Desorption of Hydrocarbons from Small Metal Clusters. Kinetics and Mechanism of Reductive Elimination of CH_3X from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$

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Mono- and dinuclear reductive eliminations of C–H bonds from monometallic hydridoalkyl complexes, important in many homogeneous catalytic processes, have been the subjects of numerous studies.[1] However, no studies of C–H reductive eliminations from isolated hydridoalkyl clusters, processes which may model hydrocarbon desorption from metal surfaces,[2] have been reported.[3] Such studies are important because the prevalence of bridging, rather than terminal, hydride and hydrocarbon ligands in polymetallic systems may be expected to result in differences in reactivity between clusters and monometallic complexes.

The cis orientations of the bridging hydrides and the methylidyne ligand of $H_3Ru_3(CX)(CO)_9$ make possible reductive elimination of either C–H or H–H bonds. When X = OMe, quantitative elimination of hydrogen occurs, forming $HRu_3(COMe)(CO)_{10}$ under CO.[5] However, the reaction of $H_3Ru_3(CX)(CO)_9$ with CO (X = Ph or CO_2Me) or with H_2/CO (X = OMe[6]) produces the corresponding CH_3X and Ru carbonyls ($Ru_3(CO)_{12}$ and $Ru(CO)_5$).[7] The molecularity of the hydride transfer was investigated with a crossover experiment. Under CO (1 atm), a mixture of $H_3Ru_3(CCO_2Et)(CO)_9$ and $D_3Ru_3(CCO_2Me)(CO)_9$ (95% deuteriated) in benzene-d_6 produced ethyl acetate (85% d_0, 15% d_1) and methyl acetate (72% d_3, 25% d_2); after correction for the ^1H content in the labeled cluster, these results are consistent with a mechanism involving at least two intramolecular and not more than one intermolecular reductive eliminations. Further control experiments are required before the intermolecularity of the formation of one of the three C–H bonds can be positively established.[20]

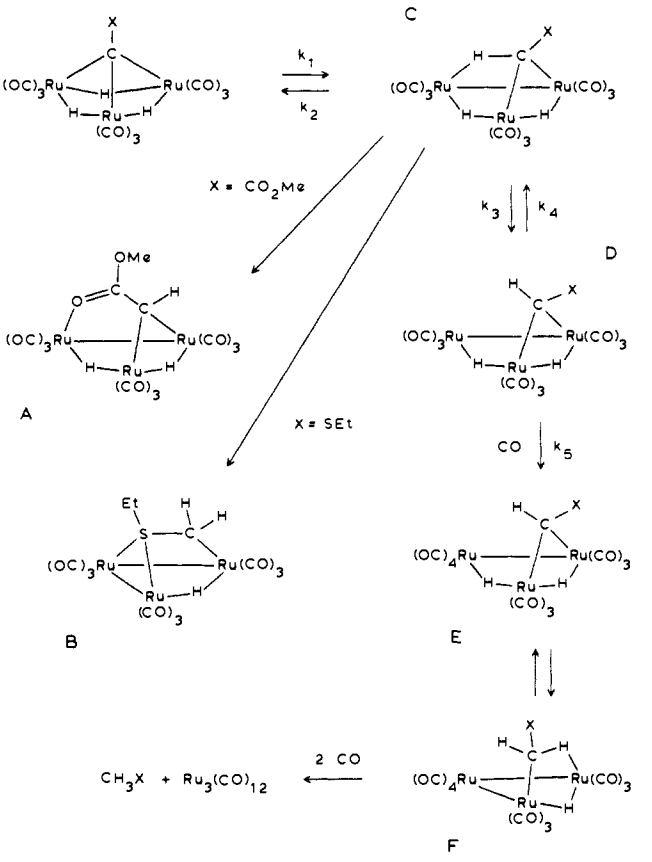

Figure 1. Proposed mechanism for reductive elimination of CH_3X from $H_3Ru_3(CX)(CO)_9$.

