Addition and Metathesis Reactions of Zirconium and Hafnium Imido Complexes

Joseph Lyndon Thorman
Iowa State University

Ilia A. Guzei
Iowa State University

Victor G. Young Jr.
University of Minnesota - Twin Cities

L. Keith Woo
Iowa State University, kwoo@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/761. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Abstract
The zirconium and hafnium imido metalloporphyrin complexes (TTP)MNAr$i$Pr (TTP = meso-5,10,15,20-tetra-p-tolylporphyrinato dianion; M = Zr (1), Hf; Ar$i$Pr = 2,6-diisopropylphenyl) were used to mediate addition reactions of carbonyl species and metathesis of nitroso compounds. The imido complexes react in a stepwise manner in the presence of 2 equiv of pinacolone to form the enediolate products (TTP)M[OC(tBu)CHC(tBu)(Me)O] (M = Zr (2), Hf (3)), with elimination of H2NAr$i$Pr. The bis(μ-oxo) complex [(TTP)ZrO]2 (4) is formed upon reaction of (TTP)ZrNAr$i$Pr with PhNO. Treatment of compound 4 with water or treatment of compound 2 with acetone produced the (μ-oxo)bis(μ-hydroxo)-bridged dimer [(TTP)Zr]2(μ-O)(μ-OH)2 (5). Compounds 2, 4, and 5 were structurally characterized by single-crystal X-ray diffraction.

Disciplines
Chemistry

Comments
Addition and Metathesis Reactions of Zirconium and Hafnium Imido Complexes

Joseph L. Thorman,† Ilia A. Guzei,‡ Victor G. Young, Jr.,∥ and L. Keith Woo‡,†

Departments of Chemistry, Iowa State University, Ames, Iowa 50011-3111, and University of Minnesota, Minneapolis, Minnesota 55455

Received August 18, 1999

The zirconium and hafnium imido metalloporphyrin complexes (TTP)M=NR(Pr) (TTP = meso-5,10,15,20-tetrap-tolyporphyrinato dianion; M = Zr (1), Hf; ArPr = 2,6-disisopropylphenyl) were used to mediate addition reactions of carbonyl species and metathesis of nitroso compounds. The imido complexes react in a stepwise manner in the presence of 2 equiv of pinacolone to form the enediolate products (TTP)M[OC(Bu)CHC(Bu)(Me)O] (M = Zr (2), Hf (3)), with elimination of H2NR(Pr). The bis(μ-oxo) complex [(TTP)ZrO] (4) is formed upon reaction of (TTP)Zr=NR(Pr) with PhNO. Treatment of compound 4 with water or treatment of compound 2 with acetone produced the (μ-oxo)bis(μ-hydroxy)-bridged dimer [(TTP)Zr(μ-O)(μ-OH)]2 (5). Compounds 2, 4, and 5 were structurally characterized by single-crystal X-ray diffraction.

Introduction

The preparation of group 4 chalcogenido complexes is an attractive goal in light of the high reactivity of metallocene and tetraazaannulene analogues described in a number of reports.1–3 Notable examples include C−H bond activation, cycloaddition, and enolate formation. Toward this end, we have developed nitrile group and chalcogenido atom transfer routes with titanium metalloporphyrin complexes. Efforts to extend this methodology to the heavier congeners has now become an area of attention. In an ongoing investigation of group 4 metalloporphyrin imido complexes, we have found a number of novel reactivity properties.4–6 We demonstrated previously that the imido complexes (TTP)M=NR(Pr) (M = Zr, Hf) exhibit reactivity with heterocumulenes to form [2 + 2] cycloaddition products.7 Further reaction has been explored with other unsaturated substrates. Among these are pinacolone and PhNO, for which we now describe results found for their reactions with zirconium and hafnium imido complexes.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a model MO40-1 Dri-Train gas purifier. Benzene, benzene-d6, toluene, THF, and hexane were freshly distilled from purple solutions of sodium benzenophenone and brought into the drybox without exposure to air. The dichloro, (TTP)MC1, imido, (TTP)M=NR(Pr) (M = Zr, Hf), and (TTP)Zr(η2-NR(Pr)C(=NBu)O) compounds were prepared according to literature procedures.3 Pinacolone was purchased from Aldrich, vacuum-transferred, and dried by passage through a plug of activated neutral alumina. Pinacolone-d3 was prepared according to a literature procedure.8 1H and 13C NMR data were acquired on Varian VXR (300 MHz) and Bruker DRX (400 MHz) spectrometers. Chemical shifts (ppm) are referenced to proton solvent standards. UV/vis spectra were recorded on a HP8452A diode array spectrophotometer and are reported as λmax in nm (log ε). Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. GCMS studies were performed on a Varian gas chromatograph coupled to an Ions 40 ion trap mass spectrometer (capillary column DB-5MS).

