MODEL STUDIES IN HYDROCARBON OXIDATION

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Progress Report (1 April - 31 November 1993)

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Introduction

The research performed during the period 1 April - 31 November 1993 has centered on an investigation of the chemistry of molecular terminal oxo complexes. In the long term, it is hoped that this research will provide results that are relevant to systems concerned with hydrocarbon oxidation. We have also carried studies of transition metal complexes that contain terminal sulfido, selenido and tellurido ligands, since a knowledge of the chemistry of the heavier congeners of this group will help provide a more complete understanding of the chemistry of transition metal oxo complexes. Furthermore, the chemistry of the metal sulfido derivatives will be directly related to hydrodesulfurization, an extremely important industrial process, for which transition metal-sulfido derivatives, *e.g.* MoS_2 , are active catalysts.

Terminal Oxo, Sulfido, Selenido and Tellurido Complexes of Zirconium

Although the transition metal oxo moiety represents by far the largest class of metal-ligand multiple bond studied to date, 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. For zirconium and hafnium, only bridging μ -oxo complexes, *e.g.* $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-O})]_3$, have been isolated previously, even though Bergman has recently provided excellent evidence that the zirconium oxo species $[\text{Cp}^*\text{Zr=O}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) may be generated as a reactive intermediate by both (i) elimination of benzene from $\text{Cp}^*\text{Zr}(\text{OH})(\text{Ph})$ and (ii) deprotonation of $\text{Cp}^*\text{Zr}(\text{OH})(\text{OSO}_2\text{CF}_3)$. The

rarity of terminal zirconium oxo complexes suggests that they are likely to be very reactive, and stimulated by Bergman's results, we have been able to isolate the first terminal zirconium oxo complex $\text{Cp}^*_2\text{Zr}(\text{O})(\text{NC}_5\text{H}_5)$ by the reaction of $\text{Cp}^*_2\text{Zr}(\text{CO})_2$ with N_2O in the presence of pyridine at 80°C (equation 1).

Modification of this approach allows the syntheses of the related terminal sulfoxo, selenido and tellurido derivatives $\text{Cp}^*_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ (equation 2).

Hence, the complete series of terminal chalcogenido complexes $\text{Cp}^*_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ ($\text{E} = \text{O, S, Se, Te}$) is now available for study. Such a result is important since we are provided with a rare opportunity to investigate the chemistry of the metal-chalcogenido moiety as a function of the chalcogen in a structurally related series of compounds.

The molecular structures of the chalcogenido complexes $\text{Cp}^{\text{Et}*}_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ ($\text{E} = \text{O, S, Se, Te}$) have been determined by single crystal X-ray diffraction. Of particular significance, the complexes $\text{Cp}^{\text{Et}*}_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$ ($\text{E} = \text{O, S, Se, Te}$) represent the first complete series of terminal chalcogenido complexes of the transition metals to be structurally characterized. Three possible covalent resonance forms may be considered to describe the metal-chalcogenido interaction, as shown below.

A detailed consideration of the changes in bond lengths for the series of chalcogenido complexes leads to the conclusion that the $\text{Zr}=\text{O}$ double bond is anomalously short.

The triply-bonded resonance structure $\overset{-}{\text{Zr}}\equiv\overset{+}{\text{E}}$ is considered to be of high energy (since it represents a 20-electron species), and so it is likely that the shortening of the $\text{Zr}=\text{O}$ bond reflects an ionic contribution $\overset{+}{\text{Zr}}-\overset{-}{\text{O}}$ which becomes more significant for the more electronegative chalcogen. Indeed, the empirical Schomaker-Stevenson equation would predict a shortening of *ca.* 0.2 Å for a $\text{Zr}-\text{O}$ bond due to a polar contribution. Thus, in addition to the resonance form $\text{Zr}=\text{O}$, it appears that the resonance form $\overset{+}{\text{Zr}}-\overset{-}{\text{O}}$ also provides an important contribution for the description of

the zirconium-oxo interaction in $\text{Cp}^{\text{Et}*}_2\text{Zr}(\text{O})(\text{NC}_5\text{H}_5)$. In contrast, for the heavier chalcogens, the lower electronegativity of E, coupled with the longer Zr-E bond length, would result in a lower Coulombic stabilization for the Zr^+-E^- resonance form. As such, the ionic contribution Zr^+-E^- would be expected to play a less significant role in describing the zirconium-chalcogenido moiety for the heavier chalcogens.

