Stereospecific Heteroatom and Hetero Group Transfer from Oxiranes, Thiiranes, and Aziridines by a Simple Alkyl Tantalocene

Grant Proulx and Robert G. Bergman*

Department of Chemistry, University of California
Berkeley, California 94720-1460

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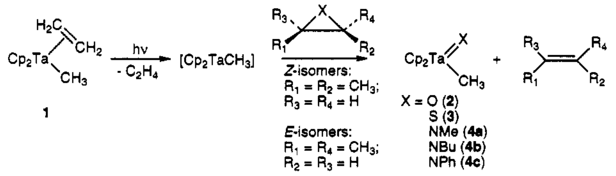
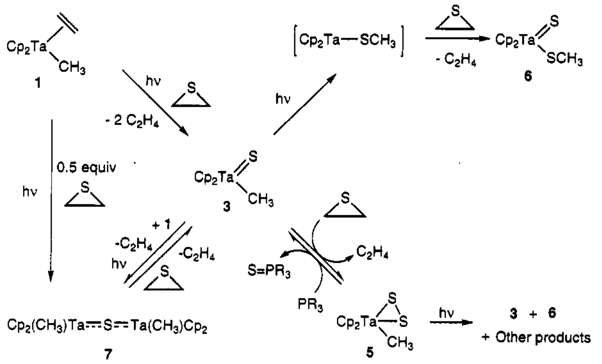
Oxygen and sulfur atom abstraction from oxiranes and thiiranes, on clean metal surfaces and in homogeneous solution, has often been studied as a way of obtaining fundamental information about carbon–oxygen and –sulfur bond cleavage that might ultimately be useful in understanding deoxygenation and desulfurization processes.[1–9] Much remains to be learned about the mechanisms of these reactions, and even less is known about the mechanism of the removal of nitrogen-containing species from commercial fuels and synthetic crudes, an important process because nitrogen compounds are poisons for re-forming and cracking catalysts and produce NO_x emissions on combustion.[10–12]

Because of their high oxygen, sulfur, and nitrene group affinity, low-valent early transition metal complexes such as group 5, d^2 species are ideal candidates for heteroatom abstraction processes.[13] Sterically demanding cyclopentadienyl ligands such as $Cp^{t\text{-Bu}}$ ($Cp^{t\text{-Bu}} = \eta^5\text{-}t\text{-BuC}_5H_4$)[14] and Cp* (Cp* = $\eta^5\text{-}C_5Me_5$)[15–19] stabilize these complexes, but they also hinder some of their further reactions. With this in mind we have investigated the photochemistry of the simple alkyltantalocene complex $Cp_2Ta(CH_3)(C_2H_4)$[20] (Cp = $\eta^5\text{-}C_5H_5$; compound **1** in Scheme 1). We have found that irradiation of **1** cleanly generates an intermediate that behaves as $Cp_2Ta(CH_3)$.[21–23] This species efficiently abstracts heteroatoms and hetero groups from the corresponding oxiranes, thiiranes, and aziridines, resulting in the formation of $Cp_2Ta({=}X)(CH_3)$ (X = O (**2**); S, (**3**); and NR (**4a–c**)) and alkene. Surprisingly, the sulfido product **3** retains a dual reactivity toward thiiranes. It undergoes further thermal sulfur atom abstraction from thiirane to give $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ (**5**) and, in a competing photochemical pathway, the sulfido thiolate complex, $Cp_2Ta({=}S)(SCH_3)$ (**6**). All the heteroatom and hetero group transfer reactions are completely stereospecific at carbon. These results constitute a rare example of nitrene group transfer from an aziridine to a metal center[24,25] (and the first one that has been demonstrated to be stereospecific) and the first formation of a soluble thiolate from a metal–alkyl sulfide species.

Scheme 1



Scheme 2



Photolysis of a C_6D_6 solution of $Cp_2Ta(C_2H_4)(CH_3)$ (**1**) in the presence of 1 equiv of *cis*-2,3-dimethyloxirane at 5 °C leads to the prompt evolution of free ethylene and (*Z*)-2-butene along with the previously characterized[26,27] oxo species, $Cp_2Ta({=}O)(CH_3)$ (**2**) in quantitative yield (^1H NMR).[28] Photolysis of the *trans*-oxide in the presence of **1** gives (*E*)-2-butene and **2**. Similarly, photolysis of **1** in the presence of 1 equiv of *cis*- or *trans*-2,3-dimethylthiirane gives $Cp_2Ta({=}S)(CH_3)$ (**3**) (81% isolated) along with the corresponding stereopure alkenes (Scheme 1). Compound **3** can be generated independently in high yield (^1H NMR) by photolysis of **1** in the presence of stoichiometric amounts of $S{=}PMe_3$.

In contrast to the above results, when 2 equiv of **1** is irradiated with 1 equiv of thiirane or $S{=}PMe_3$ (Scheme 2), the diamagnetic bridging sulfido species $Cp_2(CH_3)Ta(\mu\text{-}S)Ta(CH_3)Cp_2$ (**7**) is formed along with olefin or phosphine, respectively. This complex can be similarly obtained by the photolysis of **1** in the presence of 1 equiv of **3** and can be isolated as intensely colored blue crystals from benzene/pentane in 93% yield. Treatment of a solution of **7** with a second equivalent of thiirane or phosphine sulfide forms 2 equiv of **3** and 1 equiv of olefin or phosphine in essentially quantitative yield (^1H NMR).