(TTP)Zr(NHAr(C=NBu)O)2 (2a). This complex was formed within minutes by treatment of the imido complex, 1, with 1 equiv of pinacolone in toluene or benzene. Although complex 2a is stable in its mother liquor for days at ambient temperature and at 80 °C, it could not be isolated in an analytically pure form.1H NMR (C6D6, 400 MHz): 9.18 (s, 8H, β-H), 8.55 (d, 4H, J1H-2H = 7 Hz, meso-C6H6(CH3)2), 7.85 (d, 4H, J1H-2H = 7 Hz, meso-C6H6(CH3)2), 7.33 (d, 4H, J1H-2H = 8 Hz, meso-C6H6(CH3)2), 6.22 (m, 3H, p-p-NHAr(C=NBu)O), 3.02 (s, 1H, OC(=C(=CH2)Bu)), 2.40 (s, 12H, meso-C6H6(CH3)2), 1.35 (s, 1H, OC(=C(=CH2)Bu)), 0.96 (s, 1H, NHAr(C=NBu)O), 0.46 (6H, J1H-2H = 8.9 Hz, 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2), −0.22 (m, 2H, 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2), −0.50 (s, 9H, OC(=C(=CH2)Bu)), 1H NMR (C6D6, 400 MHz): 137.0 (OC(=C(=CH2)Bu)), 150.6, 148.6, 139.8, 137.1, 135.2 (β-pyrole), 128.5 (m-tolyl), 125.6, 124.5, 121.2 (m-p-Ar), 119.7 (m-p-Ar), 83.3 (OC(=C(=CH2)Bu)), 34.1, 29.0 (CH(Me2)), 27.3 (OC(=C(=C(CH3))), C(CH3)), 24.6 (CH(Me2)), 22.0 (CH(Me2)), 21.4 (C-tolyl).

(TTP)Zr[OC(Bu)CHC(Bu)(Me)O]2 (2). A solution of (TTP)Zr=NR(Pr) (237 mg, 0.253 mmol) and pinacolone (200 μL, 1.60 mmol) in benzene (ca. 15 mL) was stirred at 25 °C for 40 h. This dark blue solution was filtered, and the filtrate was evaporated to dryness in vacuo to yield blue 2 (204 mg, 84% yield), UV/vis (toluene): 548 (4.55), 425 (5.66), 405 (shoulder, 3.23).1H NMR (C6D6, 300 MHz): 9.21 (m, 8H, β-H), 8.47 (d, 4H, J1H-2H = 7 Hz, meso-C6H6(CH3)2), 7.93 (d, 4H, J1H-2H = 7 Hz, meso-C6H6(CH3)2), 7.25 (d, 4H, J1H-2H = 8 Hz, meso-C6H6(CH3)2), 7.25 (d, 4H, J1H-2H = 8 Hz, meso-C6H6(CH3)2), 7.25 (d, 4H, J1H-2H = 8 Hz, meso-C6H6(CH3)2), 6.22 (m, 3H, p-p-NHAr(Pr)), 3.02 (s, 1H, OC(=C(=C(=CH2)Bu))), 2.40 (s, 12H, meso-C6H6(CH3)2), 1.35 (s, 1H, OC(=C(=C(=CH2)Bu)), 0.96 (s, 1H, NHAr(Pr)), 0.46 (6H, J1H-2H = 8.9 Hz, 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2), −0.22 (m, 2H, 2.6-(CH3C6H4)2; 2.6-(CH3C6H4)2), −0.50 (s, 9H, OC(=C(=C(=CH2)Bu))), 1H NMR (C6D6, 400 MHz): 137.0 (OC(=C(=C(=CH2)Bu))), 150.6, 148.6, 139.8, 137.1, 135.2 (β-tolyl), 132.5 (β-pyrole), 128.5 (m-tolyl), 125.6, 124.5, 121.2 (m-p-Ar), 119.7 (m-p-Ar), 83.3 (OC(=C(=C(=CH2)Bu))), 34.1, 29.0 (CH(Me2)), 27.3 (OC(=C(=C(CH3))), C(CH3)), 24.6 (CH(Me2)), 22.0 (CH(Me2)), 21.4 (C-tolyl).

