). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 399.17 MHz, 23 °C): δ 3.45 (m, 4H, CHMe<sub>2</sub>), 3.23 (s, 12H, NMe<sub>2</sub>), 1.58 (s, 6H, NC(Me)N), 1.18 (d, 24H, CHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 100.63 MHz, 23 °C): δ 175.07 (NC(Me)N), 48.34 (CHMe<sub>2</sub>), 46.10 (NMe<sub>2</sub>), 25.61 (CHMe<sub>2</sub>), 11.31 (NC(Me)N). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR assignments were confirmed by DEPT, HMBC and HSQC experiments. Anal. Calcd: C, 52.01; H, 10.04. Found: C, 51.86; H, 9.98.

### Synthesis of Zr(NEt<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (7)

Zr(NEt<sub>2</sub>)<sub>4</sub> (2.344 g, 6.171 mmol) was dissolved in pentane (50 mL) and cooled to -30 °C. <sup>*i*</sup>PrN(H)C(Me)=N<sup>*i*</sup>Pr (1.761 g, 12.38 mmol) was dissolved in pentane (50 mL) and added dropwise to the pentane solution of Zr(NEt<sub>2</sub>)<sub>4</sub> (Scheme 2). The solution was stirred for 12 h and volatiles removed in vacuo affording a yellow solid (2.954 g, 5.702 mmol, 92.4% yield). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400.17 MHz, 23 °C): δ 3.71 (br, 8H,

$\text{N}(\text{CH}_2\text{CH}_3)_2$ , 3.46 (br, 4H,  $\text{CHMe}_2$ ), 1.59 (s, 6H,  $\text{NC}(\text{Me})\text{N}$ ), 1.20 (br, 24H,  $\text{CHMe}_2$ ), 1.10 (t, 12H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 100.62 MHz, 23 °C):  $\delta$  173.35 ( $\text{NC}(\text{Me})\text{N}$ ), 48.04 ( $\text{CHMe}_2$ ), 41.67 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 25.62 ( $\text{CHMe}_2$ ), 13.69 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 11.90 ( $\text{NC}(\text{Me})\text{N}$ ).  $^1\text{H}$  NMR (toluene- $d_8$ , 400.08 MHz, 23 °C):  $\delta$  3.68 (br, 8H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 3.46 (br, 4H,  $\text{CHMe}_2$ ), 1.61 (s, 6H,  $\text{NC}(\text{Me})\text{N}$ ), 1.26 (br, 24H,  $\text{CHMe}_2$ ), 1.09 (t, 12H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 100.60 MHz, 23 °C):  $\delta$  172.64 ( $\text{NC}(\text{Me})\text{N}$ ), 48.27 (br,  $\text{CHMe}_2$ ), 41.65 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 25.67 (br,  $\text{CHMe}_2$ ), 13.68 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 11.81 ( $\text{NC}(\text{Me})\text{N}$ ).  $^1\text{H}$  NMR (toluene- $d_8$ , 400.08 MHz, -60 °C):  $\delta$  3.95 (m, 4H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 3.62 (m, 4H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 3.47 (m, 2H,  $\text{CHMe}_2$ ), 3.32 (m, 2H,  $\text{CHMe}_2$ ), 1.53 (s, 6H,  $\text{NC}(\text{Me})\text{N}$ ), 1.42 (d, 6H,  $\text{CHMe}_2$ ), 1.36 (d, 6H,  $\text{CHMe}_2$ ), 1.14 (d, 6H,  $\text{CHMe}_2$ ), 1.13 (d, 6H,  $\text{CHMe}_2$ ), 1.13 (t, 12H,  $\text{N}(\text{CH}_2\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 100.60 MHz, -60 °C):  $\delta$  173.14 ( $\text{NC}(\text{Me})\text{N}$ ), 48.15 ( $\text{CHMe}_2$ ), 47.55 ( $\text{CHMe}_2$ ), 41.11 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 25.93 ( $\text{CHMe}_2$ ), 25.91 ( $\text{CHMe}_2$ ), 25.53 ( $\text{CHMe}_2$ ), 23.52 ( $\text{CHMe}_2$ ), 13.30 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ), 11.27 ( $\text{NC}(\text{Me})\text{N}$ ).  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR assignments were confirmed by HMBC and HSQC experiments. Anal. Calcd: C, 55.65; H, 10.51; N, 16.23. Found: C, 55.49; H, 10.40; N, 16.17.

### X-ray Crystallographic Studies of $\{(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)\text{Zr}[\text{MeC}(\text{N}^i\text{Pr})_2]_2\}_3$ (**2**)

The X-ray crystal structure of **2** was determined on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo source ( $K\alpha$  radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low temperature device. A suitable crystal was coated with paratone oil (Exxon) and mounted on a fiber loop under a stream of nitrogen at 100(2) K. The structure was solved by direct

methods. All non-hydrogen atoms were anisotropically refined. Empirical absorption correction was performed with SADABS.<sup>S4a</sup> Global refinements for the unit cells and data reductions were performed under the Saint program (Version 6.02). All calculations were performed using SHELXTL (Version 5.1) proprietary software package.<sup>S4b</sup>

### **Reaction of Zr(NMe<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (**1**) with O<sub>2</sub>**

*NMR-scale Reactions.* In a Young's tube, **1** (28.9 mg, 0.0626 mmol) was dissolved in benzene-*d*<sub>6</sub>. The headspace volume in the Young's tube was 2.6 mL. The solution was frozen in liquid nitrogen and nitrogen gas was removed in vacuo. O<sub>2</sub> (0.5 atm, 0.0626 mmol) was then added. Several <sup>1</sup>H NMR spectra were taken and after 3 weeks, the disappearance of **1** and the appearance of soluble species **3**, HNMe<sub>2</sub>, CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>, and an insoluble solid **4** had occurred.

In a separate test, O<sub>2</sub> (1 atm, 0.0396 mmol) was added to **1** (18.3 mg, 0.0396 mmol) in benzene-*d*<sub>6</sub>. Volume of the headspace in the Young's tube was 2.1 mL. The Young's tube was heated at 70 °C. After about ca. 12 days, the reaction was quenched in ice water and the <sup>1</sup>H NMR spectrum showed the disappearance of **1** and appearance of new peaks which corresponds to an oxo-bridged dimer **3**. <sup>1</sup>H NMR also revealed two byproducts: HNMe<sub>2</sub> (0.125 mg, 6.99% yield based on NMR) and CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> (1.09 mg, 26.9% yield based on NMR). The byproducts, HNMe<sub>2</sub> and CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> were confirmed with GC-MS. A light yellow precipitate formed which was identified to be the polymeric product **4** (9 mg, 58.4% yield).

