Ring-opening reactions of strained-ring thioethers in metal cluster complexes. Photoinduced transformation of thietane to 2-propenethiolate in a triosmium cluster complex

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of Sm(III) species is provided by the observation that the relative rates of the present reactions are consistent with general Cp'_2LnR ionic radius-rate correlations (La > Sm > Lu)[1] and that the present reactions are zero-order in substrate (Scheme I, k_{ii}[substrate] $\gg k_i$) as for other Cp'_2LnR catalysts.[1] The unimportance of divalent species in the catalytic cycle is also argued by the observation that Cp'_2Eu[18] is catalytically inactive under the present conditions. From thermochemical data[5a] we estimate that ΔH is approximately 22 kcal/mol of propylene more endothermic for the europium analogue of eq 1 and that binuclear reductive-elimination reactions (eq 7) are invari-

$$Cp'_2EuR + Cp'_2EuR' \rightarrow 2Cp'_2Eu + RR' \qquad (7)$$

$$\Delta H_{calcd} \approx -8 \text{ to } -12 \text{ kcal/mol of Eu}$$

ably exothermic (in contrast to the case for samarium). Scheme II illustrates a representative, minimum catalytic cycle that accounts for the above observations.[19]

In summary, these results offer an expedient access to organolanthanide-catalyzed hydroamination/cyclization chemistry. They also underscore the diversity that the varying redox characteristics of 4f ions can introduce in lanthanide-centered catalytic chemistry.

Acknowledgment. We are grateful to the NSF for support of this research under Grant CHE-8800813. M.R.G. thanks Rhône-Poulenc for a graduate fellowship.

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(19) (a) We are unable to detect internal olefins or their cyclization products in low substrate/catalyst ratio experiments, suggesting that proton transfer in step i (Scheme II) is to the substituted allyl carbon atom or that internal olefins are subsequently isomerized. (b) Reaction of Sm alkyls (subsequent to step iii, Scheme II) with olefin could also yield η^3-allyls[2b,5b,13b] and the corresponding heterocyclic product (an alternative to step iv). The η^3-allyl would presumably then reenter the cycle at step i.

Ring-Opening Reactions of Strained-Ring Thioethers in Metal Cluster Complexes. Photoinduced Transformation of Thietane to 2-Propenethiolate in a Triosmium Cluster Complex

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Summary: $Os_3(CO)_{11}[S(CH_2)_3]$ undergoes photoassisted ring opening, CH activation, and decarbonylation to yield $Os_3(CO)_{10}[\mu\text{-}SCH_2C(H){=}CH_2](\mu\text{-}H)$ (**2**). **2** engages in a phosphine-assisted insertion reaction between the allyl group and the hydride ligand to yield $Os_3(CO)_{10}(PMe_2Ph)[\mu\text{-}S(CH_2)_3]$ (**3**), which contains a novel thiametallacyclic ring. **3** is decarbonylated at 97 °C to yield the PMe_2Ph derivative of **2**.

The ring-opening reaction is believed to be an integral step in the desulfurization of cyclic thioethers, the principal sulfur-containing contaminants of fossil fuels.[1] Metal complexes[2] have been shown to promote this process, and it is also known to occur readily on molybdenum surfaces.[3] Due to their intrinsic strain, small-ring thioethers, such as thiiranes[4] and thietanes,[5] exhibit a greater tendency to undergo ring opening and desulfurization. Thiiranes usually undergo complete desulfurization upon reaction with metal complexes.[4] The chemistry of thietane, $S(CH_2)_3$, in metal complexes has been studied very little.[6] On metal surfaces, thietane is readily desulfurized.[5] In this report, the preliminary results of our study of the coordination and transformation of thietane by a triosmium cluster is described.

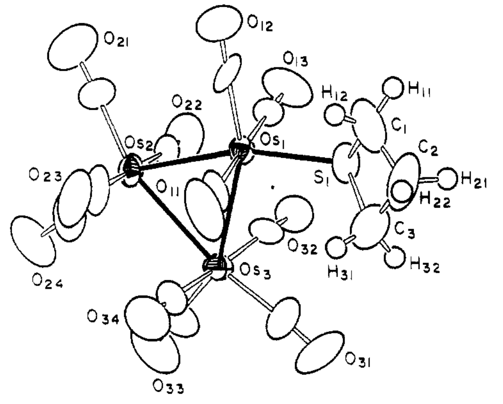

Figure 1. ORTEP diagram of $Os_3(CO)_{11}[S(CH_2)_3]$ (1) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are as follows: Os(1)-Os(2) = 2.850 (1), Os(1)-Os(3) = 2.887 (1), Os(2)-Os(3) = 2.887 (1), Os(1)-S(1) = 2.375 (5), S(1)-C(1) = 1.85 (2), S(1)-C(3) = 1.83 (2).