Zirconium and Hafnium Imido Complexes

Two new zirconium imido complexes were prepared. The first, [Zr(O)(Ph)]_2((CH=CH))_2, was prepared by reaction of (TTP)Zr(OC(Me)C(C6H4))_2 with PhNO (28.2 mg, 0.263 mmol) in toluene (ca. 15 mL) at 25 °C for 1.5 h. A dark blue solution was filtered, and the filtrate was evaporated to dryness in vacuo and recrystallized from a toluene solution layered with hexanes at −25 °C overnight to yield blue 3 (79 mg, 61% yield). UV/vis (toluene): 548, 425. 1H NMR (CD6D6, 300 MHz): 9.23 (m, 8H, β-H), 8.47 (4H, 3J_H-H = 7 Hz, meso-C6H4CH3), 7.91 (4H, 3J_H-H = 7 Hz, meso-C6H4CH3), 7.35 (4H, 3J_H-H = 8 Hz, meso-C6H4CH3), 7.24 (4H, 3J_H-H = 8 Hz, meso-C6H4CH3), 6.78 (2H, CH(NC(Pr)N)2), 0.04 (4H, OC(Bu)CHC(Bu)(Me)O), −0.32 (4H, OC(Bu)CHC(Bu)(Me)O). 13C NMR (CD6D6): 159.5 (OC-C), 150.1 (OC-C), 140.3, 137.4, 135.2 (0-tolyl), 134.5 (0-tolyl), 132.6 (β-tolyl), 132.5 (β-tolyl), 129.0 (meso-C6H4CH3), 128.2, 127.0, 125.3, 21.5 (meso-C6H4CH3). GC/MS (C6D6NO2), m/z, calc (found): [M+Na]⁺ 276.42 (277). 1H NMR (CD3D6, 300 MHz): 7.16 (m, p-C(H3)2), 0.78 (6H, m-C(H3)2), 0.26 (s, 9H, OC(Me)C(C6H4)2), 0.22 (s, 12H, meso-C6H4CH3). 13C NMR (CD3D6): 157.3 (OC-C), 151.0 (OC-C), 138.1, 137.8, 137.5 (meso-C6H4CH3), 132.9 (meso-C6H4CH3), 130.6 (β-tolyl), 127.0 (meso-C6H4CH3), 122.5, 21.5 (meso-C6H4CH3). GC/MS (CH3NO2), m/z, calc (found): [M+2]⁺ 276.42 (277).

Structure Determinations of (TTP)Zr(OC(Bu)CHC(Bu)(Me)O) (2), [(TTP)ZrO]2 (4), and [(TTP)Zr(μ-O)2(μ-OH)]2 (5). Crystal data is found in Table 1. Compound 5 was treated with attachment to a glass fiber and mounting on a Siemens SMART system for data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrices determined from reflections harvested from three sets of 20 frames. Three major swaths of frames were collected with 0.30° tilt steps in α, β, γ. The space group was determined on the basis of systematic absences and intensity statistics, and a successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of non-hydrogen atoms. These were refined with anisotropic displacement parameters.

Atom O1 was located on the crystallographic 2-fold axis and appeared to be a hydroxido ligand based on a long metal–oxygen bond length. The proton attached to O1 was assumed to be in an sp3 geometry and disordered over the two possible, partially occupied sites. The other two oxygens, bridging hydroxide (O3) and oxo (O2), were equally disordered over the crystallographic 2-fold axis and were refined with restrained metal–oxygen distances. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. There were 1.5 solvent molecules of benzene per asymmetric unit. SHELXTL DELU and SAME restraints were employed here to keep reasonable C–C distances and approximate rigid-body anisotropic displacement parameters. There were 48 restraints used altogether. Three bad reflections were omitted from the final least-squares refinement. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 program suite.

Crystals of 2 and 4 were treated in an analogous manner to that of 5. Systematic absences in the diffraction data were uniquely consistent

(9) SHELXTL-Plus V5.0; Siemens Industrial Automation, Inc.: Madison, WI, 1997.
Table 1. Crystal Data and Structure Refinements

