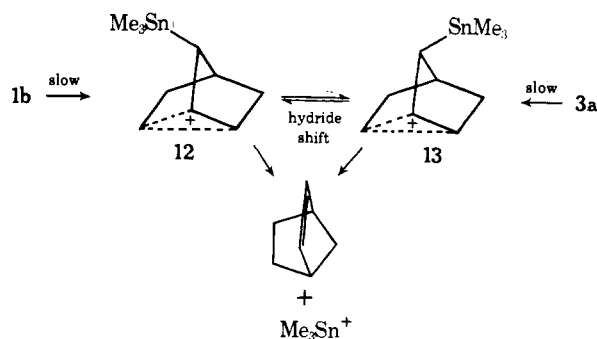ysis occurs to yield a 7-Me$_3$Sn-substituted-2-norbornyl cation which undergoes a rapid 1,2-deoxystannylation reac-

tion.[8] Similarly **4b** gives rise to an acetate mixture derived from norbornene and pseudonortricyclene. Absence of a significant rate effect argues that the Me$_3$Sn group is not involved in the rate determining step, the products resulting from subsequent competitive 1,2- and 1,3-deoxystannylation reactions. 1,3-Elimination from the endo cation, **14**, can occur with retention at the carbon-tin bond or, maintaining a preference for the W configuration, *vide infra*, from **15** concerted with or following a 6,2-hydride shift.
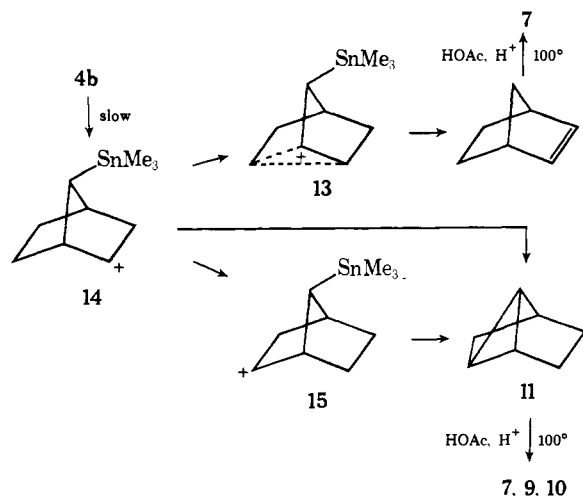
The 1000-fold rate acceleration shown by **2b** and the exclusive formation of **11** indicates a strong perference for double inversion, limiting structures for possible intermediates and transition states to those differing little from the W configuration.[9] This percaudal interaction may provide homoconjugative stabilization[10-13] if carbocationic intermediates are involved or may represent the bond making interaction in the transition state for a concerted 1,3-elimination.[14]
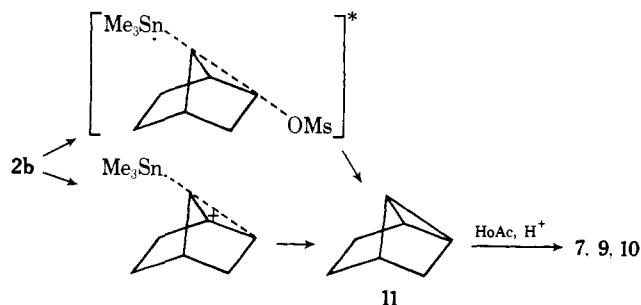
Further work on the question of concerted 1,3-eliminations and/or metal stabilized cations in these 1,3-deoxymetalation reactions is continuing.

References and Notes

(1) D. D. Davis, R. L. Chambers, and H. T. Johnson, *J. Organometal. Chem.*, **25**, C13 (1970); H. G. Kuivila and N. M. Scarpa, *J. Amer. Chem. Soc.*, **92**, 6990 (1970).

(2) H. G. Kuivila, J. L. Considine, and J. D. Kennedy *J. Amer. Chem. Soc.*, **94**, 7206 (1972); C. H. W. Jones, R. G. Jones, P. Partington, and R. M. G. Roberts, *J. Organometal. Chem.*, **32**, 201 (1971).

