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Formation of α,β-Unsaturated Imines and Successful Trapping of Oxozirconocene in a [4 + 2] Azaoxametallacyclohexene Retrocycloaddition

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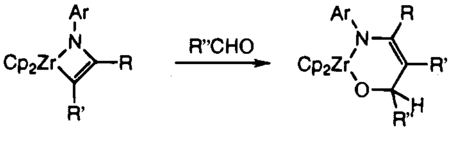
Monomeric transition metal oxo complexes (M=O), especially those involving metals in the middle of the transition series, such as W, Mo, and Re, are well-known[1,2] and are normally very stable.[3] Group 4 oxometallocene complexes have been found to be much more reactive and are often difficult to isolate. The reactive monomeric titanocene and zirconocene intermediates [$Cp^*_2Zr{=}O$] and [$Cp^*_2Ti{=}O$], containing sterically bulky (η^5-C_5Me_5) ligands, have recently been generated and trapped with various organic molecules.[4−8]

In contrast to the Cp* Group 4 oxo complexes, their unsubstituted cyclopentadienyl analogues have eluded characterization or even successful trapping by external reagents. We report here (1) the synthesis of a series of new azaoxametallacyclohexenes by migratory insertion of aldehydes into the Zr−C bonds of azametallacyclobutenes; (2) clean thermal [4 + 2] retrocycloaddition of these molecules to give α,β-unsaturated imines; and (3) a new type of trapping reaction, along with kinetic evidence, that supports the generation of monomeric $Cp_2Zr{=}O$ as a coproduct of the imines. Our results also provide support for the intervention of analogous six-membered oxametallacycle intermediates and their subsequent [4 + 2] retrocycloaddition postulated recently by Doxsee *et al.* in the reactions of titanacyclobutenes with aldehydes.[9]

Benzaldehyde reacts with the dark purple azametallacycle **1** to give a 56% yield of the orange insertion product **3** at 25 °C in 12 h (eq 1). Insertion of aldehydes into metal−carbon bonds of metallacycles has been observed in several cases,[10−12] but to our knowledge, the structures of these insertion products have been determined only by spectroscopic methods. We therefore undertook an X-ray diffraction study of the insertion product to confirm and further elucidate the structure (Figure 1).[13] The C=C bond appears to be quite localized. The phenyl ligands are twisted to reduce steric interference, and there is a slight distortion of the Zr coordination from C_{2v} symmetry due to steric interactions. The organic portion of the ring is planar, with the Cp_2ZrO moiety at an angle to the plane. The addition of 2-methylpropionaldehyde or benzaldehyde to the dark blue azametallacyclobutene **2** over a period of a few minutes at 25 °C in toluene resulted analogously in the formation of orange complexes **4** and **5a**, respectively (eq 1). We believe these to be the aldehyde insertion products illustrated in eq 1 on the basis of spectroscopic evidence and their similarity to complex **3**.



(1)

Ar = 2,6-dimethylphenyl
1 R = R' = Et
2 R =Me, R' = Ph

3 R = R' =Et, R" = Ph
4 R = Me, R' = Ph, R" = *i*-Pr
5a R =Me, R' = Ph, R" = Ph

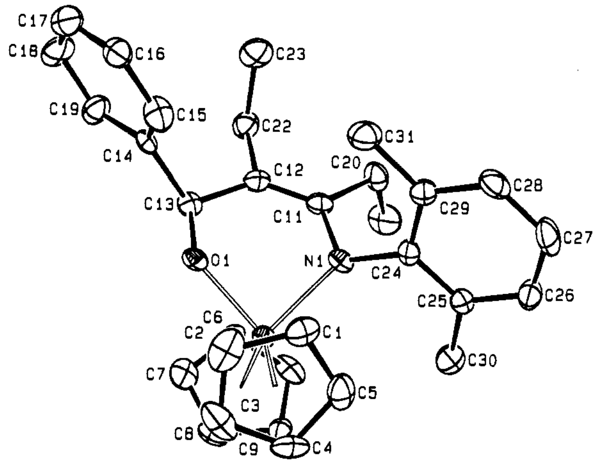


Figure 1. ORTEP diagram of the molecular structure of $Cp_2Zr(N(2,6\text{-}Me_2C_6H_3)CEt{=}CEtCH(Ph)O)$ (**3**).