<table>
<thead>
<tr>
<th>(TTP)Zr(OC(Bu)CHC(Bu)(Me)O)</th>
<th>[TTP]ZrO₂</th>
<th>[TTP]Zr₂(μ-O)(μ-OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C₁₁₀H₉₆N₄O₄Zr</td>
<td>C₁₁₀H₉₆N₄O₄Zr₂</td>
</tr>
<tr>
<td>fw</td>
<td>1182.70</td>
<td>1736.32</td>
</tr>
<tr>
<td>temp, K</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>wavelength, Å</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Cc</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>21.8318(8)</td>
<td>31.8540(16)</td>
</tr>
<tr>
<td>b, Å</td>
<td>20.7139(8)</td>
<td>16.7937(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>15.7878(8)</td>
<td>18.8770(9)</td>
</tr>
<tr>
<td>β, deg</td>
<td>112.624(1)</td>
<td>117.254(1)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>6590.2(5)</td>
<td>8977.18(1)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>density (calcd), Mg/m³</td>
<td>1.192</td>
<td>1.285</td>
</tr>
<tr>
<td>abs coeff, mm⁻¹</td>
<td>0.215</td>
<td>0.289</td>
</tr>
<tr>
<td>F(000)</td>
<td>2508</td>
<td>3600</td>
</tr>
<tr>
<td>crystal size, mm³</td>
<td>0.30 × 0.30 × 0.30</td>
<td>0.21 × 0.40 × 0.42</td>
</tr>
<tr>
<td>θ range, deg</td>
<td>141–21.97</td>
<td>24.8–28.32</td>
</tr>
<tr>
<td>index ranges</td>
<td>–22 ≤ h ≤ 22</td>
<td>–42 ≤ h ≤ 37</td>
</tr>
<tr>
<td>0 ≤ k ≤ 21</td>
<td>–16 ≤ l ≤ 16</td>
<td>0 ≤ k ≤ 20</td>
</tr>
<tr>
<td>0 ≤ l ≤ 25</td>
<td>53 684</td>
<td>22 019</td>
</tr>
<tr>
<td>no. of reflns collected</td>
<td>20 673</td>
<td>10 734 (Rint = 0.0037)</td>
</tr>
<tr>
<td>no. of indep reflns</td>
<td>7601 (Rint = 0.0037)</td>
<td>10 734 (Rint = 0.0068)</td>
</tr>
<tr>
<td>abs cor</td>
<td>empirical with SADABS</td>
<td>SADABS</td>
</tr>
<tr>
<td>max and min transm</td>
<td>0.9383</td>
<td>0.9383</td>
</tr>
<tr>
<td>refinement method</td>
<td>full-matrix least-squares on F²</td>
<td>full-matrix least-squares on F²</td>
</tr>
<tr>
<td>data/restraints/params</td>
<td>7601/233/544</td>
<td>10734/040/448</td>
</tr>
<tr>
<td>goodness-of-fit on F²</td>
<td>1.065</td>
<td>1.007</td>
</tr>
<tr>
<td>final R Indices (I &gt; 2σ(I))</td>
<td>R1 = 0.0691, wR2 = 0.1909</td>
<td>R1 = 0.0461, wR2 = 0.1068</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0828, wR2 = 0.2084</td>
<td>R1 = 0.0848, wR2 = 0.1133</td>
</tr>
<tr>
<td>largest diff peak and hole, e Å⁻³</td>
<td>1.292 and 0.690</td>
<td>0.587 and –0.435</td>
</tr>
</tbody>
</table>

Sources: PLATON calculated the upper limit of volume that can be occupied by the solvent to be 2028.3 Å³, or 30.8% of the unit volume. The program calculated 512 electrons, which corresponds to four hexane and six toluene molecules, in the unit cell for the diffuse species. A similar treatment was applied to two severely disordered toluene molecules that were identified and refined in the asymmetric unit of complex 4. PLATON calculated the upper limit of volume that could be occupied by the solvent to be 208.3 Å³, or 22.5% of the unit volume. The program calculated 812 electrons, corresponding to eight toluene molecules, in the unit cell for the diffuse species. Note that all derived data in the following tables were based on known contents. No data are given for the diffusely scattering solvent molecules.

Results

Pinacolone Coupling Mediated by (TTP)Zr=NaN₅PR₃, 1.

Upon treatment of (TTP)Zr=NaN₅PR₃, 1, with 1 equiv of pinacolone, a new species was observed within 5 min. Product analysis was achieved by ¹H NMR spectroscopy.¹¹ The observation of a three-proton multiplet at 6.22 ppm, due to the meta and para Ar₅PR₃ protons, indicated that the NaN₅PR₃ moiety had been retained in the product. This chemical shift is close to the upfield signals found for the corresponding aryl protons of the imido complex, 1, at 6.08 ppm. Additionally, the new Ar₅PR₃ isopropyl proton chemical shifts, 0.46 (d, 6H), 0.32 (3d, 6H), –0.23 (m, 2H), 2.02 ppm, remain significantly upfield of those of the free amine [2.63 (s, 2H), 1.14 (d, 12H) ppm] and only slightly downfield from those found for complex 1 [0.18 (m, 2H), 0.00 (d, 12H) ppm]. The NH amido proton was observed at 0.95 ppm, similar to the chemical shifts reported for (TTP)Hf(NH₂Ph)(NH₅Ph)₂.² Signals at 3.02 (s, 1H), 1.35 (s, 1H), and –0.50 (s, 9H) ppm signify the presence of a single bound pinacolone fragment. The large variation in chemical shifts for the two geminal protons (vide infra) was unusual but must arise because of differences in position relative to the porphyrin ring current.