(3) (a) D. D. Davis, A. J. Surmatis, and G. L. Robertson, *J. Organometal. Chem.*, **46**, C9 (1972); (b) H. T. Johnson, Ph.D. Dissertation, New Mexico State University, 1973; D. D. Davis and H. T. Johnson, *J. Organometal. Chem.*, to be submitted for publication.

(4) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(5) A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, **92**, 6140 (1970).

(6) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2822 (1966); P. G. Gassman and J. G. Macmillan *ibid.* **91**, 5527 (1969); P. G. Gassman and J. M. Hornback *ibid.*, **94**, 7010 (1972); P. G. Gassman, J. L. Marshall, and J. G. Macmillan, *ibid.*, **95**, 6319 (1973).

(7) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); infrared and nmr spectra of authentic material were kindly supplied by Professor Moore.

(8) D. D. Davis and C. E. Gray, *J. Org. Chem.*, **35**, 1303 (1970).

(9) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3194, 3195, 3917 (1967).

(10) Inversion gives rise to a structure similar to a corner-stannylated cyclopropane, while retention would initially lead to the edge-stannylated form. DePuy and McGirk[11] have proposed mercuric analogs in the electrophilic cleavages of substituted cyclopropanes.

(11) C. H. DePuy and R. H. McGirk *J. Amer. Chem. Soc.*, **95**, 2366 (1973).

(12 Charge-transfer spectral studies of organomercury and -lead compounds showed no evidence of 1,3-carbon–metal hyperconjugation.[13]

(13) W. Hanstein, H. S. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(14) Support for two-stage 1,3-eliminations as a general mechanism is discussed by F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, **95**, 3585 (1973).

Dennis D. Davis,* **Harry T. Johnson**
Department of Chemistry, New Mexico State University
Las Cruces, New Mexico 88003
Received August 24, 1974

Mechanism of Reductive Elimination. I. Dinuclear Elimination of Hydrogen from cis-Dihydridotetracarbonylosmium

Sir:

Attention has recently been called[1] to the possible importance of dinuclear elimination as a reaction mode in organo transition metal chemistry. We wish to report evidence for, and details of the mechanism of, the dinuclear elimination of hydrogen from the cis dihydride H$_2$Os(CO)$_4$.[2]

Our attention was drawn to this compound by the high stability of both it and Os(CO)$_4$(CH$_3$)$_2$ in comparison with Os(CO)$_4$(H)CH$_3$.[3,4] (The dihydride begins to decompose rapidly only at 125°, the dimethyl compound decomposes slowly even at 165°, while Os(CO)$_4$(H)CH$_3$ decomposes rapidly at 40°.) Clearly all three compounds cannot decompose by the same mechanism. Dinuclear elimination seemed likely to be occurring in one or more cases. We selected the simplest member of the series, the dihydride, for initial examination.

Under all conditions investigated the primary product of the thermal decomposition of H$_2$Os(CO)$_4$ was H$_2$Os$_2$(CO)$_8$, originally synthesized by Moss and Graham and believed to have two terminal hydrides cis to an Os–Os bond.[5] Other products, Os$_3$(CO)$_{12}$, H$_4$Os$_4$(CO)$_{12}$,[6-8] and other polynuclear hydridocarbonyls, appear subsequently. The observation that they are produced upon heating H$_2$Os$_2$(CO)$_8$ confirms that they are indeed secondary products.[9]