That sequential C–H reductive elimination occurs is suggested by isolation of substituted methylene and methyl analogues stabilized by coordination of the methylidyne substituent. Pyrolysis of $H_3Ru_3(CCO_2Me)(CO)_9$ in the absence of CO (cyclohexane solution, 70 °C, 24 h) produces $H_2Ru_3(CHCO_2Me)(CO)_9$[8] (Figure 1, structure A, 56% yield), in which the acyl oxygen is coordinated to produce a saturated cluster. Pyrolysis of $H_3Ru_3(CSEt)(CO)_9$ even under CO produces $HRu_3(CH_2SEt)(CO)_9$[10] (Figure 1, structure B[11]) in which the S atom acts as a four-electron donor.

The kinetics of these reactions have been investigated. The rate law for elimination of toluene from $H_3Ru_3(CPh)(CO)_9$ under CO pressures between 0.45 and 35 atm is given by the following equation: rate = $[acP_{CO}/(b + cP_{CO})][H_3Ru_3(CPh)(CO)_9]$, where $a = 6.5 \times 10^{-6}$ s^{-1} and $b/c = 0.47$ atm at 100 °C. The rate law is consistent with the mechanism shown in eq 1, in which an

$$H_3Ru_3(CX)(CO)_9 \rightleftarrows H_3Ru_3(CX)(CO)_9{}^* \xrightarrow{CO} \text{products} \quad (1)$$

(1) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (c) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227. (d) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (e) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (f) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376. (g) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150. (h) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (i) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447. (j) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415.

(2) (a) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283. (c) Baetzold, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 4271. (d) Shustorovich, E.; Baetzold, R. C.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 1100 and references therein.

(3) Hydrogenolysis of CH_3X from $Co_3(CX)(CO)_9$ has been investigated: (a) Seidler, P. F.; Bryndza, H. E.; Frommer, J. E.; Stuhl, L. S.; Bergman, R. G. *Organometallics* **1983**, *2*, 1701. (b) Geoffroy, G. L.; Epstein, R. A. *Inorg. Chem.* **1977**, *16*, 2795.

(4) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(5) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977.

(6) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.

(7) X = Ph, 93 ± 5%, analysis by NMR and GC; X = CO_2Me, yield 85%, analysis by NMR and GC; X = OMe, analysis by MS; $Ru_3(CO)_{12}$ and $Ru(CO)_5$, analysis by IR.

(8) Churchill, M. R.; Janik, T. J.; Duggan, T. P.; Keister, J. B., manuscript in preparation.

(9) The Os analogue has been prepared previously: Strickland, D. S. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1983.

(10) Dalton, D. M.; Keister, J. B. *J. Organomet. Chem.* **1985**, *290*, C37.

(11) The structure was established by an X-ray crystallographic study (Churchill, M. R.; Ziller, J. W., unpublished results).

(12) The rate constant for the reaction of $H_2Ru_3(CHCO_2Me)(CO)_9$ with CO (1 atm) at 70.5 °C (1.0×10^{-4} s^{-1}) is slightly greater than that for the first step.

(13) (a) Kellner, C. S.; Bell, A. T. *J. Catal.* **1981**, *71*, 288 and references therein. (b) Kobori, Y.; Naito, S.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1981**, 92. (c) Kellner, C. S.; Bell, A. T. *J. Catal.* **1981**, *67*, 175. (d) Mori, T.; Masuda, H.; Imai, H.; Miyamoto, A.; Baba, S.; Murakami, Y. *Chem. Lett.* **1981**, 831.

(14) Vites, J. C.; Jacobsen, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563.

(15) Bower, D. K.; Keister, J. B. *J. Organomet. Chem.*, in press.

(16) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

(17) (a) Poe, A.; Smith, R., presented at the XIIth International Conference on Organometallic Chemistry, Vienna, Austria, Sept 13, 1985. (b) Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1983**, *70*, 121.

(18) Additional support for reversible formation of the agostic Ru–H–C bond is the observation of rapid scrambling of the methylidyne proton and hydrides of $H_3Ru_3(CH)(CO)_9$.[19]

(19) Shapley, J. R.; VanderVelde, D. G., unpublished results.

(20) See supplementary material.

(21) For very recent reports of inverse isotope effects for reductive elimination reactions, see: (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (c) Packett, D. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 5036.