Three possible limiting isomers for this product, consistent with the ¹H NMR data, are shown in Figure 1. Distinctive ¹³C NMR resonances attributed to the bound pinacolone fragment, but not due to the tert-buty1 group, are found at 83.3 and 170.7 ppm. A HETCOR experiment revealed that the protons resonating at 3.02 and 1.35 ppm were both bound to the same carbon atom (83.3 ppm), precluding isomer 1. The proton resonating at 3.02 ppm displayed a through-space interaction with the tert-buty1 group (–0.50 ppm) in a NOESY experiment. Consequently, this proton must be cis to the tert-buty1 group. The ¹³C NMR data are incompatible with isomer 4 because the peak

(10) All software and sources of the scattering factors are contained in the SHELXTL V5.10 program library: G. Sheldrick, Siemens-AXS, Madison, WI.

(11) The large ring current of the aromatic porphyrin macrocycle provides a useful means for identifying metal-bound ligands through ¹H NMR. Upfield shifts of bound-ligand protons are commonly 1–4 ppm from those of the free ligand. The ring current effects on the ¹³C nuclei of metal-bound ligands of metalloporphyrin complexes are shifted to a smaller degree, which allows comparison of these resonances to those found in spectra of nonporphyrin metal analogues.
Zirconium and Hafnium Imido Complexes

\[ \text{Figure 1. Possible isomers from the addition reaction between complex I and pinacolone.} \]

\[ \text{Figure 2. Possible isomers of coupled-pinacolone derivatives consistent with } ^1\text{H NMR data.} \]

at 83.3 ppm is too far downfield for a C-bound enolate.\(^{(12)}\) A metalloence enolate complex, \(\text{Cp}^*\text{Zr(OH)}(\eta^1-\text{OC(=CH}_2)(\text{Bu})\), possesses similar \(^1\text{C NMR} \text{chemical shifts at 84.1 [OC(=CH}_2]=CH}_2\) and 172.8 ppm [OC(=CH}_2)(\text{Bu})]. The NMR data for the addition product are most consistent with an O-bound enolate, isomer III. The enolate complex (TPP)Zr(NAr\(^{3d}\))\([\text{OC(=CH}_2)(\text{Bu})], 2a, could not be isolated in pure form because of decomposition to intractable products during purification attempts.

The position of the olefinic proton was established by a NOESY experiment which showed through-space interactions of this hydrogen with both tert-butyl groups and the methyl group. Furthermore, the methyl group, which resonates at \(-0.69\) ppm, was also close, spatially, to the tert-butyl unit with the signal at \(-0.46\) ppm. Isomer IV was consistent with the NOESY experiment, while isomer V would exhibit an NOE interaction of the olefinic proton with only one tert-butyl group. The connectivity of the hydrocarbon backbone was definitively established by a HMBC experiment that showed two-bond coupling interactions between the olefinic proton and both carbon 3 and carbon 5 (see Figure 2 for numbering). Isomer V would contain a two-bond coupling of the olefinic proton to only one carbon atom. The chemical shifts of carbon 3 (160.0 ppm), carbon 4 (97.6 ppm), and carbon 5 (80.0 ppm) of the metallacycle backbone were assigned by HETCOR and HMBC NMR experiments.

In addition to 2-D NMR results, support for the assignment of the two tert-butyl groups in complex 2 was facilitated by deuterium labeling. Treatment of the imido complex 1 with 1 equiv of pinacolone followed by excess pinacolone-\(\text{d}_{12}\) produced complex 2 with a 9-proton singlet in the \(^1\text{H NMR} \text{spectra} \text{at} 0.04\) ppm. Conversely, treatment of complex 1 with 1 equiv of pinacolone-\(\text{d}_{12}\) and then with excess pinacolone-\(\text{d}_{6}\) produced enediolate complex 2 with a 9-proton singlet at \(-0.46\) ppm and a 3-proton singlet at \(-0.69\) ppm. These experiments also revealed that the source of the protons transferred to the imido group was the methyl group of the first pinacolone consumed. On the basis of the NMR structural analysis, the reaction sequence for pinacolone condensation with complex 1 is shown in eqs 1 and 2.

Complex 2 could also be synthesized by alternate routes. Formation of the enediolate compound 2 occurred on treatment of the ureato complex (TPP)Zr(NAr\(^{3d}\))\((\text{OC(=CH}_2)(\text{Bu})\)O) with excess pinacolone. The urea, NHA\(^{3d}\)C(=NH)\(\text{Bu})\), was a byproduct of this process. Treatment of (TPP)ZrCl\(_2\) with excess pinacolone in the presence of piperidine also resulted in the formation of complex 2. Although this was a more direct synthetic approach, it yielded impure product. A one-pot synthesis that involved adding excess pinacolone to in situ generated complex 1 produced complex 2 in a yield and purity comparable to those found for the reaction with isolated imido complex 1. Whereas the formation of complex 2 from enolate species 2a required hours to reach completion, treatment of complex 2b (the less bulky tolylamido analogue of 2a) with pinacolone resulted in the rapid formation of the enediolate compound.