Of course the dimeric nature of the primary product does

not by itself imply a dinuclear elimination mechanism. A traditional mononuclear reductive elimination followed by
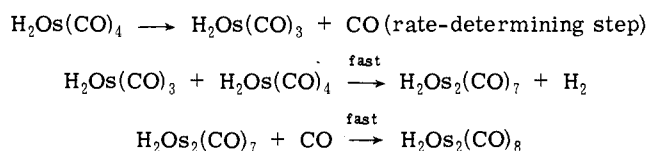
$$H_2Os(CO)_4 \longrightarrow Os(CO)_4 + H_2$$
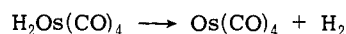
the insertion of $Os(CO)_4$ into an Os–H bond of another $H_2Os(CO)_4$ molecule would also result in the formation of $H_2Os_2(CO)_8$. Indeed, Moss and Graham originally proposed[6] that their polynuclear osmium dihydridocarbonyls resulted from such a reaction sequence. Simple elimination of H_2 might also have been expected as the reverse of the original synthesis[2] of $H_2Os(CO)_4$ by the oxidative addition of hydrogen to $Os(CO)_5$—a process likely to involve intermediate $Os(CO)_4$.

The distinction between dinuclear and mononuclear elimination mechanisms was most easily made through labeling experiments. $D_2Os(CO)_4$ was readily prepared (71% yield, 86% isotopic purity) from $Na_2Os(CO)_4$[4] and D_3PO_4 in tetraglyme. Thermolysis of mixtures of the deuteride and hydride at 105° gave HD as well as H_2 and D_2, indicating a dinuclear mechanism. The exact isotopic composition of the product gas reflects the operation of small isotope effects: $k_{HH}/k_{HD} = 1.4 \pm 0.2$, $k_{HH}/k_{DD} = 2.9 \pm 0.4$.[10]

The possible presence of an H_2–D_2–HD equilibration catalyst was checked by the prolonged thermolysis of $H_2Os(CO)_4$ under excess D_2. Although the principal product was H_2, a small amount of HD (16% of H_2) was formed, suggesting that the $H_4Os_4(CO)_{12}$–$Os_3(CO)_{12}$ secondary product system is capable of slow isotopic equilibration. (This conclusion was confirmed by observing the slow equilibration of an H_2–D_2 mixture by these compounds.) This experiment also rules out any mechanism involving the reversible dissociation of hydrogen prior to the bimolecular step; such a process would have formed $D_2Os(CO)_4$ and thus much HD as in the previous experiment.

A quantitative study of the kinetics of $H_2Os(CO)_4$ decomposition was then undertaken.[11] Under small CO pressures the reaction is first-order in $H_2Os(CO)_4$, the rate constant at 125.8° being $6.1 \pm 0.2 \times 10^{-5}$ sec^{-1}. ΔH^* is 33.7 $\pm$ 0.6 kcal/mol and ΔS^* is +6 $\pm$ 2 eu. The rate law and activation parameters suggest a rate-determining step involving carbon monoxide dissociation.[12]

Taken together, the deuterium labeling data and the kinetic results suggest the following mechanism.[13,14]

$$H_2Os(CO)_4 \longrightarrow H_2Os(CO)_3 + CO \text{ (rate-determining step)}$$

$$H_2Os(CO)_3 + H_2Os(CO)_4 \xrightarrow{\text{fast}} H_2Os_2(CO)_7 + H_2$$

$$H_2Os_2(CO)_7 + CO \xrightarrow{\text{fast}} H_2Os_2(CO)_8$$

The empty coordination site formed in the first step may allow the formation of one or more hydride bridges necessary for the dinuclear step.

This mechanism makes one unusual prediction, namely that $H_2Os(CO)_4$ successfully competes with carbon monoxide for the coordinatively unsaturated intermediate $H_2Os(CO)_3$, so that decomposition will occur faster than carbonyl exchange. The entire scheme could thus be tested by heating $H_2Os(CO)_4$ under an atmosphere of ^{13}CO and stopping the reaction after one half-life. Mass spectroscopic analysis of the isolated components showed only 4% label incorporation in the recovered $H_2Os(CO)_4$, while there was 51% label incorporation in the product $H_2Os_2(CO)_8$. The latter result exceeds the minimum (12.5%) required by the last step of the proposed mechanism and shows that $H_2Os_2(CO)_8$, unlike $H_2Os(CO)_4$, undergoes rapid carbonyl exchange under the reaction conditions.