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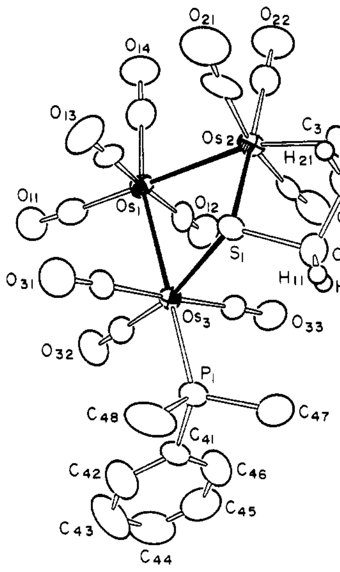
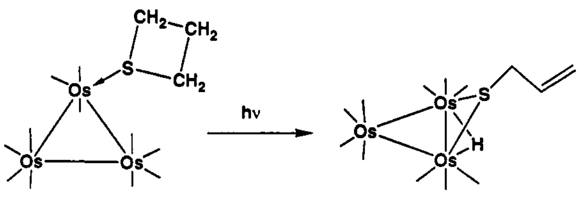


Figure 2. ORTEP drawing of $Os_3(CO)_{10}(PMe_2Ph)[\mu\text{-}S(CH_2)_3]$ (3) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å) are as follows: Os(1)–Os(2) = 2.9504 (7), Os(1)–Os(3) = 2.9559 (7), Os(2)–S(1) = 2.430 (2), Os(3)–S(1) = 2.446 (3), S(1)–C(1) = 1.85 (1), Os(2)–C(3) = 2.20 (1).

The compound $Os_3(CO)_{11}[S(CH_2)_3]$ (1) was obtained in 84% yield from the reaction of $Os_3(CO)_{11}(NCMe)$ and $S(CH_2)_3$ at 25 °C.[7] Compound 1 was characterized structurally, and an ORTEP drawing of its molecular structure is shown in Figure 1.[8,9] This is apparently the first structural characterization of thietane in a metal complex. The ligand occupies an equatorial coordination site in the cluster and is not significantly different from the structure that it exhibits in the gas phase.[10]

When subjected to UV–vis irradiation, compound 1 was decarbonylated and transformed to the new compound $Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CH_2)(\mu\text{-}H)$ (2), which is identical with the product obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ and 2-propenethiol.[11] The transformation of 1 to 2 involves both a C–S bond cleavage and a CH cleavage at the 3-position of the thietane ring (eq 1).

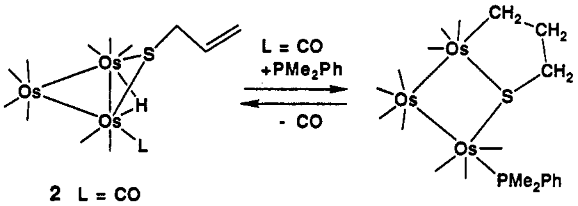


(1)

1 **2**

Curiously, we were unable to obtain 2 by a thermal decarbonylation of 1. It is known that thietanes undergo photoinduced ring-opening reactions,[12] and we suspect that this is the first step in the transformation of 1 to 2. The nature of the CH activation step is less clear, but we have observed the following transformation, which may be pertinent.

When a solution of 2 was allowed to react with PMe_2Ph, the new compound $Os_3(CO)_{10}(PMe_2Ph)[\mu\text{-}S(CH_2)_3]$ (3) was obtained in 73% yield.[13] The molecular structure of 3 was ascertained by a crystallographic analysis, and an ORTEP drawing of its structure is shown in Figure 2.[9,14] The molecule consists of an open triosmium cluster with the sulfur atom, S(1), bridging the nonbonded metal atoms Os(2) and Os(3). A trimethylene group bridges the S(1)–Os(2) bond to form the first example of a thiametallacyclopentane ring system; Os(2)–C(3) = 2.20 (1) Å and S(1)–C(1) = 1.85 (1) Å. The phosphine ligand is coordinated to Os(3). Formally, the formation of 3 is the result of an insertion of the unsaturated double bond of the allyl group into the metal–hydride bond (eq 2). The transformation, which occurs under remarkably mild conditions (25 °C), appears to be greatly promoted by the phosphine.[15] It is surprising that the phosphine ligand and the alkyl group are coordinated to different metal atoms. Efforts to learn more about the mechanism of this unusual process are in progress. When solutions of 3 were heated to 97 °C, it was decarbonylated to yield $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}SCH_2CH{=}CH_2)(\mu\text{-}H)$ (4), the PMe_2Ph derivative of 2.[16] This transformation appears to be a simple



(2)