The preceding investigation also employed hafnium in place of zirconium. Due to similarities of the two series of compounds, only the latter was addressed. The largest difference in the \(^1\text{H NMR} \text{data} \text{of} \text{the} \text{amido/enolato} \text{congeners} \text{was} \text{found} \text{for} \text{the} \text{methylene} \text{resonances}. \text{The} \text{geminal} \text{CH}_2 \text{resonances for} \text{3a (2.91, 1.18 ppm) were slightly} \text{upfield} \text{of} \text{those for} \text{2a (3.02, 1.35 ppm).} \text{Similarly, the olefinic} \text{resonance} \text{in} \text{the} \text{enediolate} \text{complex was} \text{upfield} \text{for} \text{the} \text{hafnium} \text{derivative (2.92 ppm) relative to} \text{that for} \text{the} \text{zirconium} \text{complex (3.00 ppm).} \text{Reaction} \text{times} \text{were} \text{observed} \text{to be} \text{somewhat} \text{longer} \text{for} \text{the} \text{heavier} \text{congener, as} \text{observed} \text{previously} \text{for} \text{other Hf} \text{and Zr metalloporphyrin complexes.} \text{Under identical reaction conditions, treatment of} \text{the} \text{respective imido complex, (TPP)M=NAr}^{3d}\text{M} = \text{Zr, Hf), with excess pinacolone produced the amide/enolate complex within minutes for zirconium and 1 h for hafnium.}


\(^{(13)}\) Conformational changes of the six-membered ring may serve as a possible source of disorder in the metallacycle as observed in the X-ray structure analysis.
Formation of Oxygen-Bridged Dimers 4 and 5. The bis-(μ-oxo) complex [(TTP)ZrO2], 4, was initially observed in the thermal decomposition of the N,O-bound ureato complexes (TTP)[Zr(μ2-NAr)2PC(==N-Bu)O] and (TTP)[Zr(μ2-NBuC(==NAr))O]2.14 A more facile route to complex 4 was found from the metathesis reaction between complex 1 and PhNO (eq 3).

\[
\begin{align*}
&\text{1} &\quad 2 \text{ PhNO} &\quad \rightarrow &\quad \text{2} \text{ PhN=NaPr} \\
&\text{2} &\quad Zr &\quad + &\quad \text{2} \text{ PhN=NaPr} \\
\end{align*}
\]

Dimer was formed in moderate yield along with the diazene PhN=NaPr. The 1H NMR spectrum of the bis(μ-oxo) species exhibited signals typical of zirconium metalloporphyrin complexes. The exception was an upfield shift of the β-pyrole signal to 8.44 ppm due to the face-to-face orientation of the two porphyrin rings. The β-pyrole signal remained as a singlet at 223 K in CDCl3, indicating fast rotation of the porphyrin rings relative to one another. Complex 4 readily undergoes hydrolysis upon exposure to water to produce the (μ-oxo)bis(μ-hydroxy) dimer, complex 5 (eq 4).

\[
\begin{align*}
&\text{4} &\quad + &\quad \text{H}_2\text{O} &\quad \rightarrow &\quad \text{5} \\
&\text{4} &\quad Zr &\quad + &\quad \text{H}_2\text{O} &\quad \rightarrow &\quad \text{5} \\
\end{align*}
\]

Compound 5 was found from heating a toluene solution of 5 at ~8.27 ppm (s, 2H) were found to be upfield of those reported for the tetraphenylporphyrin analogue (~6.73 ppm, s, 2H).15b

Crystal Structures of (TTP)Zr(OC(Bu)CHC(Bu)Me(O)2) (2), [(TTP)ZrO]2 (4), and [(TTP)Zr2(μ-O)(μ-OH)]2 (5). The crystallographic data for complexes 2, 4, and 5 are presented in Table 1, and selected metrical parameters are collected in Tables 2 and 3. All of the molecules exhibit typical out-of-plane displacements of the zirconium from the mean 4-Npyrrole plane for six- and seven-coordinate metals. In the case of complex 2, acquisition of high-quality crystals was not possible, despite numerous recrystallizations. These difficulties were attributed to the solvent-dependent nature of the crystals and volatile solvent molecules packed in the voids of the lattice. While extensive disorder in the enediolate ligand precluded anisotropic refinement of the carbon backbone, the oxygen atom identities were unequivocally established and were consistent with the results of spectroscopic experiments. A representation of complex 2 is given in Figure 3. The Zr–O bond distances of 1.963(6) [Zr–O1] and 1.945(7) Å [Zr–O2] compare well with those in alkoxy compounds16 but are considerably shorter than the single bonds observed in the four-atom metallacycles (TTP)Zr(μ2-NAr)2PC(==N-Bu)O]2.0667(12) Å and (TTP)Zr(μ2-NBuC(==NAr))O2. 17 Atom O1 eclipses the Zr–N2 bond within 2.0°, while atom O2 is staggered in relation to the Zr–N3 and Zr–N4 bonds by 62.5° and 26.5°, respectively. The Zr–N2 [2.290(10) Å], Zr–N4 [2.295(9) Å], and Zr–N1 [2.254(14) Å] bonds are long compared to Zr–N2 [2.177(9) Å] and Zr–N1 [2.254(8) Å] distances. These differences are likely due to contributions from nitrogen–oxygen repulsions [N2−O2 = 2.717(2) Å; N4−O2 = 2.721(2) Å].17