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intramolecular rearrangement forms an activated intermediate $H_3Ru_3(CX)(CO)_9$* prior to CO addition. Possibilities for the nature of this intermediate include structures containing (1) one or more terminal hydride ligands, (2) an agostic[4] Ru-H-C bond (Figure 1, structure C), or (3) a fully formed C-H bond and an unsaturated metal site (Figure 1, structure D) which should rapidly react with CO. The third possibility is most likely since (1) and (2) are saturated and unlikely to add CO. Entropies of activation for the limiting rate constants for disappearance of $H_3Ru_3(CX)(CO)_9$ are close to zero [+6 (±2) (Cl), +1.6 (±1.5) (Ph), and −5 (±3) (CO_2Me) eu], consistent with an intramolecular mechanism, and the enthalpies of activation are relatively large [31.4 (±0.9) (Cl), 31.4 (±0.6) (Ph), and 25.1 (±1.0) (CO_2Me) kcal/mol]. The lower value for the activation enthalpy for the CO_2Me derivative may indicate participation of the acyl moiety in the transition state; the rate constant for rearrangement of $H_3Ru_3(CCO_2Me)(CO)_9$ to $H_2Ru_3(CHCO_2Me)(CO)_9$ is the same as that for reductive elimination of methyl acetate in the presence of CO, indicating the same rate-determining step for both reactions.[12]

The deuterium isotope effects, ${}^{H}k_{obsd}/{}^{D}k_{obsd}$, for the reductive elimination from $H_3Ru_3(CX)(CO)_9$ were measured to be 1.00 (±0.05) (3.8 atm, 60 °C) for X = CO_2Me and 0.64 (±0.06) (35 atm, 100 °C) for X = Ph. Isotope effects for reductive eliminations from monometallic complexes fall in the range 1.3-3.3,[1,21] but isotope effects for the formation of hydrocarbons by hydrogenations of carbon or CO on surfaces are frequently less than 1.[13] The inverse isotope effects can be explained by the existence of equilibria involving intermediates in which the force constant of the hydrogen is higher than in the ground state. The calculated equilibrium isotope effects for intermediates having (a) a terminal hydride ligand, (b) a fully formed C-H bond, and (c) an agostic Ru-H-C bond are 0.72, 0.44, and 0.54, respectively.[20] However, normal isotope effects are found for reductive eliminations of molecular hydrogen from clusters having bridging hydrides,[5,17] arguing against (a), and these isotope effects are measured at high CO pressures, where the rate-determining step is formation of $H_3Ru_3(CX)(CO)_9$*, assumed to have a fully formed C-H bond. Then the inverse isotope effect implies the existence of a preequilibrium involving a second intermediate, different than $H_3Ru_3(CX)(CO)_9$* but of the same formulation, most likely having an agostic Ru-H-C bond.[18]

The mechanism shown in Figure 1 fully accounts for the observed rate law and deuterium isotope effects. The structure of intermediate C containing an agostic Ru-H-C bond has precedence in the formation of the isostructural species $HFe_3(HCH)(CO)_9^{1-}$ and $H_3Ru_3(HCEt)(CO)_9^{1+}$.[14,15] Intermediates E and F are based upon the structures of the analogous Os clusters.[16] The slow step in the reductive elimination process is formation of D. The rate law for this mechanism is given by eq 2, of the same form as that found experimentally. At high CO

$$\text{rate} = [k_1k_3k_5P_{CO}/(k_2k_4 + (k_2 + k_3)k_5P_{CO})][H_3Ru_3(CX)(CO)_9] \quad (2)$$

pressures the rate-determining step is formation of the activated intermediate $H_3Ru_3(CX)(CO)_9$* (D) and the observed rate constant becomes k_1k_3/k_2 if $k_2 >> k_3$. Since the isotope effect upon the value of the equilibrium constant k_1/k_2 is <1, the value of ${k_{obsd}}^{H}/{k_{obsd}}^{D}$ will be <1 if the isotope effect upon k_3 is not much > 1.

In conclusion, reductive elimination of CH_3X from $H_3Ru_3(CX)(CO)_9$ proceeds by sequential formation of the three C-H bonds, at least two of which are formed by intramolecular processes. An inverse isotope effect for reductive elimination suggests a preequilibrium between species containing Ru-H-Ru and Ru-H-C bonds.

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Supplementary Material Available: Table of kinetic data for reductive elimination of CH_3X from $H_3Ru_3(CX)(CO)_9$, X = Ph, Cl, and CO_2Me, table of analysis of mass spectral data from the crossover experiment, and calculations of equilibrium isotope effects (4 pages). Ordering information is given on any current masthead page.