*Reaction Conducted in a Schlenk Flask.* In another experiment, O<sub>2</sub> (1 atm, 2.014 mmol) was added to **1** (0.465 g, 1.007 mmol) in toluene in a Schlenk flask. The

headspace of the flask was 20.0 mL. The solution was heated at 80 °C for ca. 5 days. A pale yellow solid had precipitated from the solution. Volatiles were removed in vacuo and pentane was added. The solution was filtered and concentrated in attempts to grow crystals. Over time, a light yellow/white solid would precipitate out. An attempt to grow crystals of **3** in Et<sub>2</sub>O, hexanes and toluene was also made. The characterization of the precipitate **4** is discussed below. NMR characterization of **3**: <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400.17 MHz, 23 °C): δ 4.26 (m, 4H, CHMe<sub>2</sub>), 3.47 (m, 4H, CHMe<sub>2</sub>), 1.34 (s, 12H, NC(Me)N), 1.25 (d, 24H, CHMe<sub>2</sub>) 1.02 (d, 24H, CHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 100.63 MHz, 23 °C): δ 151.38 (NC(Me)N), 49.20 (CHMe<sub>2</sub>), 41.40 (CHMe<sub>2</sub>), 25.60 (CHMe<sub>2</sub>), 22.90 (CHMe<sub>2</sub>), 15.38 (NC(Me)N). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR assignments were confirmed by HSQC experiment.

#### **Reaction of Zr(NEt<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (**7**) with O<sub>2</sub>**

*NMR-scale Reaction.* In a Young's tube, **7** (16.5 mg, 0.0319 mmol) was dissolved in benzene-*d*<sub>6</sub>. Volume of headspace in the Young's tube was 2.3 mL. Before adding O<sub>2</sub>, the solution was frozen in liquid nitrogen and nitrogen gas was removed in vacuo. O<sub>2</sub> (1 atm, 0.0319 mmol) was then added. The solution was then heated at 70 °C for 7 days. <sup>1</sup>H NMR revealed the oxo-bridged dimer **3** and HNEt<sub>2</sub> had formed. Based on NMR the yield of HNEt<sub>2</sub> was 14.1% (2 mg). HNEt<sub>2</sub> was confirmed by GC-MS. A light yellow precipitate was identified as {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> (**4**) (7.8 mg, 62.8% yield). The NMR chemical shifts were the same for the reaction of the methyl amide analog **1** with O<sub>2</sub> to produce the oxo-bridged dimer **3**.

*Reaction Conducted in a Schlenk Flask.* In a large scale experiment, O<sub>2</sub> (1 atm,

1.06 mmol) was added to **7** (0.549 g, 1.06 mmol) in toluene in a Schlenk flask. The volume of the headspace of the Schlenk flask was 53.6 mL. The solution was heated at 80 °C for 4 days. A pale yellow solid **4** had precipitated. Volatiles were removed in vacuo and pentane was added. The solution was filtered and concentrated in an attempt to grow crystals. Over time a cloudy solution would form and it was believed the polymer **4** had formed.

### Reaction of **1** or **7** with H<sub>2</sub>O

*NMR-scale Reaction.* In a Young's NMR tube, **1** (35.3 mg, 0.0682 mmol) was dissolved in benzene-*d*<sub>6</sub>. In a separate Young's NMR tube, H<sub>2</sub>O (1.2 mg, 0.0611 mmol) was dissolved in 0.5 mL of THF. The solution of **1** in benzene-*d*<sub>6</sub> was cooled with an ice bath and the H<sub>2</sub>O/THF solution was added dropwise. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies showed the formation of **3** and HNet<sub>2</sub>. The polymer {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>]<sub>n</sub> (**4**) precipitated out of the solution. This was the same procedure used for the reaction of **1** with H<sub>2</sub>O to confirm **3** and **4**. The reactions were monitored by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. The reaction was much faster than that of **1** or **7** with O<sub>2</sub>, and was completed in a few minutes. The product mixture turned cloudy, as the result of the precipitation of the polymer {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>]<sub>n</sub> (**4**). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts of **3** are identical to those from the reactions of O<sub>2</sub> with Zr(NR<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (R = Me, **1**; Et, **7**). The amount of the solid was too small to be isolated. These observations point to the reaction in Scheme 3. Since the reactions here with H<sub>2</sub>O unlikely give peroxo products, the observations of **3** and **4** in the reactions in Scheme 3 support the assignments of **3** and **4** as the dimeric and polymeric oxo products,



ruling out that they are peroxo species.

### **Purification of H<sub>2</sub>O<sub>2</sub>**

*Caution: Extreme care should be taken when using hydrogen peroxide.*

High purity H<sub>2</sub>O<sub>2</sub> was prepared by evacuating at <0.1 torr a 20 mL of 30% aqueous H<sub>2</sub>O<sub>2</sub> solution at 23 °C till the volume of the remaining solution is ca. 2 mL.<sup>S5</sup> Since boiling points of H<sub>2</sub>O<sub>2</sub> and water are 150.2 and 100 °C, respectively, water was expected to be preferentially removed during the process. The residue, containing mostly H<sub>2</sub>O<sub>2</sub>, was then vacuum-transferred at <0.1 torr and condensed by liquid nitrogen in another Schlenk flask at -178 °C in order to remove the stabilizer in the H<sub>2</sub>O<sub>2</sub> solution. The condensed H<sub>2</sub>O<sub>2</sub> liquid was titrated three times with a 0.05 M aqueous KMnO<sub>4</sub> solution which had been standardized with potassium oxalate. The H<sub>2</sub>O<sub>2</sub> liquid was found to be 96% pure.

To standardize KMnO<sub>4</sub>, K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.2447 g, 1.47 mmol) was dissolved in deionized water (15 mL) and heated to ~70 °C. (Do not boil the solution!) Concentrated H<sub>2</sub>SO<sub>4</sub> (1 mL) was then added. After two titrations the concentration of KMnO<sub>4</sub> was 0.506 M.

To find the concentration of the hydrogen peroxide liquid, H<sub>2</sub>O<sub>2</sub> (0.0818 g, 2.40 mmol) was dissolved in deionized water (15 mL) and concentrated H<sub>2</sub>SO<sub>4</sub> (1 mL). After three titrations with KMnO<sub>4</sub> (0.506 M, 18.2 mL, 9.21 mmol) the concentration of H<sub>2</sub>O<sub>2</sub> was 95.5-96.6%.