When a solution of **3** and a second equivalent of thiirane is allowed to react at 45 °C in the dark for 2 days, a new product begins to form along with a second equivalent of olefin. The new product was isolated in 88% yield and characterized as the persulfido complex **5**.[29] The molecular structure of this persulfido–

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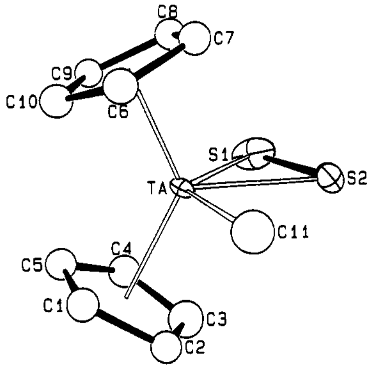

Figure 1. ORTEP diagram for the molecular structure of $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$ (**5**). Selected bond distances (Å): Ta–S1, 2.512(3); Ta–S2, 2.427(3); Ta–C11, 2.292(14); S1–S2, 2.044(6). Selected bond angles (deg): S1–Ta–S2, 48.84(14); S2–Ta–C11, 75.7(3); S1–Ta–C11, 124.5(3).

tantalum–alkyl is shown in Figure 1. This product is stable at room temperature in the absence of reducing agents. However, in the presence of PPh_3, **5** slowly reacts to regenerate complex **3** and $S{=}PPh_3$.[30]

In marked contrast to the thermal chemistry of **3**, photolysis of the sulfido complex at 5 °C in the presence of a second equivalent of *cis*- or *trans*-2,3-dimethylthiirane forms a product different from **5**. Spectral and analytical data are consistent with assignment of the identity of this material as $Cp_2Ta({=}S)(SCH_3)$ (**6**). We believe that this material forms by migratory insertion of the $Ta\text{–}CH_3$ group to the sulfido sulfur atom to give "Cp_2TaSCH_3" followed by sulfur atom abstraction from thiirane to give **6** and another equivalent of olefin.[31] It is also possible to generate **6** in low yield by irradiation of a solution of **5** (^{1}H NMR). However, due to the low conversion observed in this transformation, and the formation of significant amounts of **3** along with a number of other uncharacterized species, we do not believe that **5** is a significant intermediate in the low-temperature photolytic formation of **6** from **3**.

Complex **1** also reacts photochemically with aziridines. Upon irradiation of a C_6D_6 solution of *N*-methylaziridine and **1**, formation of 2 equiv of ethylene is observed along with >95% (^{1}H NMR) of the imido complex $Cp_2Ta({=}NCH_3)(CH_3)$ (**4a**). Similar reactions were observed using *N*-phenyl- or *N*-(*n*-butyl)aziridine, leading to ethylene and $Cp_2Ta({=}NR)(CH_3)$ (R = *n*-Bu (**4b**); Ph (**4c**)). Using *cis*- or *trans*-2,3-dimethyl-*N*-methylaziridine (Scheme 1), the imido complex **4a** is obtained along with >95% of the (*Z*)- or (*E*)-2-butene, respectively (^{1}H NMR).

As illustrated in Scheme 1, we believe that the oxygen, sulfur, and nitrene group transfer reactions observed in the photochemical reaction of **1** reported here take place via the initial formation of Cp_2TaCH_3 or a solvate of this species.[32] This reactive Ta(III) intermediate then rapidly abstracts O, S, or NR from the three-membered rings. A variety of mechanisms have been suggested for the deoxygenation of epoxides to form metal–oxo species and for the reverse process, the epoxidation of olefins by metal–oxo complexes, and Bercaw and his colleagues have published a detailed analysis of epoxide deoxygenation by a tantalum system similar to the one reported here.[17] Analogous studies of nitrene group transfer have not been performed, presumably due to the lack of previously known complexes that undergo this reaction.[24] In both the nitrene transfer reactions and the sulfide/persulfide transformation, we believe that the unusual reactivity of this system is due, in part, to the lack of sterically bulky ligands on the tantalum.[33] This allows easier attack of the hetero ring at Ta or Ta=S and (in the sulfur case) facilitates phosphine-mediated reconversion of the persulfido to the sulfido complex.[34] Although we have not yet carried out detailed mechanistic studies of our reactions, the preliminary stereochemical data mentioned above argue against mechanisms involving long-lived radical, carbocation, or carbanion intermediates. The simplest mechanism that can be postulated involves concerted atom or group transfer from the ring to the metal center. However, stereospecific formation and decomposition of heterometallacycles cannot be ruled out at present. Efforts to distinguish these alternatives are presently underway in our laboratory.

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Supplementary Material Available: Complete spectral and analytical data for **3**, **4a–c**, and **5–7** and tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, and intramolecular distances and angles for **5** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(30) Our ability to reversibly interconvert the sulfido and persulfido complexes suggests the possibility that a tantalum-catalyzed thiirane desulfurization might be carried out catalytically. However, preliminary data indicate that the catalytic activity of **3** is small at 45 °C, showing no better than a 20% increase in the rate of sulfur transfer compared to the uncatalyzed phosphine/thiirane reaction.

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(32) We find no evidence that $Cp_2Ta(CH_3)$ equilibrates with the isomer $Cp_2Ta({=}CH_2)(H)$ as reported in bulkier systems.

(33) For example, desulfurization of the more hindered $(t\text{-}BuCp)_2Ta(S_2)(H)$ with PR_3 requires several hours in refluxing toluene whereas we observed the parent $Cp_2Ta(S_2)(CH_3)$ to undergo desulfurization at 45 °C over several hours. See ref 14.

(34) In the sulfur-atom abstractions above, the formation of the C–S bond in the conversion of **3** to **6** is essentially the microscopic reverse of the C–S bond cleavage that was observed by Bercaw for η^2-thioaldehyde–hydride derivatives of permethyltantalocene. See ref 15.