Heating the aldehyde insertion product **5a** resulted in the formation of the α,β-unsaturated imine **6a** in 72% yield (Scheme 1). A white insoluble precipitate, believed to be an oligomeric zirconocene oxide,[14,15] was formed during the course of the reaction. In previous studies we have found that Cp_2ZrMe_2 is an extremely effective water scavenger, reacting quickly and stoichiometrically with water at room temperature to form the known[16] μ-oxo complex $[Cp_2ZrMe]_2O$ (**7**) and methane. To ensure that the thermolysis of **5a** was occurring under completely anhydrous conditions, we added an excess of Cp_2ZrMe_2 to the zirconacycle **5a** in solution at room temperature. NMR analysis showed the immediate appearance of a small amount (1−3%) of **7** due to scavenging of trace water in solution but no further reaction with the excess dimethyl complex present. The dry solution was then heated to 45 °C to effect conversion of **5a** to the imine. Under these conditions, no white precipitate was formed; instead, a quantitative additional amount (based on **5a**) of $[Cp_2ZrMe]_2O$ grew in as the retrocycloaddition reaction proceeded. No other zirconium-containing products were observed.

The observations summarized above support the mechanism illustrated in Scheme 1, in which thermal decomposition of **5a** produces imine **6a** and monomeric $Cp_2Zr{=}O$, as would be

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[1] Nugent, W. A.; Mayer, J. A. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[2] Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401 and references therein.

[3] Apparent exceptions among organometallic oxo compounds include certain Cp*Re oxo complexes (Herrmann, W. A. *J. Organomet. Chem.* **1986**, *300*, 111) and $Cp^*_2W{=}O$ (Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391).

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[9] Doxsee, K. M.; Mouser, J. K. *Tetrahedron Lett.* **1991**, *32*, 1687.

[10] Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1991**, *113*, 8889.

[11] Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

[12] Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994.

[13] The X-ray diffraction studies were carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Details of this study are provided as supplementary material.

[14] Our identification of the precipitate is based on reaction stoichiometry. To our knowledge, an insoluble oligomeric zirconocene oxide has not been characterized, although the slightly soluble trimeric species $[Cp_2ZrO]_3$ has been previously characterized (see following reference). A small peak (averaging about 5% of conversion) at δ 6.21 in C_6D_6, corresponding to $[Cp_2ZrO]_3$, is usually observed in our experiments.

[15] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

[16] Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.

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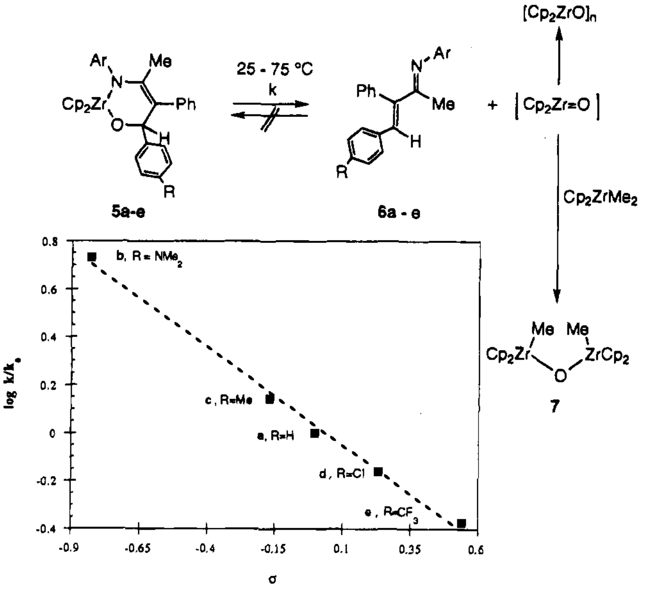
Scheme 1



expected from a simple retrocycloaddition reaction. The oxozirconium complex oligomerizes in the absence of Cp_2ZrMe_2, but in the presence of the dimethyl complex, it is efficiently trapped to give the μ-oxo complex **7**.[17] To obtain kinetic support for this mechanism, the rate of retrocycloaddition in C_6H_6 was measured. With no dimethyl complex present as a trap, the disappearance of starting material was monitored by UV/vis spectroscopy at temperatures between 45 and 75 °C. The reaction was also followed by NMR spectroscopy to confirm that the appearance of imine product exhibited the same rate behavior as the disappearance of starting material. The retrocycloaddition exhibited excellent first-order kinetics at each temperature.[18] An Eyring plot of the rate data gave activation parameters $\Delta H^{\ddagger} = 26.5$ kcal/mol and $\Delta S^{\ddagger} = 3.48$ eu. The positive entropy is consistent with a unimolecular rate-determining step, although its magnitude is somewhat smaller than that measured for retro-Diels–Alder reactions; this may indicate a relatively early transition state.