## Reaction of **1** with H<sub>2</sub>O<sub>2</sub>

*Caution: Extreme care should be taken when using hydrogen peroxide.*

*NMR-scale Reaction.* In a Young's tube, **1** (13.6 mg, 0.0294 mmol) was dissolved in benzene-*d*<sub>6</sub>. H<sub>2</sub>O<sub>2</sub> (0.7 μL, 0.0297 mmol) was then added. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra revealed the oxo-bridged dimer **3**, HNMe<sub>2</sub> and CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>. A precipitate formed and was presumed to be {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> (**4**). The NMR chemical shifts were the same for the reaction of the methyl amide analog **1** with O<sub>2</sub> to produce the oxo-bridged dimer **3**.

*Reaction Conducted in a Schlenk Flask.* In a large scale experiment, H<sub>2</sub>O<sub>2</sub> (26.5 mg, 0.780 mmol) in THF (20 mL) at 0 °C was added to **1** (356.7 mg, 0.772 mmol) in THF (15 mL) and cooled to -50 °C. It was allowed to stir overnight and volatiles were removed in vacuo. The <sup>1</sup>H NMR spectrum revealed the oxo-bridged dimer **3**. A precipitate formed and was presumed to be {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> (**4**).

*Reactions of Solid **1** with H<sub>2</sub>O<sub>2</sub>.* High purity H<sub>2</sub>O<sub>2</sub> (0.4 μL, 0.0170 mmol) was added directly on powders of Zr(NMe<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (**1**, 17.1 mg, 0.0370 mmol) in a glovebox. This was an attempt to minimize the contact of the product, peroxo **2**, with unreacted **1** by not using a solvent. As soon as the liquid H<sub>2</sub>O<sub>2</sub> was added via syringe to the powders of **1**, a spark with smoke occurred. This observation suggests that {(μ-η<sup>2</sup>:η<sup>2</sup>-O<sub>2</sub>)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>]<sub>3</sub> (**2**) is a very unstable and reactive compound (Scheme 3).

## Characterization of {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> (**4**)

It is presumed that the polymer {(μ-O)Zr[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>]<sub>n</sub> (**4**) is the same for the reactions of **1** and **7** with O<sub>2</sub>. For the characterization here, the polymer **4** was prepared

from the reaction of **7** with O<sub>2</sub>. The solid-state <sup>13</sup>C NMR spectrum of **4** (Figure S1) shows peaks at 14.19 ppm for NC(*Me*)N, 23.27 ppm for -CH*Me*<sub>2</sub>, 46.34 ppm for -CHMe<sub>2</sub>, and 152.35 ppm for NC(*Me*)N. The IR spectrum (Figure S2) shows a C=N peak at 1641 cm<sup>-1</sup>. A TGA experiment was performed under N<sub>2</sub>, the sample was heated from room temperature to 1000 °C at a rate of 10 °C per minute (Figure S3). There was a 36.21% loss which accounted for one amidinate ligand to be removed and **4** is considered to be a stable compound at room temperature. Anal. Calcd: C, 49.31; H, 8.79; N, 14.38. Found: C, 49.24; H, 8.71; N, 14.29.

### Mass Spectrometric Studies of **2** and the Reactions between **1** or **7** and H<sub>2</sub>O in Air

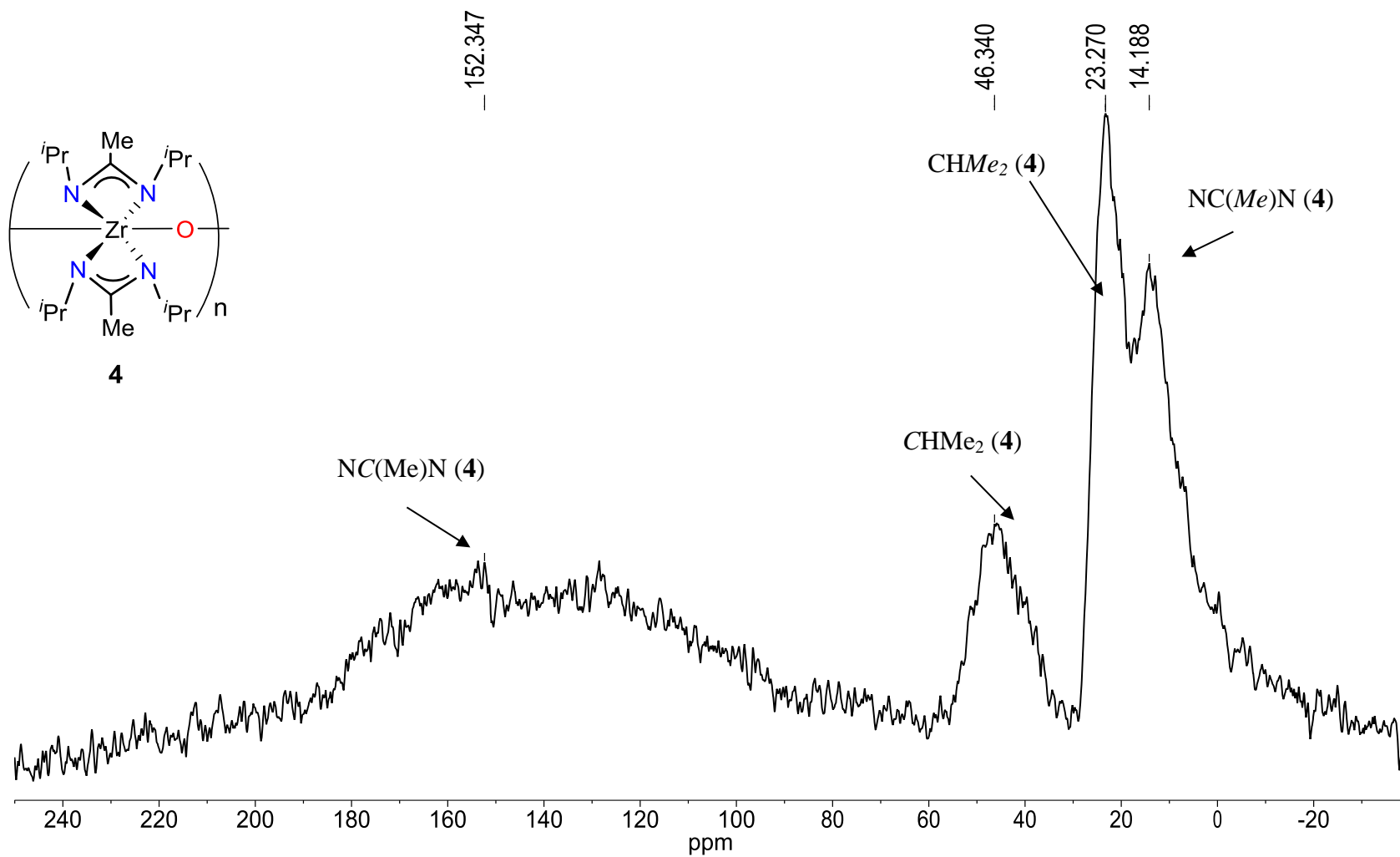
Zirconium has five stable isotopes and in MS displays a unique isotopic pattern. It is easy to determine whether a compound has one Zr atom or two Zr atoms because their MS patterns are very different. Crystals of **2** (which contained **1**) were added to a heated stream of He gas at 400 °C and the peroxo dimer **5** (Figure 2) was observed along with **3**. It is believed that the high temperature converted the crystals of **2** to its more stable oligomer which is the peroxo dimer **5**.

