Reactions of zirconium amide amidinates with dioxygen.

Observation of an unusual peroxo 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. O₂ (Airgas) was purified by passing it through a P₂O₅ column. Deionized H₂O was degassed and stored in a Schlenk flask. High purity H₂O₂ was prepared from 30% aqueous H₂O₂ solution (Fischer Scientific, reagent grade) and its purification is discussed below. Na₂SO₄, KMnO₄, K₂C₂O₄ and H₂SO₄ were bought from Fischer Scientific and used without further purification. N,N’-Diisopropylcarbodiimide, LiNMe₂ and MeLi (1.6 M in Et₂O) were purchased from Acros and used without further purification. ZrCl₄ (Strem) was sublimed...
at 170 °C before use. Li[MeC(NPr)₂] was prepared by the reaction of N,N’-diisopropylcarbodiimide with MeLi by an approach similar to that of Hessen et al. S₁

Zr(NMe₂)₄ and Zr(NEt₂)₄ were prepared according to literature. S₂ ¹H and ¹³C{¹H} 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%20DART%20Technology/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 iPrN(H)C(Me)=NPr**

*iPrN(H)C(Me)=NPr* has been prepared by two different groups; Oshima and
Miller. They have reported $^1$H NMR spectra of $^{i}$PrN(H)C(Me)=N$^{i}$Pr in CDCl$_3$ and CD$_3$CN, respectively. We are reporting its $^1$H and $^{13}$C{$_^1$H} NMR spectra at 208 K in toluene-$d_8$ and in benzene-$d_6$ at 23 °C.

Li[MeC(N$^{i}$Pr)$_2$] (5.893 g, 39.77 mmol) was dissolved in THF (50 mL) and H$_2$O (0.80 mL, 0.80 g, 44.42 mmol) was added via syringe. The solution was allowed to stir for 20 min and Et$_2$O (100 mL) was added. Na$_2$SO$_4$, a drying agent, was added to the solution and stirred for 12 h, followed by filtration. Et$_2$O in the filtrate was removed at 23 °C. The liquid product $^{i}$PrN(H)C(Me)=N$^{i}$Pr was distilled from the liquid residue at 115 °C and ~0.1 Torr. We have found that at room temperature the $^1$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 $^1$H and $^{13}$C{$_^1$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 $^1$H NMR these efforts were not successful.

$^1$H NMR (benzene-$d_6$, 400.17 MHz, 23 °C): δ 3.85 (br, 2H, CHMe$_2$), 3.01 (br, 1H, NH), 1.36 (s, 3H, NC(Me)N), 1.13 (d, 12H, CHMe$_2$); $^{13}$C{$_^1$H} NMR (benzene-$d_6$, 100.62 MHz, 23 °C): δ 151.58 (NC(Me)N), 45.29 (br, CHMe$_2$), 24.22 (CHMe$_2$), 15.71 (NC(Me)N). $^1$H NMR (toluene-$d_8$, 400.17 MHz, 23 °C): δ 3.74 (br, 1H, NH), 3.33 (br, 2H, CHMe$_2$), 1.43 (s, 3H, NC(Me)N), 1.04 (d, 12H, CHMe$_2$); $^{13}$C{$_^1$H} NMR (toluene-$d_8$, 100.62 MHz, 23 °C): δ 151.55 (NC(Me)N), 45.18 (br, CHMe$_2$), 24.18 (CHMe$_2$), 15.47 (NC(Me)N). $^1$H NMR (toluene-$d_8$, 400.17 MHz, -65 °C): δ 4.71 (br, 1H, NH), 4.28 (m, 1H, CHMe$_2$), 3.47 (m, 1H, CHMe$_2$), 1.60 (s, 3H, NC(Me)N), 1.22 (d, 6H, CHMe$_2$), 1.11
(d, 6H, CHMe₂); $^{13}$C{¹H} NMR (toluene-$d_8$, 100.62 MHz, -65 °C): δ 152.11

(NC(Me)N), 49.04 (CHMe₂), 41.10 (CHMe₂), 25.58 (CHMe₂), 22.54 (CHMe₂), 15.79

(NC(Me)N). DART-MS: Calculated $m/z = 143.15482$ [M+H⁺], Found $m/z = 143.15488$

[M+H⁺]; 0.419 ppm difference.