In addition to establishing a series of $\text{Zr}=\text{E}$ double bond lengths, we have also sought to provide a comparison between terminal $\text{Zr}=\text{E}$ double and $\text{Zr}-\text{E}$ single bond lengths. As expected, each $\text{Zr}=\text{E}$ double bond is substantially shorter than the corresponding $\text{Zr}-\text{E}$ single bond, the difference ranging from 0.19 Å for oxygen to 0.15 Å for tellurium. However, it is particularly noteworthy that the relative decrease in the length of the double bond, compared to that of the single bond, is greatest for the oxo derivative (9.6 % decrease) and least for the tellurido derivative (5.0 % decrease). Such an observation is presumably a reflection of the general abilities of oxygen and tellurium to partake in multiple bonding.

Reductive Coupling of Chalcogenido Ligands

The reductive-coupling of chalcogenido ligands (and the microscopic reverse, oxidative-cleavage) represents an important fundamental transformation. For example, the formation of a metal dioxo complex from dioxygen may involve oxidative-cleavage. We have observed the first well-defined example of the reductive-coupling of chalcogenido ligands by studying the chemistry of $\text{W}(\text{PMe}_3)_4(\text{Te})_2$. Thus, addition of Bu^tNC to $\text{W}(\text{PMe}_3)_4(\text{Te})_2$ results in reductive-coupling of the tellurido ligands to give the η^2 -ditellurido derivative $\text{W}(\text{PMe}_3)(\text{CNBu}^t)_4(\eta^2\text{-Te}_2)$ (equation 3).

Examination of the coordination modes of the Bu^tNC ligands in $\text{W}(\text{PMe}_3)(\text{CNBu}^t)_4(\eta^2\text{-Te}_2)$ offers some insight into the coupling reaction. Thus, $\text{W}(\text{PMe}_3)(\text{CNBu}^t)_4(\eta^2\text{-Te}_2)$ exhibits two types of Bu^tNC ligands, namely (i) two mutually *trans* Bu^tNC ligands that possess effectively linear geometries at nitrogen with C-N-Bu^t bond angles of $167(2)^\circ$, and (ii) two mutually *cis* Bu^tNC ligands that are markedly bent at nitrogen, with C-N-Bu^t bond angles of $138(1)^\circ$ and $146(2)^\circ$. Although not as common as linear coordination, bent coordination of isocyanides isprecedented. The occurrence of a bent isocyanide ligand is indicative of extensive π -back-bonding and is therefore associated with a resonance form of the type $\text{M}=\text{C}=\ddot{\text{N}}-\text{R}$, in contrast to $\bar{\text{M}}-\text{C}\equiv\overset{+}{\text{N}}-\text{R}$ for linear coordination. Therefore, as a consequence of the strong π -acceptor character, which reduces electron density at the tungsten center and thereby stabilizes the lower valence state, the Bu^tNC ligands would be expected to promote the reductive-coupling of the two tellurido ligands. In contrast, the strong σ -donor PMe_3 ligands (with little π -acceptor character) stabilize higher valence states and so would be expected to inhibit the reductive-coupling of the two tellurido ligands.

It is anticipated that an understanding of the factors that influence the interconversion of $[\text{M}](\text{Te})_2$ and $[\text{M}](\eta^2\text{-Te}_2)$ moieties will also have implications for the coupling and cleavage of ligands in other systems, such as the interconversion of $[\text{M}](\text{O})_2$ and $[\text{M}](\eta^2\text{-O}_2)$ groups.

Publications Citing DOE Support

1. "Isocyanide-Induced Coupling of Terminal Tellurido Ligands: The Synthesis and Structure of $\text{W}(\text{PMe}_3)(\text{CNBu}^t)_4(\eta^2\text{-Te}_2)$." Daniel Rabinovich and Gerard Parkin, *J. Am. Chem. Soc.* **1993**, *115*, 9822.
2. "Terminal Oxo, Sulfido, Selenido and Tellurido Complexes of Zirconium, $(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Zr}(\text{E})(\text{NC}_5\text{H}_5)$: Comparison of Terminal Zr-E Single and Zr=E Double Bond Lengths." William A. Howard and Gerard Parkin, *J. Am. Chem. Soc.* in press.

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