Since the reactions of Zr(NR<sub>2</sub>)<sub>2</sub>[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub> (R = Me, **1**; Et, **7**) with O<sub>2</sub> or water have been studied, it was of interest to see what products would be detected in MS from the reactions. In MS, there is a brief exposure time for the sample to enter into the gas phase. The exposure to O<sub>2</sub> was not of concern because it takes days for **1** or **7** to react with O<sub>2</sub>.

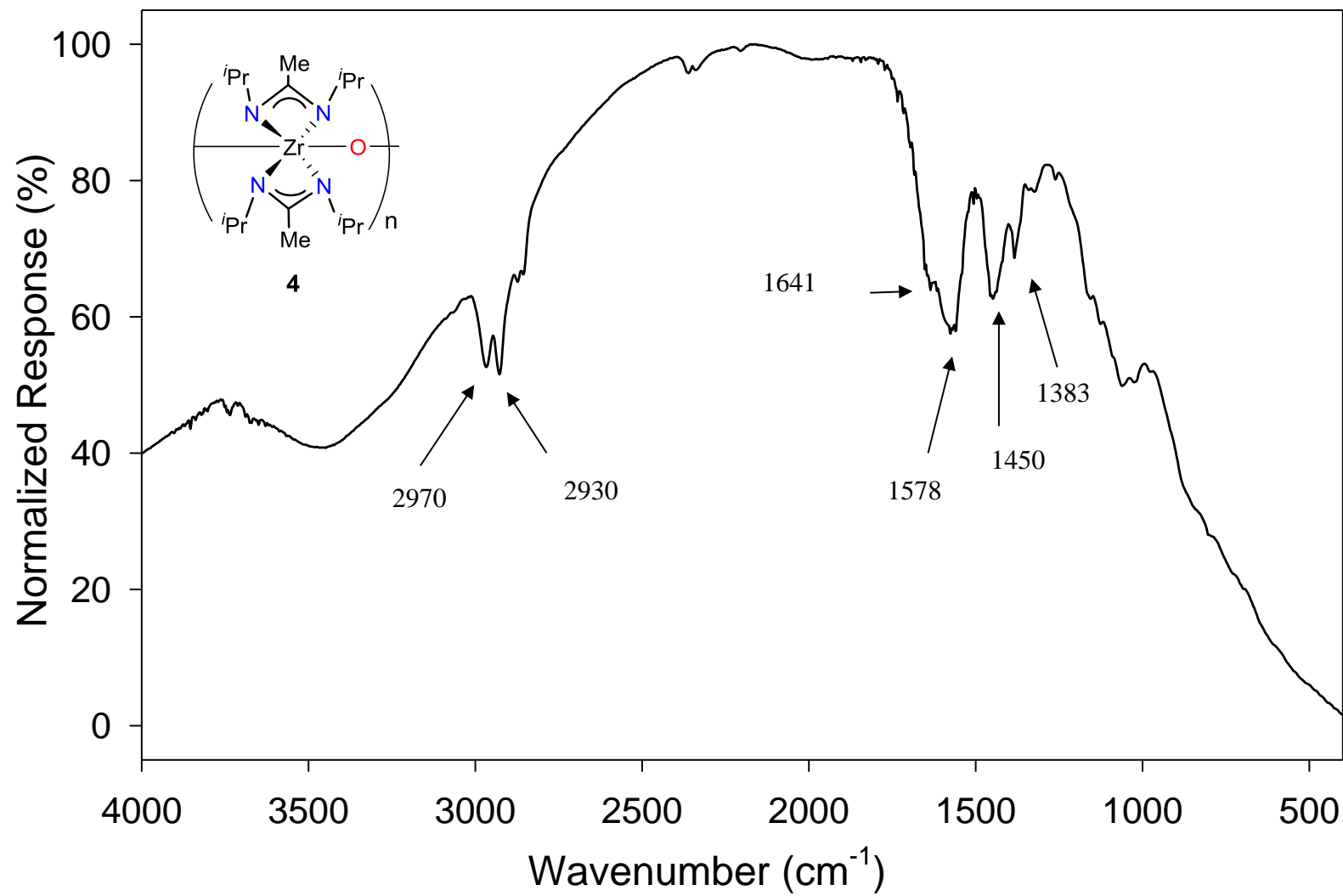
Solid powders of **1** or **7** were kept in a sealed vial under nitrogen until the MS analysis by a JEOL AccuTOF™ DART (Direct Analysis in Real Time) mass

spectrometer was heated to 200 °C. The powders were collected on the sealed end of a capillary tube and added quickly to the heated stream of He gas in air. Compounds **1** or **7** reacted with H<sub>2</sub>O in air and the volatile products [M+H<sup>+</sup>] (species+H<sup>+</sup>) were then analyzed by MS.