Thus, in this dihydride at least, thermal reductive elimination of molecular hydrogen does not occur, loss of carbon

monoxide and subsequent dinuclear elimination occurring instead. It is worth noting that (1) loss of CO is also the primary photoprocess occurring upon irradiation of $H_2Os(CO)_4$ in an argon matrix at 20°K[15] and (2) loss of molecular hydrogen does occur as the principal fragmentation mode of the parent ion $H_2Os(CO)_4$ in the mass spectrometer. We are currently investigating the extent to which these dinuclear processes also occur in the reactions of the related alkyl species.

References and Notes

(1) P. S. Braterman and R. J. Cross, Chem. Soc. Rev., **2**, 271 (1973), and references therein.
(2) F. L'Eplattenier and F. Calderazzo, Inorg. Chem., **6**, 2092 (1967).
(3) F. L'Eplattenier and C. Pelichet, Helv. Chim. Acta, **53**, 1091 (1970), and references therein.
(4) R. D. George, S. A. R. Knox, and F. G. A. Stone, J. Chem. Soc., Dalton Trans., 972 (1973).
(5) J. R. Moss and W. A. G. Graham, Chem. Commun., 800 (1969).
(6) J. R. Moss and W. A. G. Graham, J. Organometal. Chem., **23**, C47 (1970).
(7) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, Chem. Commun., 477 (1971).
(8) C. R. Eady, B. F. G. Johnson, and J. Lewis, J. Organometal. Chem., **57**, C84 (1973).
(9) A previous brief report[6] of the thermolyses of $H_2Os(CO)_4$ and $H_2Os_2(CO)_8$ reported products not incompatible with our observations, although the sequence $H_2Os(CO)_4 \rightarrow H_2Os_2(CO)_8 \rightarrow H_4Os_4(CO)_{12}$ and $Os_3(CO)_{12}$ has not hitherto been established.
(10) The stated uncertainty reflects the slow H_2–D_2 equilibration (vide infra).
(11) The reactions were run in concentrated mesitylene solution and followed by nmr with octamethylcyclotetrasiloxane as internal standard.
(12) Although the rate is independent of p_{CO} up to the highest experimentally practical pressure (600 mm), this observation is not at all inconsistent with a dissociative mechanism; the concentration of CO in the liquid phase is quite small compared to the concentration of $H_2Os(CO)_4$ (about 0.4 M). Since the rate-determining step must be unimolecular and is demonstrably not the loss of molecular hydrogen, there is in any case no chemically plausible alternative.
(13) A similar mechanism has been proposed for the loss of hydrogen from the monohydride $HCo(CO)_4$ by Ungvary and Marko.[14] However, they postulate equilibrium dissociation of a carbonyl group prior to the bimolecular elimination step.
(14) F. Ungvary and L. Marko, J. Organometal. Chem., **20**, 205 (1969).
(15) A. J. Rest, personal communication of unpublished work.

John Evans, Jack R. Norton*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received August 22, 1974

MINDO/3 Study of the Thermolysis of Dioxetane. Role of the Triplet State[1]

Sir:

The thermolysis of derivatives (**1**) of 1,2-dioxetane to pairs of carbonyl derivatives (**2**) is a well known chemiluminescent process. The emission of light is due to phosphorescence of one of the product molecules, this being formed in its triplet state. While estimates of the quantum yield vary,[2-6] most lie in the range 0.5–1.0, implying that intersystem crossing is taking place with high efficiency. As Kearns[7] has pointed out, it is difficult to see how this could be the case unless the intersystem crossing is an integral part of the reaction, the transition state corresponding to the point at which the singlet and triplet surfaces cross. This argument has not, however, been pressed, presumably because of the long held view that such a process would necessarily have a very low frequency factor.[8] The frequency factors for dissociation of dioxetanes seem in fact to be "normal."