2 L = CO
4 L = PMe$_2$Ph
3

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[7] One equivalent of thietane (5 μL) was allowed to react with $Os_3(CO)_{11}NCCH_3$ (60 mg, 0.065 mmol) in 60 mL of CH_2Cl_2 at 25 °C for 1 h. The product 1 was isolated by chromatography (TLC) on silica gel by elution with a 5/1 hexane/CH_2Cl_2 solvent mixture; yield 52 mg, 84%. IR (ν(CO), cm^{-1}; in hexane): 2111 w, 2057 s, 2036 s, 2022 vs, 2010 m, 2004 m, 1993 m, 1997 m, 1970 w, 1958 w. ^1H NMR (δ; in $CDCl_3$); 3.65 (t, 4 H, J_{H-H} = 8 Hz), 2.84 (s, br, 2 H). Yellow crystals of 1 were grown from a hexane solution by slow evaporation at 25 °C. Anal. Calcd for 1: C, 17.65; H, 0.63. Found: C, 17.66; H, 0.62.

[8] Crystal data for 1: space group $P2_1/c$, a = 9.020 (2) Å, b = 11.673 (3) Å, c = 19.7000 (4) Å, β = 94.21 (2)°, Z = 4. An empirical absorption correction was applied to the data. The structure was solved by direct methods and was refined (1947 reflections) to the final residuals R = 0.034 and R_w = 0.035.

[9] Diffraction measurements were made on a Rigaku AFC6S diffractometer 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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[11] An 80-mg (0.086-mmol) amount of 1 in 80 mL of hexane was photolyzed (high-pressure Hg lamp, external source) under a nitrogen purge for 2 h at 25 °C. The solution changed from yellow to orange/red. The unreacted 1 was separated from a mixture of red $Os_4(CO)_{12}(\mu_2\text{-}S)$ and yellow 2 by column chromatography (silica gel with hexane solvent). The mixture of products was then separated by TLC on alumina to yield 15 mg of pure $Os_3(CO)_{10}(\mu\text{-}SCH_2CHCH_2)(\mu\text{-}H)$ (2; 22%, based on amount of 1 consumed). IR (ν(CO), cm^{-1}; in hexane): 2107 w, 2068 m, 2059 s, 2048 w, 2025 sh, 2020 vs, 2000 m, 1989 m, 1987 m, 1946 vw. ^1H NMR (δ; in $CDCl_3$): 5.81 (m, 1 H, J_{H-H} = 7 Hz), 5.27 (m, 2 H)8, 3.03 (m, 2 H), −17.44 (s, 1 H). Anal. Calcd for 2: C, 16.88; H, 0.65. Found: C, 17.14; H, 0.58. To corroborate its identity further, 2 was also prepared (yield 76%) by the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ and 1 equiv of allyl mercaptan at 25 °C in CH_2Cl_2 for 2 h.

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[13] A 4-μL (0.028-mmol) amount of PMe_2Ph was allowed to react with 2 (8 mg, 0.009 mmol) in 15 mL of hexane for 30 min at 25 °C. The product was isolated by TLC on silica gel. This yielded 7 mg (73%) of yellow $Os_3(CO)_{10}(PMe_2Ph)[\mu\text{-}S(CH_2)_3]$ (3). IR (ν(CO), cm^{-1}; in hexane): 2098 w, 2060 m, 2036 m, 2011 s, 1999 sh, 1994 m, 1979 m, 1974 m, 1960 m. ^1H NMR (δ; in $CDCl_3$): 7.54–7.44 (m, 5 H), 2.29 (t, 2 H, J_{H-H} = 6.7 Hz), 2.17 (d, 6 H, J_{H-P} = 9.7 Hz), 1.69 (t, 2 H, J_{H-P} = 9.7 Hz), 1.69 (t, 2 H, J_{H-H} = 5.8 Hz), 1.32 (m, 2 H). Orange crystals of 3 were grown from solution in a hexane/CH_2Cl_2 (5/1) solvent mixture by slow evaporation at 25 °C. Anal. Calcd for 3: C, 23.73; H, 1.61. Found: C, 23.55; H, 1.55.

[14] Crystal data for 3: space group $P2_1/n$, a = 10.536 (2) Å, b = 18.131 (3) Å, c = 14.174 (2) Å, β = 99.57 (1)°, Z = 4. An empirical absorption correction was applied. The structure was solved by direct methods and was refined (2780 reflections) to the final residuals R = 0.024 and R_w = 0.026.

[15] Interestingly, this insertion reaction is not promoted by CO under similar conditions.

