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Supplementary Material Available: Experimental procedures and spectral and analytical data for all aldol reaction products (7 pages). Ordering information is given on any current masthead page.

Ring Opening and Oligomerization of Thiirane by Hexaosmium Carbonyl Cluster Complexes

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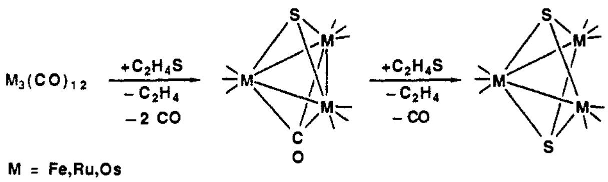
Metal complexes have played central roles in the initiation and propagation of many important polymerization reactions.[1] Studies of the reactions of metal carbonyl cluster complexes with epi-sulfides have shown sulfur transfer and alkene elimination to be the preferred reaction pathway (e.g., eq 1).[2] Although thiirane,



(1)

C_2H_4S, is able to serve as a ligand through coordination of the sulfur atom,[3] very little is known about the nature of the ring opening and eventual elimination of alkene in these reactions. The desulfurization of thiirane on a clean molybdenum (110) surface is believed to occur by an intramolecular elimination of ethylene without the formation of a thiolate intermediate.[4] We have now investigated the reactions of $Os_6(CO)_{17}(NCMe)$[5] (**1**) and $Os_6(CO)_{16}(NCMe)_2$[5] (**2**) with thiirane and have observed a pattern of ring opening and oligomerization that involves interactions of the metal atoms of the cluster functioning as a group.

1 (50.7 mg, 0.03 mmol) was allowed to react with 19 μL (0.33 mmol) of $(CH_2)_2S$[6] in 50 mL of CH_2Cl_2 solvent at reflux for 50 min. From this mixture, we have isolated by TLC 6.7 mg of the known compound $Os_6(CO)_{17}(\mu_4\text{-}S)$ (**3**),[7] 13% yield; and 13.8 mg of the new compound $Os_6(CO)_{17}[\mu_3\text{-}S(CH_2)_2S]$ (**4**), 26% yield.[8]

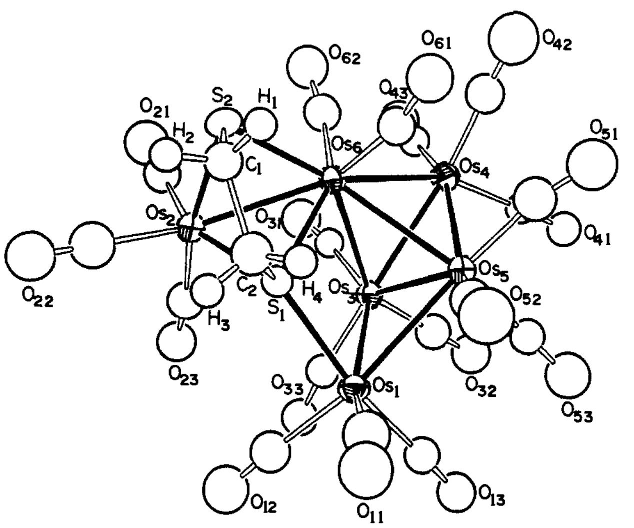


Figure 1. An ORTEP diagram of $Os_6(CO)_{17}[\mu\text{-}S(CH_2)_2S]$ (**4**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Os(1)–Os(3) = 2.872 (2), Os(1)–Os(5) = 2.880 (2), Os(2)–Os(6) = 2.814 (2), Os(3)–Os(4) = 2.778 (2), Os(3)–Os(5) = 2.725 (2), Os(3)–Os(6) = 2.897 (2), Os(4)–Os(6) = 2.862, Os(5)–Os(6) = 2.894 (2), Os(1)–S(1) = 2.380 (7), Os(2)–S(1) = 2.353 (7), Os(2)–S(2) = 2.389 (7), Os(6)–S(1) = 2.324 (7), Os(6)–S(2) = 2.401 (7).

