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Terminal Zirconium Oxo Complexes: Synthesis, Structure, and Reactivity of $(\eta^5\text{-}C_5Me_4R)_2Zr(O)(NC_5H_4R')$

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The transition metal oxo moiety ($M{=}O \leftrightarrow M^{-}{\equiv}O^{+}$) represents by far the largest class of metal–ligand multiple bonds studied to date. Although in part this reflects the important roles that metal oxo complexes play in many industrial and biological processes,[1-3] it must also be recognized that the common occurrence of such complexes undoubtedly derives from the thermodynamic stability imparted by the strong metal–oxo multiple bond. However, terminal oxo complexes are *not* ubiquitous for all the transition metals. In particular, molecular terminal oxo complexes of the group 4 transition metals (Ti, Zr, and Hf) are rare and are known only for titanium.[4,5] For zirconium and hafnium, only bridging μ-oxo complexes, *e.g.* $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}O)]_3$,[6] have been isolated previously.[7] Here we report the synthesis, structure, and reactivity of the complexes $(\eta^5\text{-}C_5Me_4R)_2Zr(O)(NC_5H_5)$ (R = Me, Et), which, to our knowledge, are the first isolated zirconium complexes with *terminal* oxo ligands.

Bergman's recent mechanistic and reactivity studies have provided excellent evidence that the zirconium oxo species $[Cp^*_2Zr{=}O]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) may be generated as a reactive intermediate by both (i) elimination of benzene from $Cp^*_2Zr(OH)(Ph)$ and (ii) deprotonation of $Cp^*_2Zr(OH)(OSO_2CF_3)$.[8] More recently, Andersen has shown that the reaction of Cp^*_2Ti with N_2O in the presence of pyridine allows the related titanium oxo species $[Cp^*_2Ti{=}O]$ to be stabilized as the pyridine adduct, $Cp^*_2Ti(O)(NC_5H_5)$,[5,9] analogous to the way in which Bergman stabilized the zirconium sulfido complex $Cp^*_2Zr(S)(NC_5H_5)$.[8] Stimulated by these results, we believed that the related zirconium oxo complex $Cp^*_2Zr(O)(NC_5H_5)$ could be isolated under suitable conditions. However, at the outset, the appropriate choice of zirconium starting material was not obvious since (i) the corresponding zirconium starting material $[Cp^*_2Zr]$ is unknown, (ii) the divalent derivative $Cp^*_2Zr(CO)_2$ has been reported to be unreactive toward N_2O,[10] (iii) the complex $Cp^*_2Zr(\eta^2\text{-}C_2Ph_2)$ reacts with N_2O to give a four-membered oxametallacycle $Cp^*_2Zr(\eta^2\text{-}OC_2Ph_2)$ and not an oxo derivative,[11] and (iv) the reactive intermediate $[Cp^*_2Zr{=}O]$, generated by deprotonation of $Cp^*_2Zr(OH)(OSO_2CF_3)$, could not be trapped with pyridine.[8a,12]

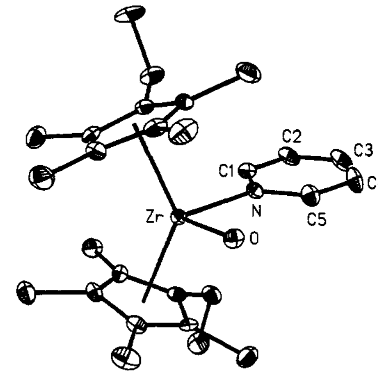
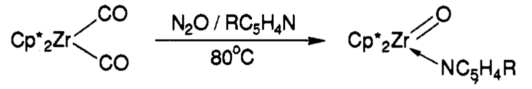


Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$. Selected bond distances (Å) and angle (deg): Zr–O 1.804(4), Zr–N 2.363(5); O–Zr–N 90.9(2).

We have previously observed that the sulfido complex $Cp^*_2Zr(S)(NC_5H_5)$ may be obtained by the reaction of the dicarbonyl $Cp^*_2Zr(CO)_2$ with sulfur in the presence of pyridine.[13] Prompted by this observation, and the results of Andersen and Bergman described above, we discovered that the zirconium oxo complexes $Cp^*_2Zr(O)(NC_5H_4R)$ (R = H, Bu^t) could also be isolated from the reaction of $Cp^*_2Zr(CO)_2$ with N_2O in the presence of the appropriate pyridine at 80 °C (eq 1).[14,15]



$$Cp^*_2Zr(CO)_2 \xrightarrow[80\,^{\circ}C]{N_2O\,/\,RC_5H_4N} Cp^*_2Zr(O)(NC_5H_4R) \qquad (1)$$