**Synthesis of Zr(NMe₂)₂[MeC(N'Pr)₂]₂ (1)**

Zr(NMe₂)₄ (1.601 g, 5.984 mmol) was dissolved in pentane (50 mL) and cooled to

-30 °C. ¹PrN(H)C(Me)=N'Pr (1.758 g, 12.36 mmol) was dissolved in pentane (50 mL)

and added dropwise to the solution of Zr(NMe₂)₄ (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). ¹H NMR (benzene-$d_6$, 399.17 MHz, 23 °C): δ 3.45 (m, 4H,

CHMe₂), 3.23 (s, 12H, NMe₂), 1.58 (s, 6H, NC(Me)N), 1.18 (d, 24H, CHMe₂); $^{13}$C{¹H}

NMR (benzene-$d_6$, 100.63 MHz, 23 °C): δ 175.07 (NC(Me)N), 48.34 (CHMe₂), 46.10

(NMe₂), 25.61 (CHMe₂), 11.31 (NC(Me)N). ¹H and $^{13}$C{¹H} 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(NEt₂)₂[MeC(N'Pr)₂]₂ (7)**

Zr(NEt₂)₄ (2.344 g, 6.171 mmol) was dissolved in pentane (50 mL) and cooled to

-30 °C. ¹PrN(H)C(Me)=N'Pr (1.761 g, 12.38 mmol) was dissolved in pentane (50 mL)

and added dropwise to the pentane solution of Zr(NEt₂)₄ (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). ¹H NMR (benzene-$d_6$, 400.17 MHz, 23 °C): δ 3.71 (br, 8H,
X-ray Crystallographic Studies of \{\(\mu-\eta^2-\eta^2\)-O\}_2\text{Zr}[\text{MeC(N}^\prime\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 anisotypically refined. Empirical absorption correction was performed with SADABS.\textsuperscript{S4a} 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.\textsuperscript{S4b}

**Reaction of Zr(NMe\textsubscript{2})\textsubscript{2}[MeC(N^\textit{i}Pr)\textsubscript{2}]\textsubscript{2} (1) with O\textsubscript{2}**

*NMR-scale Reactions.* In a Young’s tube, 1 (28.9 mg, 0.0626 mmol) was dissolved in benzene-\textsubscript{d\textsubscript{6}}. 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\textsubscript{2} (0.5 atm, 0.0626 mmol) was then added. Several \textsuperscript{1}H NMR spectra were taken and after 3 weeks, the disappearance of 1 and the appearance of soluble species 3, HNMe\textsubscript{2}, CH\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2}, and an insoluble solid 4 had occurred.

In a separate test, O\textsubscript{2} (1 atm, 0.0396 mmol) was added to 1 (18.3 mg, 0.0396 mmol) in benzene-\textsubscript{d\textsubscript{6}}. 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 \textsuperscript{1}H NMR spectrum showed the disappearance of 1 and appearance of new peaks which corresponds to an oxo-bridged dimer 3. \textsuperscript{1}H NMR also revealed two byproducts: HNMe\textsubscript{2} (0.125 mg, 6.99% yield based on NMR) and CH\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2} (1.09 mg, 26.9% yield based on NMR). The byproducts, HNMe\textsubscript{2} and CH\textsubscript{2}(NMe\textsubscript{2})\textsubscript{2} 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\textsubscript{2} (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 Et₂O, hexanes and toluene was also made. The characterization of the precipitate 4 is discussed below. NMR characterization of 3: \(^1\)H NMR (benzene-\(d_6\), 400.17 MHz, 23 °C): \(\delta\) 4.26 (m, 4H, CHMe₂), 3.47 (m, 4H, CHMe₂), 1.34 (s, 12H, NC(Me)N), 1.25 (d, 24H, CHMe₂) 1.02 (d, 24H, CHMe₂); \(^{13}\)C\(^{1}\)H NMR (benzene-\(d_6\), 100.63 MHz, 23 °C): \(\delta\) 151.38 (NC(Me)N), 49.20 (CHMe₂), 41.40 (CHMe₂), 25.60 (CHMe₂), 22.90 (CHMe₂), 15.38 (NC(Me)N). \(^1\)H and \(^{13}\)C\(^{1}\)H NMR assignments were confirmed by HSQC experiment.