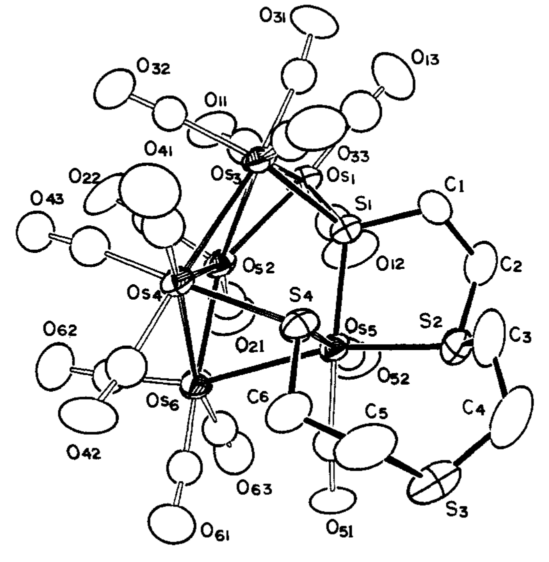


Figure 2. An ORTEP drawing of $Os_6(CO)_{16}[\mu_4\text{-}S(CH_2CH_2S)_3]$ (**7**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are Os(1)–Os(2) = 2.738 (2), Os(1)–Os(3) = 2.870 (2), Os(2)–Os(3) = 2.767 (1), Os(2)–Os(4) = 2.820 (1), Os(2)–Os(6) = 2.587 (2), Os(3)–Os(4) = 2.980 (2), Os(4)–Os(6) = 2.977 (1), Os(5)–Os(6) = 2.930 (1), Os(5)–S(1) = 2.404 (6), Os(5)–S(2) = 2.432 (6), Os(5)–S(4) = 2.428 (6).

Compound **4** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analysis.[9,10] An ORTEP drawing of **4** is shown in Figure 1. Four of the six osmium atoms, Os(3), Os(4), Os(5), and Os(6), are arranged in the shape of a closed tetrahedron. The Os(3)–Os(5) edge of this group is bridged by an $Os(CO)_3$ group, Os(1), and a second $Os(CO)_3$ group, Os(2), is bonded to the cluster at Os(6). An ethanedithiolate group bridges

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(8) Compound **4** was isolated by TLC on silica gel by elution with a hexane/CH_2Cl_2, 2/1, solvent mixture. For **4**: IR (ν(CO) cm^{-1} in CH_2Cl_2) 2100 (w), 2081 (m), 2067 (vs), 2024 (s, br); ^1H NMR (in CD_3CN) 3.28 (s, br), 3.26 (s, br). Satisfactory elemental analyses for C and H have been obtained.

(9) Dark orange crystals of **4** were grown by slow evaporation of solvent from CH_2Cl_2 solutions at 25 °C, space group, $P2_1/n$, a = 10.101 (2) Å, b = 17.953 (3) Å, c = 16.193 (3) Å, β = 94.75 (1)°, Z = 4. An empirical absorption correction was applied to the data. The structure was solved by direct methods and was refined (2968 reflections) to the final residuals, R = 0.034 and R_w = 0.035.

(10) Diffraction measurements were made on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX.

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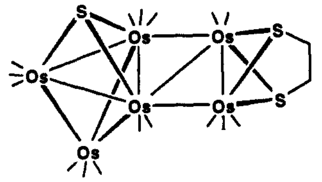
the Os(2)–Os(6) bond. S(2) is bonded to Os(2) and Os(6), but S(1) is a triply bridging atom that is bonded to Os(1), 2.380 (7) Å, Os(2), 2.353 (7) Å, and Os(6), 2.324 (7) Å, and presumably serves as a five-electron donor to the three metal atoms. The bonding within the dithiolato ligand is similar to that in other bridging ethanedithiolate groups.[11] The presence of two sulfur atoms bonded to the C_2H_4 group suggests that a sulfur atom, possibly a sulfido ligand transferred to **1** in a prior reaction with thiirane,[12] has played a role in the thiirane ring-opening process.

The importance of ring-opening processes is even more profound in the reaction of **2** with thiirane. From the reaction of 25 mg (0.015 mmol) of **2** with 8.9 μL (0.15 mmol) of thiirane in 25 mL of refluxing CH_2Cl_2 for 30 min, we have isolated by TLC the complexes $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (**5**),[13] 15% yield, $Os_6(CO)_{16}(\mu_3\text{-}S)[\mu\text{-}S(CH_2)_2S]$ (6),[14] 8% yield, a trace of **4**, 1% yield, and $Os_6(CO)_{16}[\mu_4\text{-}S(CH_2CH_2S)_3]$ (**7**),[15] 10% yield. Compounds **6** and **7** have been characterized by single-crystal X-ray diffraction analyses.[10,16] Compound **6** contains both a triply bridging sulfido ligand and a bridging ethanedithiolate group as shown by the line structure below.