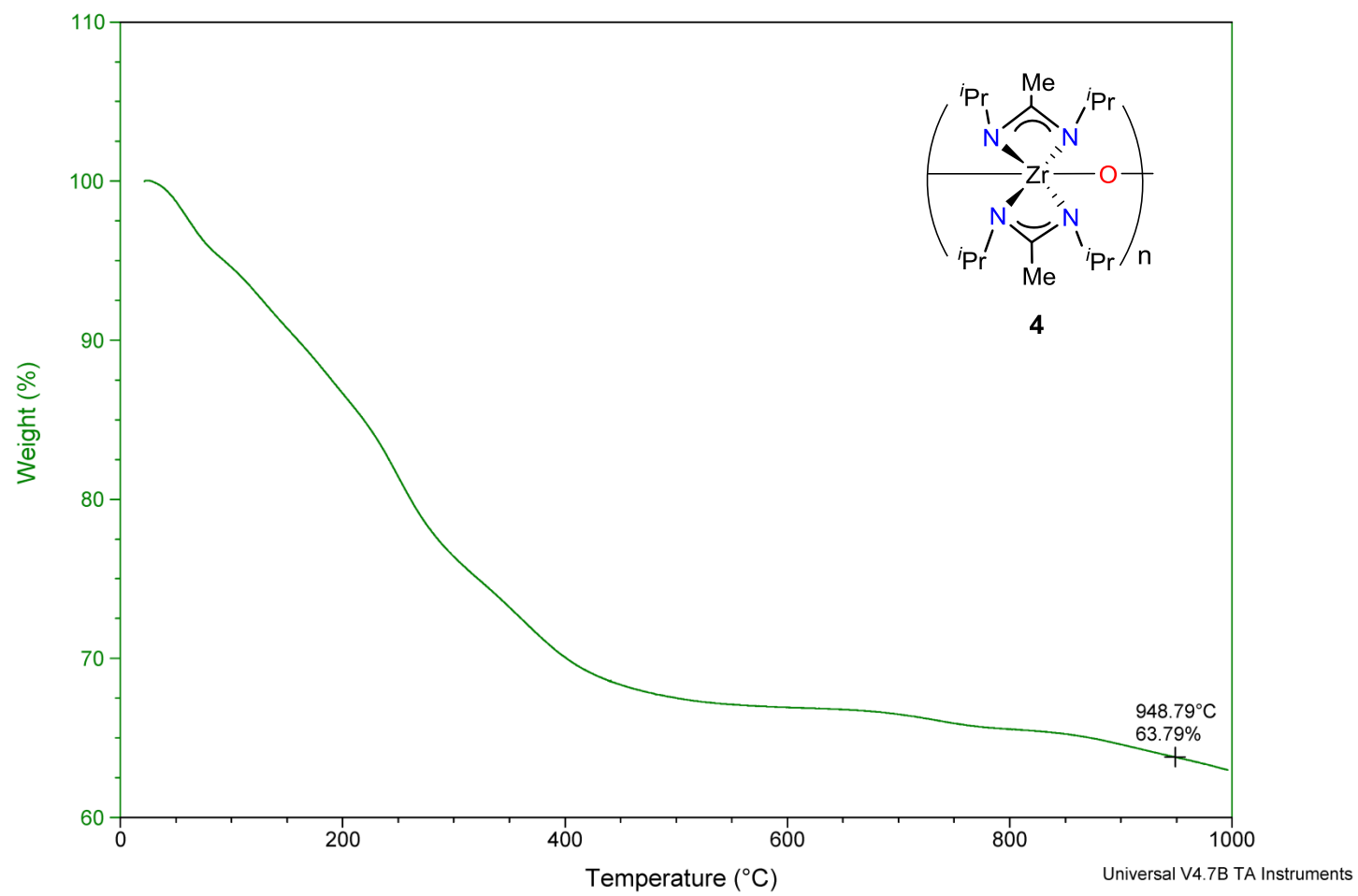
Since the reactions of both **1** and **7** with water give the same products, it was not surprising that the same products are observed in MS. The MS analyzer detected three zirconium and oxygen containing products: oxo monomer **9**, oxo dimer **3**, and a dihydroxyl complex **10** as shown in Scheme 5. The calculated mass for [9+H<sup>+</sup>] is 389.18579 *m/z*, and the cation was observed at 389.18249 *m/z*. The calculated and observed isotopic patterns for [9+H<sup>+</sup>] are given in Figure S4. The calculated mass for [10+H<sup>+</sup>] is 407.19635 *m/z*, and the cation was observed at 407.19077 *m/z*. The calculated and observed isotopic patterns for [10+H<sup>+</sup>] are shown in Figure S5. The calculated mass for [3+H<sup>+</sup>] is 777.36375 *m/z*, and the cation was observed at 777.37085 *m/z*. The calculated and observed isotopic patterns for [3+H<sup>+</sup>], a two Zr atoms complex, are shown in Figure S6. Also, the cations {Zr(NR<sub>2</sub>)[MeC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>}<sup>+</sup> (R = Me, Et) were observed and are likely formed by the MS process. The calculated and observed isotopic patterns for [1-NMe<sub>2</sub><sup>+</sup>] and [2-NEt<sub>2</sub><sup>+</sup>] are given in Figures S7 and S8, respectively.



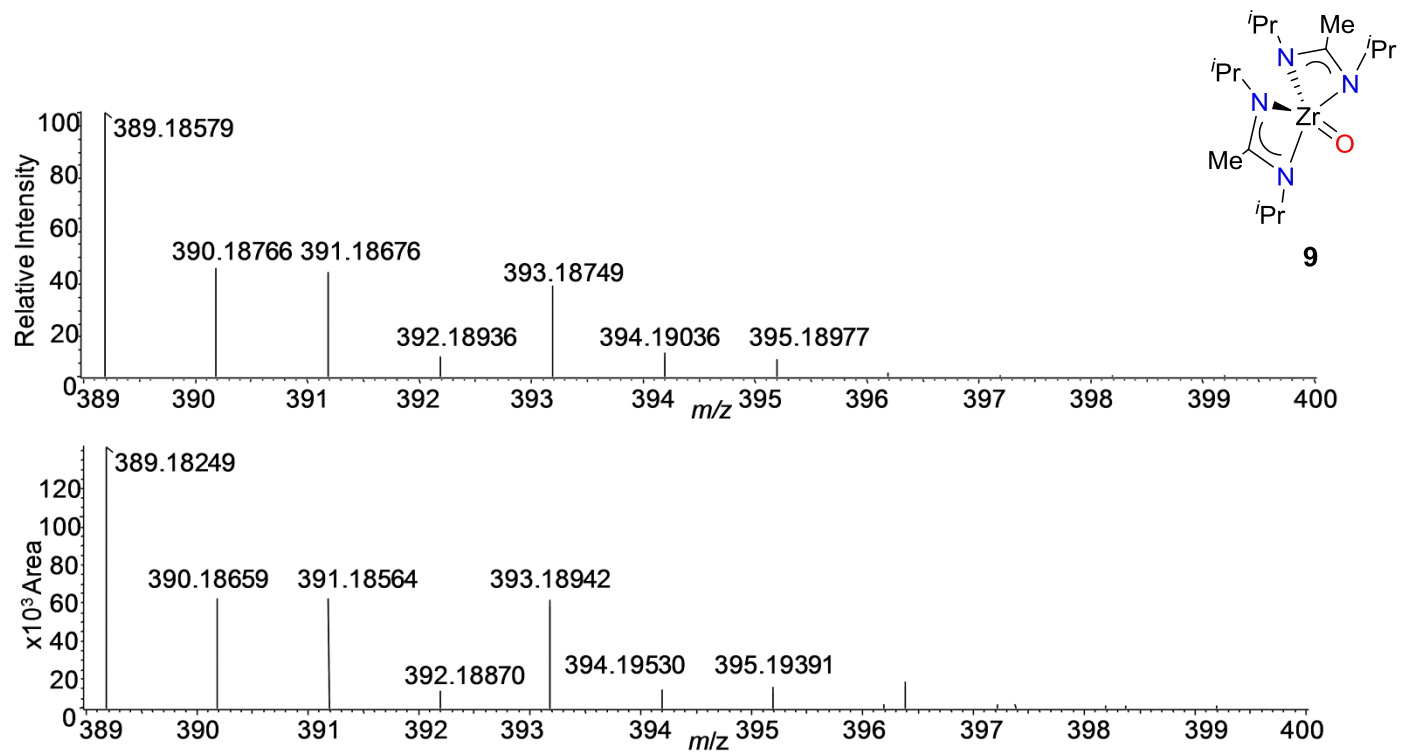
**Figure S1.** Solid-state  $^{13}\text{C}$  NMR spectrum of **4**.