The tetramethylethylcyclopentadienyl analogue $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$ may also be synthesized by a similar procedure. Significantly, the molecular structure of $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$ has been determined by X-ray diffraction, as shown in Figure 1, thereby confirming the presence of a terminal oxo ligand in these complexes.[16] Notably, the Zr=O bond length [1.804(4) Å] in $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$ is substantially shorter than the Zr–O single bonds in the related hydroxy complexes $Cp^*_2Zr(OH)_2$ [1.975(8) and 1.982(7) Å],[17] $Cp^*_2Zr(OH)_2{\cdot}(H_2O)$

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(9) In the absence of pyridine, Bottomley has reported that an oxo-bridged complex $Cp^*Ti(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_5CH_2)(\mu\text{-}O)_2TiCp^*$ is obtained. Bottomley, F.; Egharevba, G. O.; Lin, I. J. B.; White, P. S. *Organometallics* **1985**, *4*, 550–553.

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(12) Furthermore, both $Cp^*_2Zr(OH)_2$ and $Cp^*_2Zr(OH)Cl$ have also been considered as potential precursors to a terminal zirconium oxo complex (ref 17), but the success of this approach has not been reported.

(13) Howard, W. A.; Parkin, G. *Organometallics*, in press.

(14) All new complexes have been fully characterized, and the molecular structures of $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$, $Cp^*_2Zr\{\eta^2\text{-}OC(H)(Bu^t)OC(H)(Bu^t)O\}$, $Cp^*_2Zr\{\eta^1\text{-}OC(Ph){=}CH_2\}(OH)$, $Cp^*_2Zr(NHPh)(OH)$, and $Cp^*_2Zr(\eta^2\text{-}NH_2NPh)(OH)$ have been determined by single-crystal X-ray diffraction.

(15) Unidentified products are obtained in the absence of pyridine, in contrast to the previous report which describes that $Cp^*_2Zr(CO)_2$ is inert to N_2O (ref 10).

(16) $(\eta^5\text{-}C_5Me_4Et)_2Zr(O)(NC_5H_5)$ is orthorhombic, $Pc2_1n$ (No. 33), a = 9.681(3) Å, b = 14.124(3) Å, c = 18.134(3) Å, V = 2479.5(7) Å^3, Z = 4.

(17) Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 456–458.

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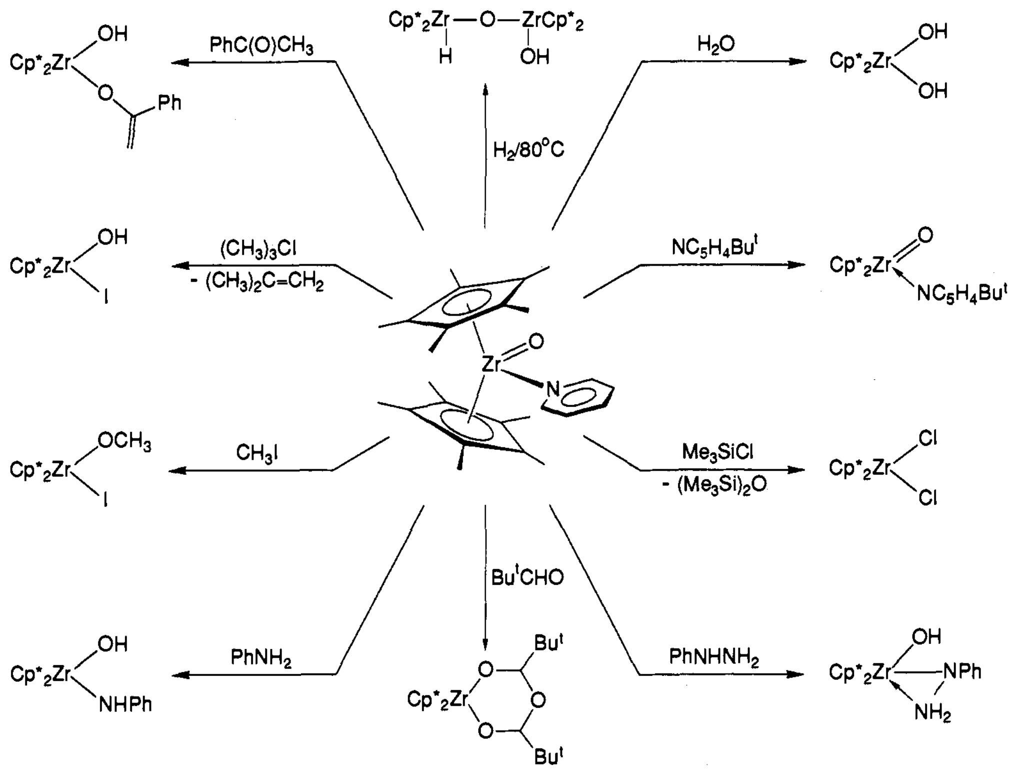
Scheme I. Reactivity of Cp*$_2$Zr(O)(NC$_5$H$_5$)