Measurement of the rate in the presence of both negligible and large amounts of added Cp_2ZrMe_2 had no effect on the measured rate constants.[19] Addition of imine **6a** also had a negligible effect on the rate.[20] These experiments demonstrate that the dimethyl complex reacts with an intermediate, most likely $Cp_2Zr{=}O$, generated after the rate-determining step, and furthermore that the formation of the oxo complex and imine is not detectably reversible (Scheme 1). Reverse reaction of $Cp_2Zr{=}O$ with an α,β-unsaturated imine was also sought by examining the retrocycloaddition of p-NMe_2-substituted metallacycle **5e** with an excess of p-CF_3-substituted imine **6e**. This combination was chosen because complex **5b** undergoes retrocycloaddition readily at room temperature, whereas **5e** is completely stable under these conditions. However, no exchange to give **5e** was observed at room temperature over several days as **5b** decomposed to imine **6e** and $[Cp_2Zr{=}O]_n$. This once again supports a mechanism involving no reversion of $Cp_2Zr{=}O$ and **6** back to **5**.

The effect of electronically different substituents was investigated by examining the retrocycloaddition of a series of metallacycles **5a–e** having different substituents on the phenyl group α to the oxygen atom, prepared by migratory insertion reactions of the appropriate aldehydes. Once again, clean first-order kinetics were observed in each case. A Hammett plot of the data is shown in Scheme 1; the ϱ value for the reaction is -0.8. This indicates that there is a buildup of positive charge in the transition state on the carbon α to the oxygen, or alternatively that the starting material **5** is stabilized by electron-withdrawing substituents on the phenyl ring. In order to obtain information about which of these interpretations is more likely, a preliminary investigation of the dependence of the reaction rate on solvent polarity was undertaken. When the retrocycloaddition was repeated in tetrahydrofuran (dielectric constant $(\epsilon) = 7.58$) rather than benzene ($\epsilon = 2.28$), the rate was actually slightly slower, favoring the latter explanation. This initial-state effect may be due to inductive stabilization of a partial negative charge on the oxygen α to zirconium.

In summary, we believe our results provide strong evidence that thermal decomposition of azaoxametallacycles of type **5** involves simple [4 + 2] retrocycloaddition, analogous to organic retro-Diels–Alder reactions, and that monomeric $Cp_2Zr{=}O$ is generated. Efforts are under way aimed at studying the mechanisms of these reactions in more detail and at locating other reagents that might be capable of trapping the monomeric oxo complex so that more might be learned about its chemical properties.

Acknowledgment. We acknowledge Dr. F. J. Hollander, director of the University of California, Berkeley, X-ray diffraction facility (CHEXRAY), for performing the crystal structure determination of complex **3**. Support for this work was provided by the National Institutes of Health (Grant No. R37GM25459).

Supplementary Material Available: Spectroscopic and analytical data for complexes **2–6a**; tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, and intramolecular distances and angles for **3**; and representative kinetic plots (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(17) A control experiment verified that Cp_2ZrMe_2 does not react with the products of **5** → **6** + $[Cp_2ZrO]_n$ if added after the reaction is complete.

(18) The rate constants for the retrocycloaddition **5a** → **6a** + $[Cp_2ZrO]_n$ in C_6H_6 followed by UV/vis spectroscopy are as follows: 45.0 °C, $(2.63 \pm 0.01) \times 10^{-5}\ s^{-1}$; 54.6 °C, $(8.2 \pm 0.2) \times 10^{-5}\ s^{-1}$; 63.6 °C, $(28.2 \pm 0.2) \times 10^{-5}\ s^{-1}$; 73.6 °C, $(87.3 \pm 0.5) \times 10^{-5}\ s^{-1}$.

(19) When the retrocycloaddition reaction **5c** → **6c** + $[Cp_2Zr{=}O]$ was followed by UV/vis spectroscopy in C_6H_6 at 45 °C in the absence and presence of excess Cp_2ZrMe_2, the rate constants varied only slightly: 0 equiv of Cp_2ZrMe_2, $k = (3.6 \pm 0.1) \times 10^{-5}\ s^{-1}$; 9 equiv of Cp_2ZrMe_2, $k = (3.46 \pm 0.03) \times 10^{-5}\ s^{-1}$; 25 equiv of Cp_2ZrMe_2, $k = (3.13 \pm 0.03) \times 10^{-5}\ s^{-1}$.

(20) When the retrocycloaddition reaction **5e** → **6e** + $[Cp_2Zr{=}O]$ was followed by UV/vis spectroscopy in C_6H_6 at 75 °C in the absence and presence of excess **6e**, the rate constants varied only slightly: 0 equiv of **6e**, $k = (3.97 \pm 0.03) \times 10^{-4}\ s^{-1}$; 3.5 equiv of **6e**, $k = (3.12 \pm 0.08) \times 10^{-4}\ s^{-1}$; 8 equiv of **6e**, $k = (4.7 \pm 0.1) \times 10^{-4}\ s^{-1}$; *ca.* 10 equiv of **6e**, $k = (3.45 \pm 0.03) \times 10^{-4}\ s^{-1}$.