**Reaction of Zr(NEt₂)₂[MeC(N'^iPr)₂]₂ (7) with O₂**

**NMR-scale Reaction.** In a Young’s tube, 7 (16.5 mg, 0.0319 mmol) was dissolved in benzene-\(d_6\). Volume of headspace in the Young’s tube was 2.3 mL. Before adding O₂, the solution was frozen in liquid nitrogen and nitrogen gas was removed in vacuo. O₂ (1 atm, 0.0319 mmol) was then added. The solution was then heated at 70 °C for 7 days. \(^1\)H NMR revealed the oxo-bridged dimer 3 and HNEt₂ had formed. Based on NMR the yield of HNEt₂ was 14.1% (2 mg). HNEt₂ was confirmed by GC-MS. A light yellow precipitate was identified as \{((\mu-O)Zr[MeC(N'^iPr)₂]₂\}_n (4) (7.8 mg, 62.8% yield). The NMR chemical shifts were the same for the reaction of the methyl amide analog 1 with O₂ to produce the oxo-bridged dimer 3.

**Reaction Conducted in a Schlenk Flask.** In a large scale experiment, O₂ (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 H₂O**

*NMR-scale Reaction.* In a Young’s NMR tube, 1 (35.3 mg, 0.0682 mmol) was dissolved in benzene-\(d_6\). In a separate Young’s NMR tube, H₂O (1.2 mg, 0.0611 mmol) was dissolved in 0.5 mL of THF. The solution of 1 in benzene-\(d_6\) was cooled with an ice bath and the H₂O/THF solution was added dropwise. \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR spectroscopies showed the formation of 3 and HNEt₂. The polymer \{((\mu-O)Zr[MeC(N^nPr)_2]₂\}ₙ (4) precipitated out of the solution. This was the same procedure used for the reaction of 1 with H₂O to confirm 3 and 4. The reactions were monitored by \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR spectroscopies. The reaction was much faster than that of 1 or 7 with O₂, and was completed in a few minutes. The product mixture turned cloudy, as the result of the precipitation of the polymer \{((\mu-O)Zr[MeC(N^nPr)_2]₂\}ₙ (4). The \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR chemical shifts of 3 are identical to those from the reactions of O₂ with Zr(NR₂)₂[MeC(N^nPr)_2]₂ (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 H₂O 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$_2$O$_2$**

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

High purity H$_2$O$_2$ was prepared by evacuating at $<$0.1 torr a 20 mL of 30% aqueous H$_2$O$_2$ solution at 23 °C till the volume of the remaining solution is ca. 2 mL.$^{55}$ Since boiling points of H$_2$O$_2$ and water are 150.2 and 100 °C, respectively, water was expected to be preferentially removed during the process. The residue, containing mostly H$_2$O$_2$, was then vacuum-transferred at $<$0.1 torr and condensed by liquid nitrogen in another Schlenk flask at -178 °C in order to remove the stabilizer in the H$_2$O$_2$ solution. The condensed H$_2$O$_2$ liquid was titrated three times with a 0.05 M aqueous KMnO$_4$ solution which had been standardized with potassium oxalate. The H$_2$O$_2$ liquid was found to be 96% pure.

To standardize KMnO$_4$, K$_2$C$_2$O$_4$ (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$_2$SO$_4$ (1 mL) was then added. After two titrations the concentration of KMnO$_4$ was 0.506 M.

