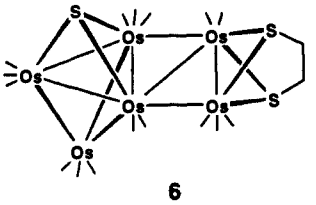
the Os(2)-Os(6) bond. S(2) is bonded to Os(2) and Os(6), but S(1) is a triply bridging atom that is bonded to Os(1), 2.380 (7) Å, Os(2), 2.353 (7) Å, and Os(6), 2.324 (7) Å, and presumably serves as a five-electron donor to the three metal atoms. The bonding within the dithiolato ligand is similar to 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.



6

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.

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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.

(11) (a) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. D.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329. (b) Rakowski DuBois M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

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

(13) Adams, R. D.; Horváth, I. T.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 1533.

(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); ^1H NMR (δ in $CDCl_3$) 3.00 (d, d, d; $J_{H\text{-}H}$ = 13.0 Hz, $J_{H\text{-}H}$ = 8.1 Hz, $J_{H\text{-}H}$ = 5.0 Hz, 1 H), 2.90 (d, d, d; $J_{H\text{-}H}$ = 13.0 Hz, $J_{H\text{-}H}$ = 8.1 Hz, $J_{H\text{-}H}$ = 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); ^1H NMR (δ in CD_2Cl_2) 5.32 (d, t, $J_{H\text{-}H}$ = 2.0 Hz, $J_{H\text{-}H}$ = 2.0, 1 (H), 3.53 (d, d, $J_{H\text{-}H}$ = 13.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, 1 H), 3.36 (d, d, $J_{H\text{-}H}$ = 12.3 Hz, $J_{H\text{-}H}$ = 3.4 Hz, 1 H), 3.25 (d, $J_{H\text{-}H}$ = 14.8 Hz, 1 H), 3.00 (t, $J_{H\text{-}H}$ = 13.0 Hz, 1 H), 2.35 (m, 4 H), 2.00, $J_{H\text{-}H}$ = 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, β = 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, α = 99.58 (2)°, β = 100.76 (1)°, γ = 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.

(17) A metal complex containing a 4,7-octanedithiolato ligand prepared by a different method has been structurally characterized.[18]

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A Remarkable Alkane Protonolysis Reaction: Observation of Stoichiometric Hydrogen Formation

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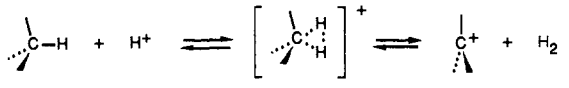
Since its independent discovery in 1967 by Olah[1] and Hogeveen,[2] the formation of carbocations by protonolysis of alkanes with strong acids such as $HSbF_6$ has become a well-known and much-studied process.[3] Although the reaction appears simple, its mechanism has been a subject of controversy for 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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(4) Stoichiometric hydrogen formation has been reported in the initial stages of an alkane protonolysis reaction: Bassir, M.; Torck, B.; Hellin, M. *New J. Chem.* **1987**, *11*, 437-441. In addition, Wuest has observed stoichiometric hydrogen evolution in a specialized case: Erhardt, J. M.; Wuest, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 6363-6364.

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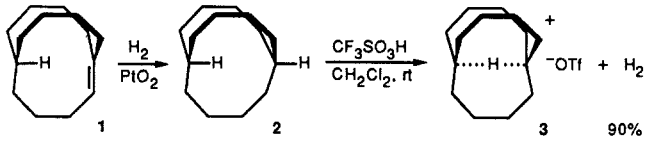
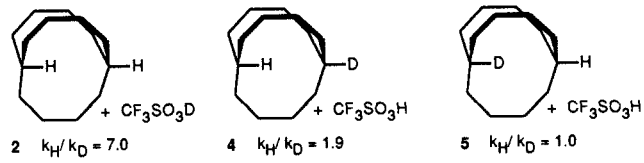
not the reactive oxidizing agent in $HSbF_6$ solutions. One particularly appealing explanation[10] is that the pentacoordinate RH_2^+ intermediate is intercepted and reduced by SbF_5 prior to the escape of H_2. Some recent work by Sorensen[11] has cast doubt on this explanation, however, leading him to state that "we...cannot really accept that the solution C-H protonation of alkanes...is an important pathway in the RH → R^+ reaction".