**Figure S12.** IR spectrum of **4** in KBr.

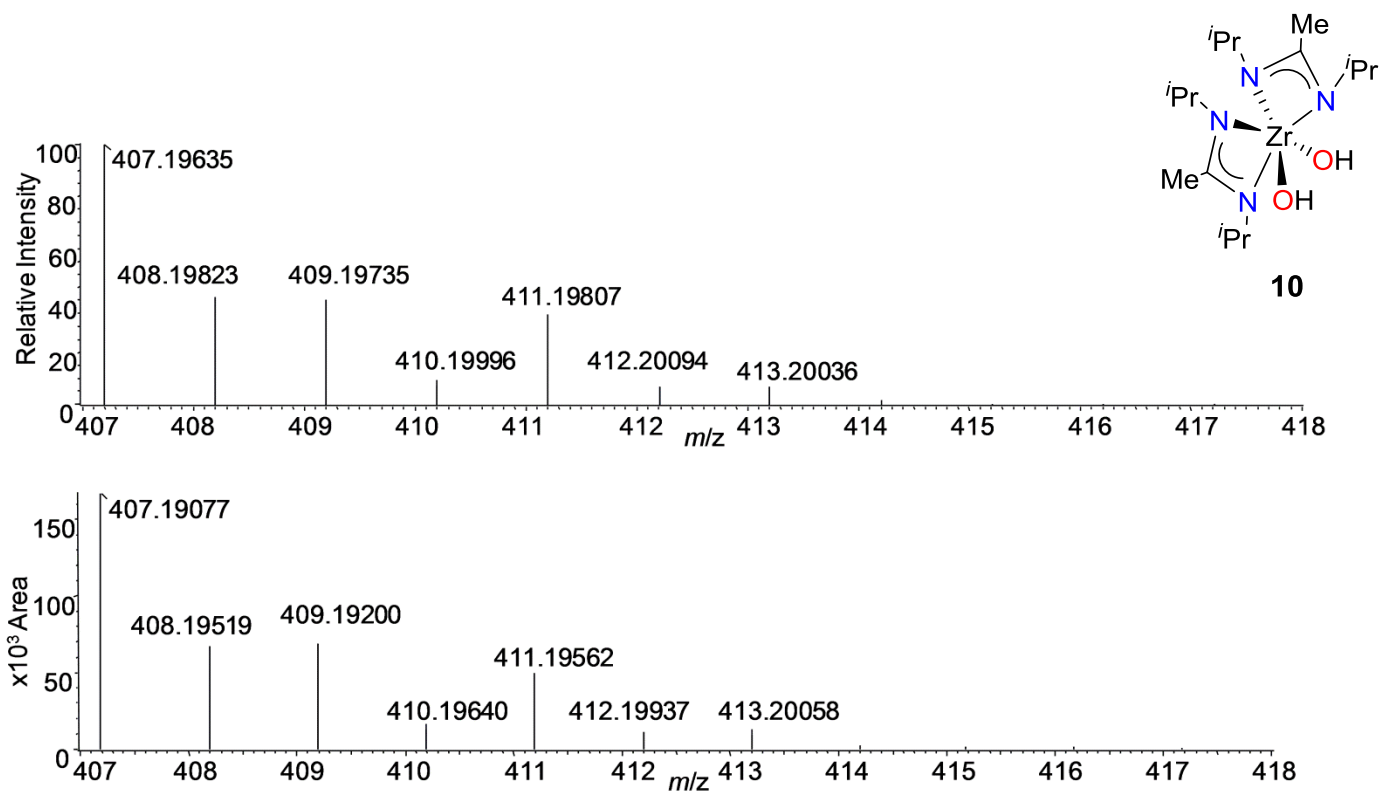


**Figure S3.** TGA of **4**.

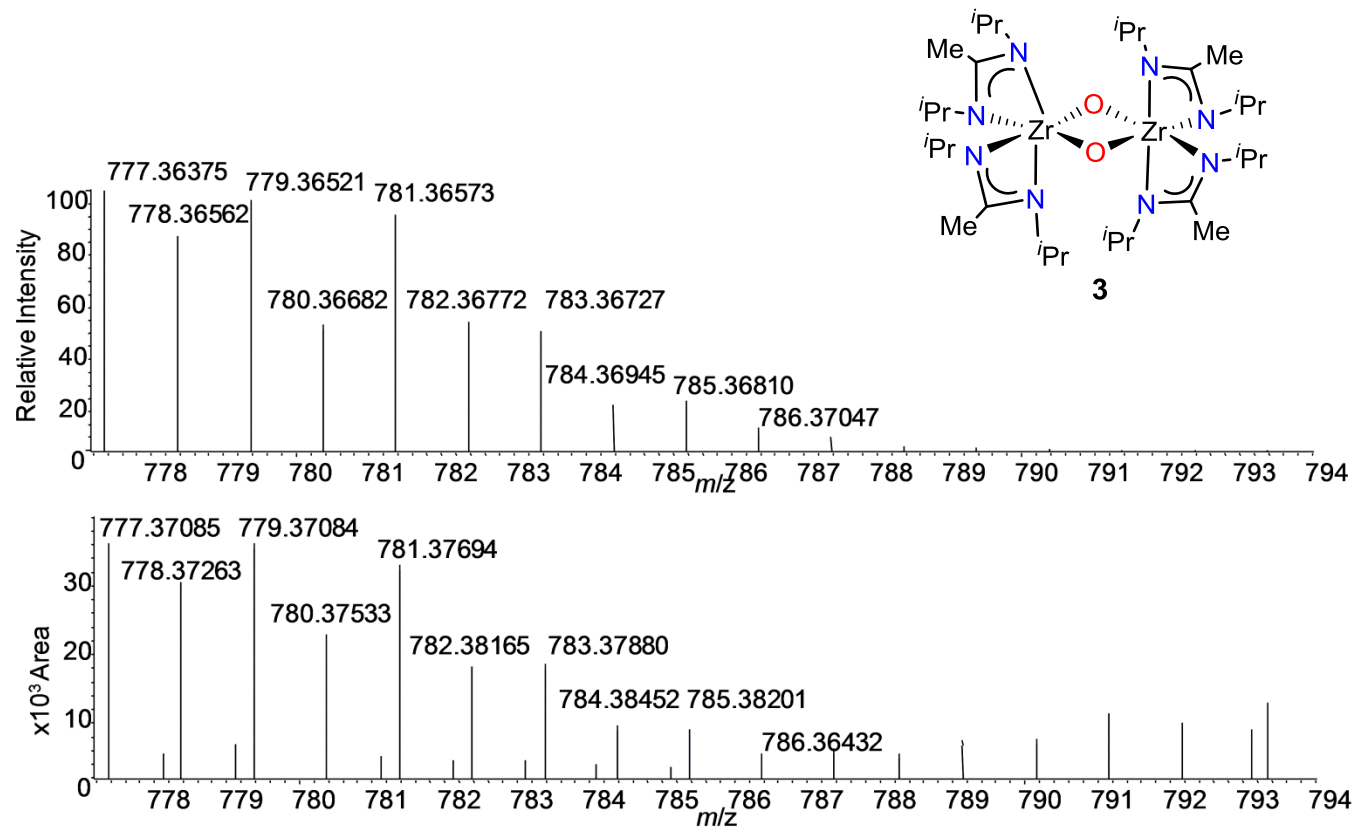


**Figure S4.** (Top) Calculated and (Bottom) Observed MS for [**9**+H<sup>+</sup>].





**Figure S5.