5-(Trifluoromethyl)bacteriorhodopsin Does Not Translocate Protons

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We wish to report that a proper fit of the retinal chromophore in the bacteriorhodopsin (bR) binding site is necessary for proton pumping. Bacteriorhodopsin[1], the pigment contained in the purple membrane of *Halobacterium halobium*, functions as a light-driven proton pump and converts solar energy into a proton gradient that is coupled to ATP synthesis.[2] The retinal chromophore is covalently linked to Lys-216[3] of the apoprotein via a protonated Schiff base (SBH^+) linkage.[4,5] There are two forms of bR,[2,6] the light-adapted bR^{LA} absorbing at 570 nm and the dark-adapted bR^{DA} absorbing at 560 nm, the chromophores of which are respectively *all-trans*-retinal and a 1:1 mixture of *trans*- and 13-*cis*-retinal. Both forms undergo a photocycle but only bR^{LA} translocates protons. The red shift to 570 nm in bR from 440 nm (in MeOH) in retinal/butylamine-SBH^+ has been attributed to electrostatic interactions between the protonated chromophore and the protein within the binding site (external point charge model, Figure 1).[7,8]

The present studies with 5-(trifluormethyl)(5-TFM)-5-norretinal[9] were undertaken in order to investigate the effect of electronic perturbation on the point charges near the β-ionone ring. Incubation of retinal oxime free apo-membrane[10] with *trans*-5-TFM-retinal (HEPES buffer, pH 7.0) in the dark for 60 min resulted in smooth formation of pigment (5-TFM-bR), the "dark-regenerated" pigment, λ_{max} 465 nm (Figure 2a). Irradiation

(1) (a) Oesterhelt, D.; Stoeckenius, W. *Nature (London) New Biol.* **1971**, *233*, 149-152. (b) Oesterhelt, D.; Stoeckenius, W. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2853-2857.

(2) *Methods Enzymol.* **1982**, *88*, Biomembranes Part I.

(3) (a) Bayley, H.; Huang, K. S.; Radhakrishnan, R.; Ross, A. H.; Tagakaki, Y.; Khorana, H. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2225-2229. (b) Lemke, H. D.; Oesterhelt, D. *FEBS Lett.* **1981**, *128*, 255-260. (c) Muller, E.; Johnson, A. H.; Akhtar, M. *FEBS Lett.* **1981**, *130*, 187-193.

(4) Lewis, A.; Spoonhower, J.; Bogomolni, R. A.; Lozier, R. H.; Stoeckenius, W. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 4462-4464.

(5) (a) Rothschild, K. J.; Marrero, H. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4045-4047. (b) Bagley, K.; Dollinger, G.; Eisenstein, L.; Singh, A. K.; Zimanyi, L. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4972-4976.

(6) Kouyama, T.; Bogomolni, R. A.; Stoeckenius, W. *Biophys. J.* **1985**, *48*, 201-208.

(7) (a) Nakanishi, K.; Balogh-Nair, V.; Arnaboldi, M.; Tsujimoto, K.; Honig, B. *J. Am. Chem. Soc.* **1980**, *102*, 7945-7947. (b) Spudich, J. L.; McCain, D. A.; Nakanishi, K.; Okabe, M.; Shimizu, N.; Rodman, H.; Honig, B.; Bogomolni, R. A. *Biophys. J.* **1986**, *46*, 479-483.

(8) The planar 6-s-trans ring/chain conformation takes into account the evidence from NMR: Harbison, G. S.; Smith, S. O.; Pardeon, J. A.; Courtin, J. M. L.; Lugtenburg, J.; Herzfeld, J.; Mathies, R. A.; Griffin, R. G. *Biochemistry* **1985**, *24*, 6955-6962.

(9) Taguchi, T.; Hosoda, A.; Kobayashi, Y. *Tetrahedron Lett.* **1985**, *26*, 6209-6212.

(10) Bayley, H.; Radhakrishnan, R.; Huang, K. S.; Khorana, H. G. *J. Biol. Chem.* **1981**, *256*, 3797-3801.

0002-7863/86/1508-6077$01.50/0 © 1986 American Chemical Society