β-elimination process that results in a release of the alkenyl grouping and closure of the cluster. This transformation demonstrates the existence of a relatively facile CH activation process that leads to the formation of an uncoordinated 2-propenethiolato group, such as that found in **2**. It is possible that an intermediate similar to **3** was traversed en route to **2**. Efforts to confirm this are currently in progress. This observation of the involvement of thiametallacylces in the cluster chemistry of thietane appears to contrast significantly with the proposed transformations of thietane on metal surfaces.[5,17]

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Gong Chen for help with the structural analyses.

Supplementary Material Available: Tables of crystal data, positional anisotropic thermal parameters, and bond distances and angles for the structural analysis of compounds **1** and **3** (15 pages); tables of structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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(16) A solution of **3** (16 mg) in heptane (20 mL) was heated to reflux for 1 h. The product **4** was isolated in 60% yield by TLC on alumina. IR (ν(CO), cm^{-1}; (in hexane): 2091 m, 2051 s, 2014 vs, 1999 m, 1989 m, 1967 m, 1947 w, 1943 w. ^{1}H NMR (δ; in CDCl$_3$): 7.53–7.35 (m, 5 H), 5.73 (m, 1 H), 5.17–5.12 (m, 2 H), 2.81 (dd, 1 H, $J_{\text{H-H}}$ = 12.7 Hz, $J_{\text{H-H}}$ = 7.0 Hz), 2.54 (m, 1 H, $J_{\text{H-H}}$ = 12.7 Hz, $J_{\text{H-H}}$ = 7.0 Hz), 2.29 (d, 3 H, $J_{\text{P-H}}$ = 10 Hz), 2.26 (d, 3 H, $J_{\text{P-H}}$ = 10 Hz), −17.03 (d, 1 H, $J_{\text{P-H}}$ = 26 Hz). The reverse of this reaction (CO addition) has not yet been achieved. The PPh$_3$ derivative of **2** was prepared by a similar sequence of insertion/ligand addition to yield the PPh$_3$ analogue of **3** and a subsequent decarbonylation. The PPh$_3$ derivative of **2** was characterized crystallographically.

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Synthesis and X-ray Crystal Structure of $[\mathrm{Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2}]_\infty$: The First Detailed Structural Characterization of a Lithium Dialkylcuprate Aggregate

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Summary: The use of SMe$_2$ (dimethyl sulfide) as both ligand and solvent has allowed the first X-ray structural characterization of a lithium alkylcuprate aggregate. The title compound $[\mathrm{Li_2Cu_2(CH_2SiMe_3)_4(SMe_2)_2}]_\infty$ (**1**) was synthesized by the reaction of 2 equiv of LiCH$_2$SiMe$_3$ with CuBr in SMe$_2$. Its structure consists of infinite chains of the dimeric units Li$_2$Cu$_2$(CH$_2$SiMe$_3$)$_4$ linked by weakly bridging SMe$_2$ ligands that bind to the lithium centers. The Li$_2$Cu$_2$ array is almost planar, and the α-carbons of the alkyl groups reside in alternating positions approximately 1.3 Å above and below the metal plane. The Li–S distances, 2.65–2.71 Å, are long, and the Li–C bonds, ~2.2 Å, are short. Thus, the Li atoms are relatively strongly bonded to the α-carbons of the alkyl group. The Cu–C distances are ~1.956 Å, which is close to the values in arylcuprates. The structure of **1** is significantly different, in certain details, from that predicted for Li$_2$Cu$_2$Me$_4$ on the basis of spectroscopy and theoretical calculations.

Since their introduction over 20 years ago[1] organocuprate (Gilman) reagents have proved extremely valuable in organic synthesis.[2] They are normally represented by the formula "LiCuR$_2$",[3] but they are believed to be associated into higher aggregates in solutions of ether—the solvent in which they are normally employed. For example, "LiCuPh$_2$" crystallizes as the "trimeric" ionic species $[\mathrm{Li_2Cu_3Ph_6}]^-$ from ether or THF solution mixtures along with a countercation of solvated or complexed lithium.[4] In addition, the self-complexing cuprate Li$_2$Cu$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)$_4$ is a dimer in both solution[5] and the solid state.[6] These two structures, and that of the related species [Li(THF)$_4$][LiCu$_4$Ph$_6$],[7] constitute the extent of the currently available detailed structural knowledge of associated lithium diorganocuprates. The scarcity of data for these compounds is further underlined by the absence of a detailed (X-ray) structure for any lithium dialkylcuprate aggregate. In addition, only two crystal structures of neutral copper(I) alkyls, the tetramer Cu$_4$(CH$_2$SiMe$_3$)$_4$[8] and the dimer [(2-(Me$_3$Si)$_2$CCuC$_5$H$_4$N)$_2$],[9] have been published. Even though the structures of the separated mononuclear dialkylcuprate ions $[\mathrm{Cu(C(SiMe_3)_3)_2}]^-$[10] and $[\mathrm{CuMe_2}]^-$[11,12]

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