** (Top) Calculated and (Bottom) Observed MS for [**10**+H<sup>+</sup>].



**Figure S6.** (Top) Calculated and (Bottom) Observed MS for [**3**+H<sup>+</sup>].

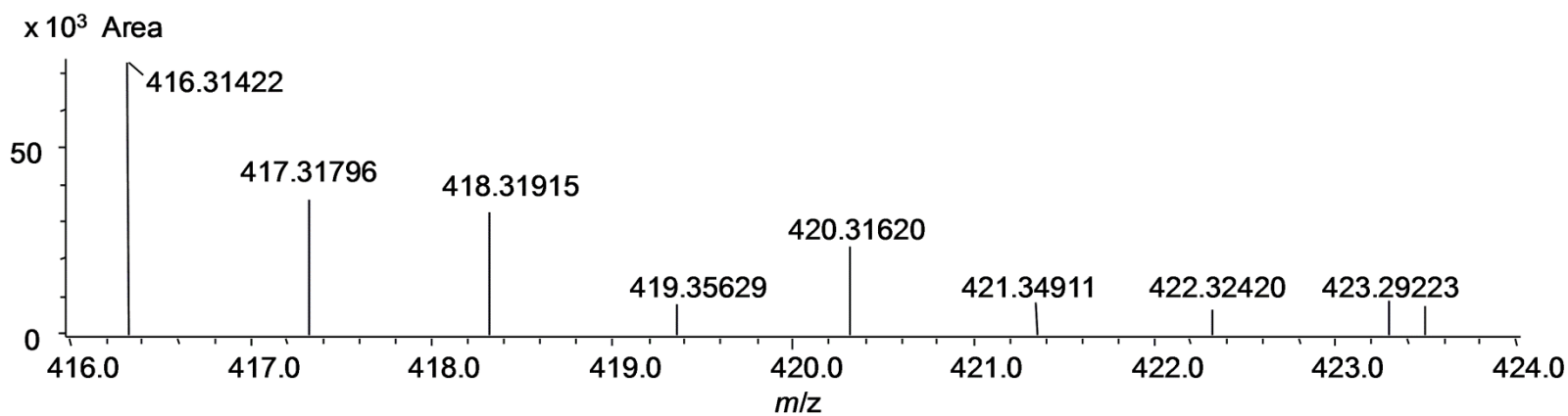
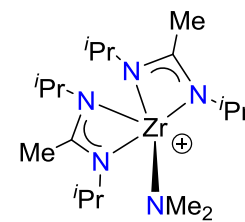
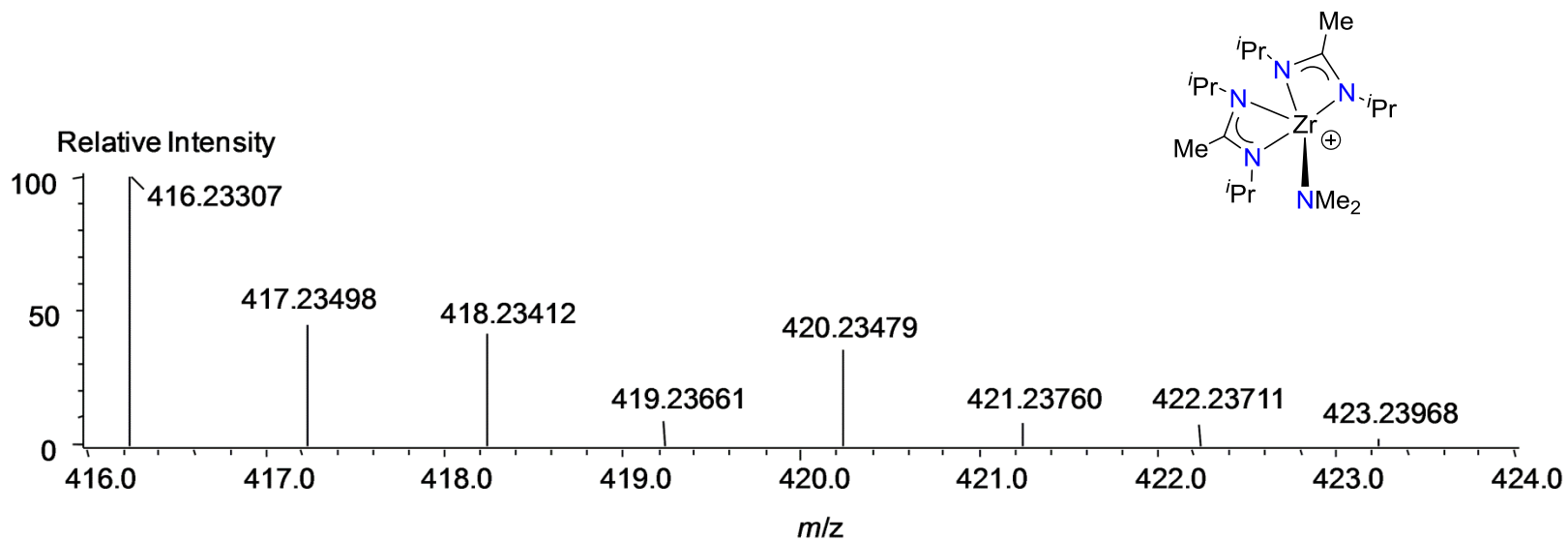
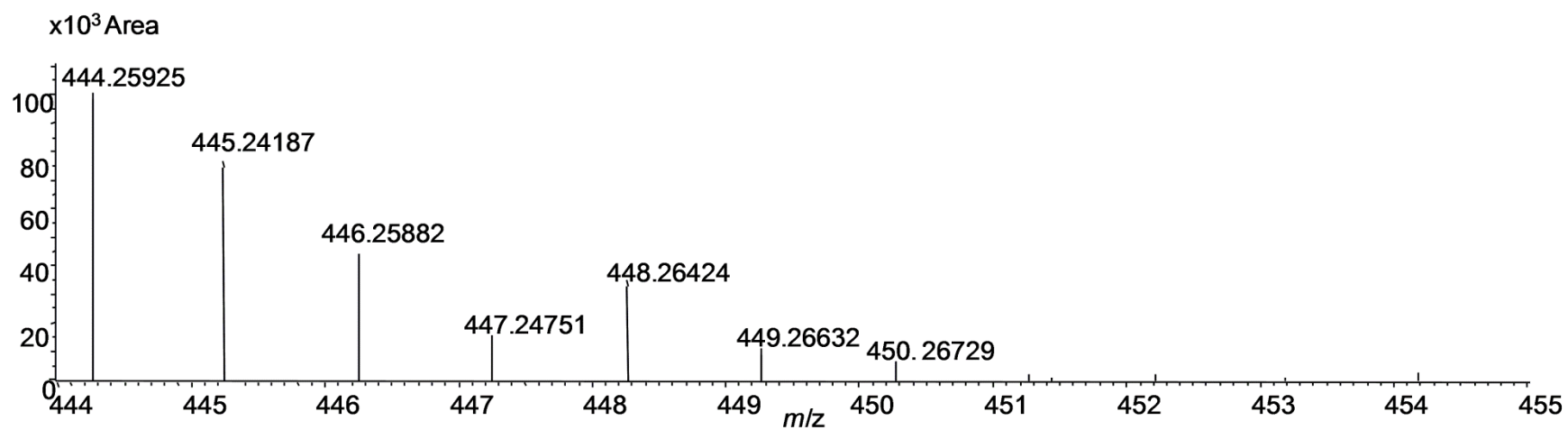