Table 2. Selected Bond Distances (Å) for Complexes 2, 4, and 5

<table>
<thead>
<tr>
<th>Complex</th>
<th>Zr−O1</th>
<th>Zr−O2</th>
<th>Zr−N1</th>
<th>Zr−N2</th>
<th>Zr−N3</th>
<th>Zr−N4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.963</td>
<td>1.945</td>
<td>2.254</td>
<td>2.290</td>
<td>2.177</td>
<td>2.295</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Zr displacement from N plane.

(14) A bis(μ-oxo) complex was reported previously, but no details on characterization were provided: Sewchok, M. G.; Haushalter, R. C.; Merola, J. S. Inorg. Chem. Acta 1988, 144, 47. (b) The isolated octaethylporphyrin analogue of complex 4 has been characterized by 1H NMR: Brand, H.; Arnold, J. Organometallics 1993, 12, 3655.

(h) The bis(μ-oxo) complex was reported previously, but no details on characterization were provided: Sewchok, M. G.; Haushalter, R. C.; Merola, J. S. Inorg. Chem. Acta 1988, 144, 47. (b) The isolated octaethylporphyrin analogue of complex 4 has been characterized by 1H NMR: Brand, H.; Arnold, J. Organometallics 1993, 12, 3655.

(h) The bis(μ-oxo) complex was reported previously, but no details on characterization were provided: Sewchok, M. G.; Haushalter, R. C.; Merola, J. S. Inorg. Chem. Acta 1988, 144, 47. (b) The isolated octaethylporphyrin analogue of complex 4 has been characterized by 1H NMR: Brand, H.; Arnold, J. Organometallics 1993, 12, 3655.
resulting from O–N interactions. The Zr1–Zr1A (3.0584(5) Å) and the O–O distances (2.5014 Å) are similar to those of previously described bridging zirconium porphyrin complexes.15a,b

Three common distortions from planarity of the porphyrin macrocycle were observed in complex 4.19 The doming effect was readily perceived in the deviations of the four pyrrole nitrogens from the 24-atom porphyrin plane [N1 (N1), 7 (N2), 17 (N3), and 9 (N4) pm]. The meso carbon atoms alternate above and below the mean 24-atom plane [15 (C5), 12 (C10), 16 (C15), and 12 (C20) pm] in a ruffling deformation. Although the saddle deformation of the porphyrin ring is perturbed by the presence of the other two distortions, it is observed in the deviations of the β-pyrrole atoms above and below the core porphyrin plane [−24 (C2), −15 (C3), 10 (C7), 1 (C8), −29 (C12), −19 (C13), 8 (C17), 2 (C18) pm].

The samples of [(TTP)Zr]2(μ-O)(μ-OH)2, 5, produced in this work are closely related to the previously described tetraphenylporphyrin derivatives [(TPP)Zr(μ-OH)2]215a and [(TPP)Zr]2(μ-O)(μ-OH)2.15b However, the OH proton resonance in complex 5 (8.27 ppm) was significantly shifted from those of the tetrahydroxy- (6.79 ppm) and the tetraphenylporphyrin dihydroxy analogues (6.73 ppm). Consequently, compound 5 was examined in a single-crystal X-ray diffraction study. The zirconium coordination environment and metrical parameters are unremarkable from those previously described by Kim and co-workers for [(TPP)Zr]2(μ-O)(μ-OH)2. However, the presence of staggered porphyrin rings in complex 5 (Figure 5) is in marked contrast to the other structurally characterized oxygen-bridged Zr and Hf metalloporphyrin species.15 The most acute torsion angle present in complex 5 involving a Zr–Npyrrole bond is 22.2° (N3–Zr1–Zr1A–N2A), whereas the corresponding angle in the TPP species is only 7.8°. The intramolecular

Discussion

Coupling of Pinacolone by (TTP)M=NArPr (M = Zr, Hf). The reactivity of the nitrene group in terminal zirconium and hafnium imido complexes has been documented in a number of studies.20 A comparable example of a Zr dX moiety reacting with a ketone occurs with Cp*2Zr(μ-O)(py) and acetophenone,
with aldehydes or ketones generally results in the formation of \( \eta^1 \)- or \( \eta^2 \)-bound \( \beta \)-hydroxy ketone complexes.\(^{22}\) However, as shown in Scheme 2, deprotonation of the \( \eta^2 \)-hydroxy ketone complex by the strong base NHAr\(^{-} \) results in the formation of a unique chelated enediolate product.\(^{23}\)