[1.976(2)–2.028(3) Å],[18] and Cp*$_2$Zr(OH)Cl [1.950(2) Å],[17] and also the trimeric oxo derivative [Cp$_2$Zr(μ-O)]$_3$ [1.950(6)–1.966(5) Å].[6] The Zr═O bond length in (η^5-C$_5$Me$_4$Et)$_2$Zr(O)(NC$_5$H$_5$) is also shorter than the Zr–O interactions in the infinite chain anion [Zr(O)(μ-O)$_2$$^{2-}$]$_\infty$ that is present in Cs$_2$ZrO$_3$ [1.91(2) and 2.091(6) Å].[19]

The terminal oxo ligand in Cp*$_2$Zr(O)(NC$_5$H$_5$) is also characterized by a ν(Zr═O) IR absorption at 780 cm^{-1},[20] which may be compared with the values for related metallocene oxo complexes: Cp*$_2$Ta(O)H (850 cm^{-1}),[21] Cp*$_2$W═O (860 cm^{-1}),[22] Cp$_2$W═O (799–879 cm^{-1}),[23] and Cp$_2$Mo═O (793–868 cm^{-1}).[23] As such, the zirconium–oxo interaction in 18-electron Cp*$_2$Zr(O)(NC$_5$H$_5$) is best represented as a Zr═O double bond, with little triple bond Zr$^-$≡O$^+$ character.

The highly reactive nature of the terminal zirconyl group in Cp*$_2$Zr(O)(NC$_5$H$_5$) is illustrated in Scheme I, in which the Zr═O moiety reacts with both polar (X$^{\delta+}$–Y$^{\delta-}$) and nonpolar substrates to give products Cp*$_2$Zr(OX)(Y) that may be considered to be derived by a formal 1,2-addition across the Zr═O double bond (Scheme I). In particular, the facile reaction with H$_2$ at 80 °C to give [Cp*$_2$Zr(H)](μ-O)[Cp*$_2$Zr(OH)],[24] presumably via the intermediate [Cp*$_2$ZrH(OH)], underscores the high reactivity of this oxo complex. Furthermore, reaction with Me$_3$SiCl results in complete abstraction of oxygen from the zirconium center to give the dichloride Cp*$_2$ZrCl$_2$ and (Me$_3$Si)$_2$O.

As expected by analogy with Bergman's work, Cp*$_2$Zr(O)(NC$_5$H$_5$) undergoes a cycloaddition reaction with PhCN to give the six-membered metallacycle Cp*$_2$Zr{η^2-OC(Ph)NC(Ph)N}.[8] In addition, we have also observed a cycloaddition reaction with the aldehyde Bu^{t}CHO to give the six-membered metallacycle Cp*$_2$Zr{η^2-OC(H)(Bu^t)OC(H)(Bu^t)O}. However, in marked contrast, cycloaddition reactions are not observed with the methyl ketones RC(O)CH$_3$ (R = Me, Bu^t, Ph). In preference, the oxo group deprotonates the ketone with the resultant formation of an enolate derivative, Cp*$_2$Zr(OH){η^1-OC(R)═CH$_2$}.[25] The basicity of the oxo ligand is also illustrated by its ability to dehydrohalogenate alkyl iodides to give the hydroxy–iodide derivative Cp*$_2$Zr(OH)I and eliminate the olefin. Thus, whereas CH$_3$I specifically undergoes 1,2-addition across the Zr═O group giving Cp*$_2$Zr(OCH$_3$)I, (CH$_3$)$_3$CI specifically undergoes dehydrohalogenation resulting in the formation of the hydroxy–iodide derivative Cp*$_2$Zr(OH)I and (CH$_3$)$_2$C═CH$_2$.

In summary, the terminal zirconium oxo complexes (η^5-C$_5$Me$_4$R)$_2$Zr(O)(NC$_5$H$_5$) have been synthesized, and the high reactivity associated with the Zr═O moiety is manifested by its reduction with H$_2$ and its ability to dehydrohalogenate alkyl halides and enolize methyl ketones.

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Supplementary Material Available: Tables of crystal structure data for (η^5-C$_5$Me$_4$Et)$_2$Zr(O)(NC$_5$H$_5$) and characterization data for all new compounds (28 pages); listing of observed and calculated structure factors for (η^5-C$_5$Me$_4$Et)$_2$Zr(O)(NC$_5$H$_5$) (12 pages). Ordering information is given on any current masthead page.

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(20) ν(Zr═O) is assigned by comparison of the IR spectra of Cp*$_2$Zr(O)(NC$_5$H$_5$), Cp*$_2$Zr(S)(NC$_5$H$_5$), Cp*$_2$Zr(Se)(NC$_5$H$_5$), and Cp*$_2$Zr(Te)(NC$_5$H$_5$).

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(25) For examples of some related zirconium enolate complexes, see ref 11b.