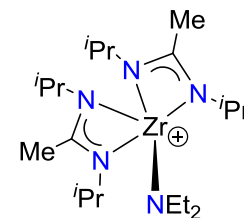
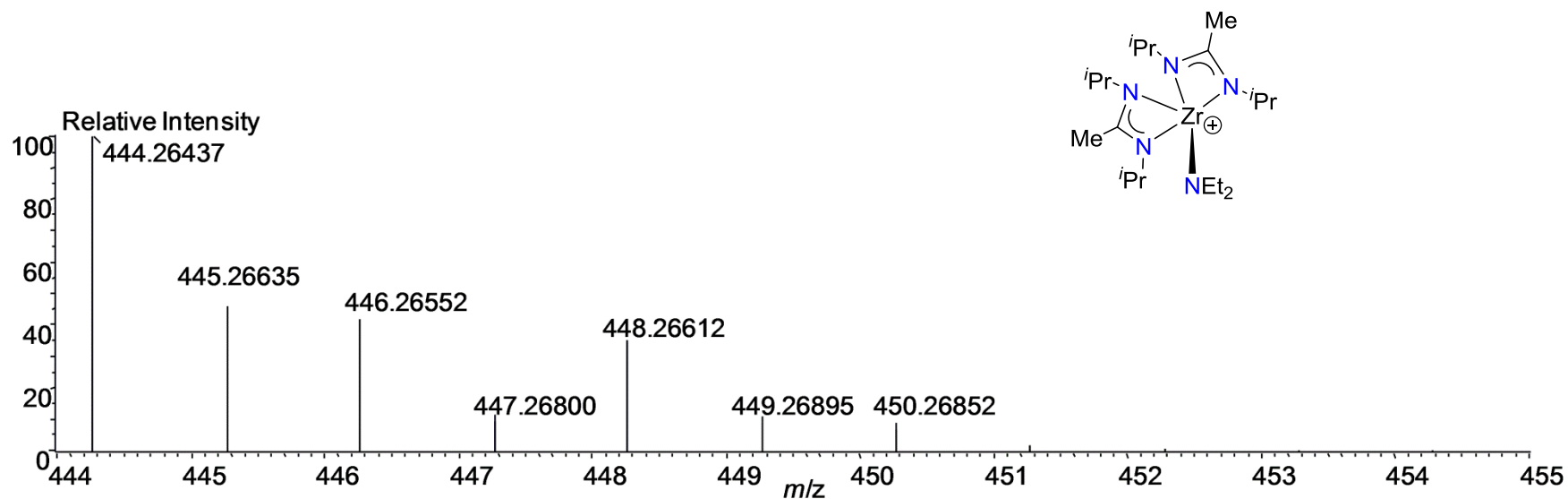


Figure S7. (Top) Calculated and (Bottom) Observed MS of  $[1-NMe_2]^+$ .



**Figure S8.** (Top) Calculated and (Bottom) Observed MS of  $[7-NEt_2]^+$ .

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