Intractable mixtures were obtained from the addition of acetone to 1 or 2a. However, the reaction between (TTP)Zr(\( \text{NHAr}^{\text{Bu}} \))[\( \text{OC}(==\text{CH}_3)\)(\text{Bu})], 2a, and 2-octanone resulted in a new enediolate complex, (TTP)Zr[\( \text{OC}(/\text{Bu})\text{CH(\text{hexyl})MeO} \]). Thus, this synthetic methodology may be extended to other ketones.

**Bridging Oxo Complexes.** An atom transfer route for the preparation of terminal oxo species of titanium porphyrin complexes was extended to Zr for the production of complex 4.\(^{24}\) Thus, the metathesis reaction between (TTP)Zr(\text{NHAr}^{\text{Bu}}) and nitrosobenzene cleanly produced the \( \mu \)-oxo dimer 4. The postulated transient monomeric oxo species (TTP)Zr\( \equiv \text{O} \) could not be trapped in the presence of excess THF or pyridine. Compound 4 is unreactive toward \text{BuNCO}, ketones, amines, and alcohols, including phenol. This lack of reactivity appears to be based, in part, on steric factors, since compound 4 is quickly hydrolyzed to compound 5. Further reactivity of complex 5 was not observed in the presence of phenol, tert-butylamine, aniline, or ZnEt\(_2\). A comparison of the structurally characterized oxygen-bridged complexes [(TTP)H\(_2\)(\( \mu \)-OH)\(_2\)-\( \mu \)-O)],\(^{15c}\) [(TTP)Zr(\( \mu \)-OH)\(_2\)(\( \mu \)-O)],\(^{15b}\) and \((\text{OEP})\text{Zr}(\text{O}-\text{H})_2\)-(7,8-\text{C}_5\text{B}_9\text{H}_12)\(^{15b}\) shows near-eclipsing of an M–O bond with an M–N bond and the presence of eclipsed porphyrin rings. This has been attributed to the presence of the \text{N} bond and the presence of eclipsed porphyrin rings. As the intramolecular steric properties of tetraphenylporphyrin are expected to be equivalent to those of tetratolylporphyrin, \( \pi \text{Zr} \text{d}–\pi \text{Zr} \) interactions between the Zr and O atoms in complexes 4 and 5 are not readily apparent.\(^{25}\)

It is interesting to note the structure of the only other known six-coordinate zirconium metalloporphyrin complex containing two O-bound ligands, (OEP)Zr(O(Bu))\(_2\).\(^{14b}\) First, the O–Zr–O angle of 90.08(9)° is rather large for this class of molecules.\(^{26}\) Second, the zirconium out-of-plane distance of 1.06 Å is the largest value reported for six-coordinate zirconium metalloporphyrin complexes. Although these features were attributed primarily to the steric bulk of the O(Bu) ligands, Zr–O \( \pi \)–bonding would most likely be enhanced by such an arrangement.\(^{27}\) Zirconium lies further toward the porphyrin plane and contains an O1–Zr1–O2 angle of 78.56(8)° in complex 4. The presence of \( \pi \text{Zr} \text{d}–\pi \text{Zr} \) interactions is expected in complex 4, albeit somewhat diminished, as evident in the metrical parameters described above.

**Conclusion**

New examples of the novel reactivity possessed by zirconium and hafnium imido metalloporphyrin complexes have been demonstrated. These complexes mediate the stepwise coupling

---

of pinacolone in the formation of an enediolate compound. Mixed-ketone condensation products are also possible. Moreover, we have developed direct synthetic routes to zirconium metalloporphyrin complexes containing bridging oxygen ligands. \((\text{TTP})\text{Zr}=\text{NArPr}\) undergoes metathesis with nitrosobenzene to produce the \(\mu\)-oxo-bridged dimer, \([[\text{TTP}]\text{ZrO}]_2\), 4. The bis(\(\mu\)-hydroxo)(\(\mu\)-oxo) dimer \([[\text{TTP}]\text{Zr}](\mu\text{-OH})_2(\mu\text{-O})\), 5, is a hydrolysis product of complex 4. Also of interest is the unique structural characteristic of staggered porphyrin rings found for complexes 4 and 5. This is in marked contrast to the eclipsed conformers known for other Zr and Hf analogues.

**Acknowledgment.** We are grateful for financial support from the Camille and Henry Dreyfus Foundation.

**Supporting Information Available:** X-ray crystallographic files in CIF format, for 2, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.