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Compound **7** is considerably more complex. Details of its molecular structure are shown in Figure 2. The molecule contains a 4,7-dithiaoctanedithiolato ligand (the atoms of this ligand are connected by solid bonds) coordinated to a very open cluster of six metal atoms. Five of the metal atoms are arranged in a nearly planar array, while the sixth, Os(5), extends out from this group and is extensively coordinated by the 4,7-dithiaoctanedithiolato ligand.[17] The terminus S(1) is a triple bridge, while the other terminus S(4) bridges only two metal atoms. Only one of the thioether links is bonded to a metal atom, S(2) to Os(5), Os(5)–S(2) = 2.432 (6) Å. One can imagine the formation of the 4,7-dithiaoctanedithiolato ligand by a sulfur-induced ring opening and oligomerization of three thiirane molecules. Metal complexes containing thiolato ligands have been shown to promote the ring-opening polymerization of episulfides.[19]

While the mechanism of the initial ring-opening and chain propagation steps have yet to be established, it does appear that high nuclearity cluster complexes possess novel abilities to produce episulfide ring-opening and oligomerization processes that do not lead to the loss of alkene. This could be related to the ability of large clusters to produce more extensive and extended coordination of the dithiolate chains.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supplementary Material Available: Tables of crystal data, positional and anisotropic thermal parameters, and bond distances and angles for the structural analysis of compounds **4** and **7** (22 pages); tables of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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(12) By an independent reaction it was shown that **3** was not the precursor to **4**.

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(14) For **6**: (IR, ν(CO) cm^{-1}, in hexane) 2101 (m), 2080 (vs), 2068 (vs), 2046 (s), 2024 (s), 2004 (s), 1951 (w), 1937 (w); ^{1}H NMR (δ in $CDCl_3$) 3.00 (d, d, d; J_{H-H} = 13.0 Hz, J_{H-H} = 8.1 Hz, J_{H-H} = 5.0 Hz, 1 H), 2.90 (d, d, d; J_{H-H} = 13.0 Hz, J_{H-H} = 8.1 Hz, J_{H-H} = 5.0 Hz, 1 H), 2.73 (m, 2 H).

(15) Compound **7** is a slow moving band that was eluted from the base line of the TLC plate with pure CH_2Cl_2 solvent. For **7**: (IR, ν(CO) cm^{-1}, in hexane) 2088 (m), 2058 (s), 2048 (vs), 2017 (m), 2004 (m), 1981 (w); ^{1}H NMR (δ in CD_2Cl_2) 5.32 (d, t, J_{H-H} = 2.0 Hz, J_{H-H} = 2.0, 1 (H), 3.53 (d, d, J_{H-H} = 13.8 Hz, J_{H-H} = 2.3 Hz, 1 H), 3.36 (d, d, J_{H-H} = 12.3 Hz, J_{H-H} = 3.4 Hz, 1 H), 3.25 (d, J_{H-H} = 14.8 Hz, 1 H), 3.00 (t, J_{H-H} = 13.0 Hz, 1 H), 2.35 (m, 4 H), 2.00, J_{H-H} = 14.2 Hz, 2 H).

(16) Dark red-brown crystals of **6** were grown from CH_2Cl_2/hexane, 10/1, solutions at −5 °C, space group, $P2_1/c$, $a = 14.674$ (2) Å, $b = 9.803$ (1) Å, $c = 21.303$ (2) Å, $\beta = 101.30$ (1)°, $Z = 4$. An empirical absorption correction was applied. The structure was solved by direct methods and was refined (2626 reflections) to the final values of the residuals, $R = 0.031$, $R_w = 0.031$. Dark red crystals of **7** were grown from CH_2Cl_2/benzene, 20/1, solutions at −5 °C. They were found to contain 1.5 equiv of benzene per unit of complex space group, $P\bar{1}$, $a = 11.806$ (2) Å, $b = 17.894$ (5) Å, $c = 9.982$ (1) Å, $\alpha = 99.58$ (2)°, $\beta = 100.76$ (1)°, $\gamma = 93.95$ (2)°, $Z = 2$. An empirical absorption correction was applied. The structure was solved by direct methods and was refined (3514 reflections) to the final values of the residuals, $R = 0.042$, $R_w = 0.040$.

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A Remarkable Alkane Protonolysis Reaction: Observation of Stoichiometric Hydrogen Formation

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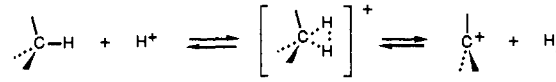
Since its independent discovery in 1967 by Olah[1] and Hogeveen,[2] the formation of carbocations by protonolysis of alkanes with strong acids such as $HSbF_6$ has become a well-known and much-studied process.[3] Although the reaction appears simple, its mechanism has been a subject of controversy for more than two decades because a nonstoichiometric amount of hydrogen is usually produced.[4] Thus, the "obvious" mechanism involving protonation of an alkane C–H bond to yield an intermediate with a three-center, two-electron C–H–H bond, followed by loss of H_2, cannot be correct in most instances.



Numerous rationalizations for the nonstoichiometric formation of H_2 have been offered,[5-9] many of which conclude that H^+ is

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