To find the concentration of the hydrogen peroxide liquid, H$_2$O$_2$ (0.0818 g, 2.40 mmol) was dissolved in deionized water (15 mL) and concentrated H$_2$SO$_4$ (1 mL). After three titrations with KMnO$_4$ (0.506 M, 18.2 mL, 9.21 mmol) the concentration of H$_2$O$_2$ was 95.5-96.6%.
Reaction of 1 with H$_2$O$_2$

*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-$d_6$. H$_2$O$_2$ (0.7 µL, 0.0297 mmol) was then added. The $^1$H and $^{13}$C{$^1$H} NMR spectra revealed the oxo-bridged dimer 3, HNMe$_2$ and CH$_3$(NMe$_2$)$_2$. A precipitate formed and was presumed to be {((μ-O)Zr[MeC(N′Pr)$_2$]$_2$)$_n$ (4). The NMR chemical shifts were the same for the reaction of the methyl amide analog 1 with O$_2$ to produce the oxo-bridged dimer 3.

*Reaction Conducted in a Schlenk Flask.* In a large scale experiment, H$_2$O$_2$ (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 $^1$H NMR spectrum revealed the oxo-bridged dimer 3. A precipitate formed and was presumed to be {((μ-O)Zr[MeC(N′Pr)$_2$]$_2$)$_n$ (4).

*Reactions of Solid 1 with H$_2$O$_2$.* High purity H$_2$O$_2$ (0.4 µL, 0.0170 mmol) was added directly on powders of Zr(NMe$_2$)$_2$[MeC(N′Pr)$_2$]$_2$ (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$_2$O$_2$ was added via syringe to the powders of 1, a spark with smoke occurred. This observation suggests that {((μ-η$^2$:η$^2$-O$_2$)Zr[MeC(N′Pr)$_2$]$_2$)$_3$ (2) is a very unstable and reactive compound (Scheme 3).

**Characterization of {((μ-O)Zr[MeC(N′Pr)$_2$]$_2$)$_n$ (4)***

It is presumed that the polymer {((μ-O)Zr[MeC(N′Pr)$_2$]$_2$)$_n$ (4) is the same for the reactions of 1 and 7 with O$_2$. For the characterization here, the polymer 4 was prepared...
from the reaction of 7 with O₂. The solid-state ¹³C NMR spectrum of 4 (Figure S1) shows peaks at 14.19 ppm for NC(Me)N, 23.27 ppm for -CHMe₂, 46.34 ppm for -CHMe₂, and 152.35 ppm for NC(Me)N. The IR spectrum (Figure S2) shows a C=N peak at 1641 cm⁻¹. A TGA experiment was performed under N₂, 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 H₂O 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(NR₂)₂[MeC(N'Pr)₂]₂ (R = Me, 1; Et, 7) with O₂ 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 O₂ was not of concern because it takes days for 1 or 7 to react with O₂.

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
The 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 H₂O in air and the volatile products [M+H⁺] (species+H⁺) 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⁺] is 389.18579 m/z, and the cation was observed at 389.18249 m/z. The calculated and observed isotopic patterns for [9+H⁺] are given in Figure S4. The calculated mass for [10+H⁺] is 407.19635 m/z, and the cation was observed at 407.19077 m/z. The calculated and observed isotopic patterns for [10+H⁺] are shown in Figure S5. The calculated mass for [3+H⁺] is 777.36375 m/z, and the cation was observed at 777.37085 m/z. The calculated and observed isotopic patterns for [3+H⁺], a two Zr atoms complex, are shown in Figure S6. Also, the cations {Zr(NR₂)[MeC(NiPr)₂]₂}⁺ (R = Me, Et) were observed and are likely formed by the MS process. The calculated and observed isotopic patterns for [1-NMe₂⁺] and [2-NEt₂⁺] are given in Figures S7 and S8, respectively.
Figure S1. Solid-state $^{13}$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⁺].
Figure S5. (Top) Calculated and (Bottom) Observed MS for [10+H⁺].
Figure S6. (Top) Calculated and (Bottom) Observed MS for [3+H⁺].
Figure S7. (Top) Calculated and (Bottom) Observed MS of $[\text{I-NMe}_2^+]$.
Figure S8. (Top) Calculated and (Bottom) Observed MS of [7-NEt₂⁺].
Additional references

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