Clearly,[3a] the ease of carbocation formation from an alkane should depend both on the stability of the cation being formed and on the acid strength of the medium. If a stable enough carbocation is formed, it should be possible to carry out the protonolysis reaction by using weaker acids than are normally employed, thereby obviating the need for the HX/MX_n combination that appears to be the source of the trouble. We have shown in a detailed study carried out over the last four years that the hydrido-bridged *in*-bicyclo[4.4.4]-1-tetradecyl cation **3** is the most stable cycloalkyl cation known.[12] It therefore occurred to us that this cation might be formed from the corresponding alkane **2** under conditions that could allow the use of mild protic acids in the absence of an added Lewis acid. If so, it would present a unique opportunity to study a little-understood reaction.

Warming a dilute solution of **2** to 40 °C in glacial acetic acid resulted in the slow disappearance (approximately 10% completion after 1 week) of alkane starting material and the formation of cation **3**. Use of trifluoroacetic acid led to a more rapid reaction, but use of trifluoromethanesulfonic acid gave the cleanest results. When alkene **2** in a minimal volume of CH_2Cl_2 was added to CF_3SO_3H at 0 °C and gas evolution was measured,[13] more than 90% of the theoretical amount of H_2 was produced in 1 h (E_{act} = 13.5 kcal/mol) and a clean solution of cation **3** was obtained, clearly identified by its distinctive one-proton NMR absorption at δ -3.46. Quenching the solution resulted in recovery of alkene **1** in 75% isolated yield.



To gain further information about the protonolysis reaction, isotope experiments using deuterated trifluoromethanesulfonic acid, CF_3SO_3D, on unlabeled alkane **2** were carried out, and a large solvent kinetic isotope effect k_H/k_D = 7.0 at 0 °C was measured as determined by disappearance of starting material and appearance of alkene **1**.[14] Similar experiments using CF_3SO_3H on the labeled *out*-deuteriobicyclo[4.4.4]tetradecane **4**[15] gave a moderate primary isotope effect k_H/k_D = 1.9 at 0 °C. By contrast, the labeled *in*-deuterio substrate **5** showed no detectable remote isotope effect.[16] Taken together, the three results are consistent with a nonconcerted reaction whose rate-limiting step involves breakage of both the alkane C-H bond and the acid O-H bond. Were the reaction concerted, one would expect a measurable remote isotope effect in substrate **5**. Were loss of H_2 from a protonated intermediate rate-limiting, one would not expect a large solvent isotope effect on **2** but would expect some exchange of the outside bridgehead hydrogen in **2** on reaction with CF_3SO_3D.[17] No exchange of the outside bridgehead hydrogen was observed, however, when the reaction of unlabeled alkane **2** in CF_3SO_3D was allowed to go to partial completion and the recovered starting material was analyzed by mass spectroscopy.



2 k_H/k_D = 7.0 4 k_H/k_D = 1.9 5 k_H/k_D = 1.0

In summary, this work provides a clearcut example of stoichiometric hydrogen evolution in an alkane protonolysis reaction and provides good evidence that the RH → RH_2^+ → $R^+ + H_2$ pathway is a viable mechanism for carbocation formation in simple alkanes. We are unable to detect the presumed RH_2^+ intermediate, but it seems likely that a triangular structure with a closed three-center bond is energetically preferred over an alternative linear structure with an open C-H-H three-center bond.[3d] Note that the small primary isotope effect we observed is consistent with a nonlinear transition state.[18]

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Isolation and Characterization of a Covalent Selenocysteine Intermediate in the Glycine Reductase System

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Selenocysteine occurs in the bacterial enzymes glycine reductase, formate dehydrogenase, and hydrogenase and the mammalian enzyme glutathione peroxidase.[1] The mechanistic role of this residue remains largely unknown. It has been postulated to function as a redox center, but there is little evidence supporting this suggestion.[2] We have investigated the mechanism of action of glycine reductase (eq 1) because of the unusual chemical re-

$$^+NH_3CH_2COO^- + P_i + 2e^- \rightarrow CH_3COOPO_3^{2-} + NH_4^+ \quad (1)$$

action catalyzed,[3] i.e., the reductive cleavage of a carbon-nitrogen bond. We have proposed the mechanism shown in Scheme I.[3] Clostridial glycine reductase consists of proteins A, B, and C.[5]

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