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Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (5 pages); a listing of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

(10) Fe-P bond distances in low-valent carbonyliron complexes usually fall in the range of 2.17-2.35 Å. See, e.g.: (a) Knoll, K.; Huttner, G.; Wasiecionek, M.; Zsolnai, L. *Angew. Chem.* 1984, 96, 708; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 739. (b) Lal De, R.; Vahrenkamp, H. *Z. Naturforsch.*, B: *Anorg. Chem., Org. Chem.* 1986, B41, 273. (c) Arif, A. M.; Cowley, A. H.; Pakulsky, M. *J. Am. Chem. Soc.* 1985, 107, 2553. (d) Huttner, G.; Mohr, G.; Friedrich, G.; Schmid, H. G. *J. Organomet. Chem.* 1978, 160, 59. (e) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, 107, 729.

Competitive H-O and H-C Bond Activation in the Reaction of CH₃OH with (OC)₃Mn⁻

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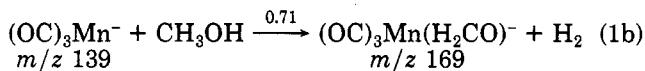
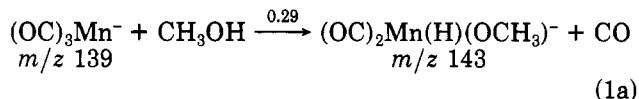
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Summary: The activation of the H-O and H-C bonds in CH₃OH are shown to be competitive in the reaction with (OC)₃Mn⁻ by product studies and kinetic deuterium isotope effects.

Three oxidative addition pathways involving the H-C,¹ H-O,^{2,3} and C-O bonds³ have been suggested for the reactions of coordinatively unsaturated transition-metal complexes with alcohols. We wish to report the results of product studies and kinetic deuterium isotope effects for the reaction of the 14-electron complex (OC)₃Mn⁻ with CH₃OH which support intermolecular H-C and H-O oxidative addition as the two competitive channels.

Our gas-phase studies are carried out in a previously described flowing afterglow (FA) apparatus in a fast flow of helium buffer gas ($P_{\text{He}} = 0.7$ torr, $\bar{v} = 57$ m s⁻¹, 298 K).⁴ A mixture containing major signals of (OC)₃Mn⁻ (m/z 139) and (OC)₄Mn⁻ (m/z 167) and a small signal of (OC)₅Mn⁻ (m/z 195) is produced by dissociative electron attachment of energetic electrons with Mn₂(CO)₁₀.⁵ Neither (OC)₄Mn⁻ or (OC)₅Mn⁻ react with CH₃OH, H₂O, or alkanes.

Addition of gaseous CH₃OH to the fast helium flow containing (OC)₃Mn⁻ produced a fast decay of the signal for (OC)₃Mn⁻ (m/z 139) and generated two product ions at m/z 143 and 169 (Table I and eq 1). The ion at m/z



143 is the (adduct - CO)⁻ analogous to the product formed by the oxidative addition of H₂O to (OC)₃Mn⁻.^{5,6} Although (OC)₂Mn(H)(OH)⁻ undergoes one H/D exchange when allowed to react with D₂O,⁷ no H/D exchange was observed between the m/z 143 ion and D₂O or CH₃OD, indicating the absence of the HO ligand. The m/z 143 ion reacted with SO₂ to yield (O₂S)Mn(H)(OCH₃)⁻ (m/z 151) by loss of both CO ligands which implies multiple Mn-to-O bonding in m/z 143 with the CH₃O ligand serving as a multielectron donor.⁵ The product ion at m/z 169 (eq 1b) is the (adduct - H₂)⁻ analogous to the olefin product ions generated by dehydrogenation of alkanes by (OC)₃Mn⁻.⁸ Reaction of the m/z 169 ion with SO₂ yields (OC)₃Mn(S-O₂)⁻ (m/z 203) with exclusive loss of H₂CO suggesting that H₂O is η²-bound in the ion at m/z 169.⁶

The reactions of (OC)₃Mn⁻ with various deuteriated methanol molecules were examined to determine the source of H₂ in the major product channel 1b and the kinetic deuterium isotope effects on both product forming channels. The elimination of HD in the reactions of (OC)₃Mn⁻ with CH₃OD and CD₃OH yielding (OD)₃Mn(H₂CO)⁻ (m/z 169) and (OC)₃Mn(D₂CO)⁻ (m/z 171), respectively, establish the origin of H₂ in channel 1b as the H-O bond and a H-C bond in the CH₃OH molecule (Table I).

The kinetic and product data for the reactions of (OC)₃Mn⁻ with CH₃OH, CH₃OD, CD₃OH, and CD₃OD are given in Table I. Although the errors in the reproducibility of the rate constants and product channel branching fractions are significant, we have calculated the rate constants for the separate product forming channels by using the average k_{total} and average branching fractions. The good agreement in the two values each obtained for k_{CH_3} and k_{CD_3} in these experiments strongly suggests that the initial intermolecular oxidative addition of the H-C and D-C to (OC)₃Mn⁻ is rate limiting in channel 1b and that the intramolecular migration of H or D from oxygen to the metal is fast and does not contribute to the rate. A similar conclusion was reached for the inter- and intramolecular steps in the related dehydrogenation of alkanes by (OC)₃Mn⁻.⁸ With use of the average of the two values for k_{CH_3} and k_{CD_3} , $k_{\text{CH}_3}/k_{\text{CD}_3} \approx 2.4$.

The rate constant k_{OD} derived in the reactions of (OC)₃Mn⁻ with CH₃OD and CD₃OD will have the larger error since these channels involve the smallest product ion signal intensities. However, the good agreement in the two results in Table I support $k_{\text{OD}} \approx 4.8 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ in these reactions. Thus, $k_{\text{OH}}/k_{\text{OD}} \approx 7$ is calculated for channel 1a involving oxidative addition of the H-O bond

(1) *Chem. Eng. News* 1985, 53 describes the paper of Professor R. G. Bergman given at the PAC CHEM 1984 meeting, and private communications with Professor Bergman. Products of exclusive H-C oxidative addition were observed or inferred by J. C. Hayes and P. O. Stoutland when mixtures of [c-C₃(CH₃)₃][(CH₃)₂P]Ir(H)₂ in *tert*-butyl alcohol or ethanol were irradiated in the condensed phase.

(2) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* 1985, 107, 6403.

(3) McElvany, S. W.; Allison, J. *Organometallics* 1968, 5, 416, 1219.

(4) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1985, 107, 4123. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* 1980, 102, 6491.

(5) McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* 1986, 108, 3105.

(6) The reverse of the present oxidative addition reactions involving selective reductive elimination of CH₃OH from (Me₃P)₂(Cl)(OC)Rh(H)(OCH₃) and of H₂CO from (Me₃P)₂(Cl)(OC)Rh(H)(CH₂OH) was recently proposed: Milstein, D. *J. Am. Chem. Soc.* 1986, 108, 3525.

(7) We believe that the fast, single H/D exchange observed in the reaction of (OC)₂Mn(H)(OH)⁻ with D₂O occurs on the HO ligand via a four-centered intermediate or transition state. If (OC)₂Mn(H)(OH)⁻ had oxidatively added D₂O, the possible products could be the starting complex ion containing one and two deuteriums (m/z 144 and 145) formed by retroaddition along with the HD elimination product (OC)₂Mn(OH)(OD)⁻; (OC)Fe(H)(OH)⁻ slowly added H₂O to yield (OC)Fe(OH)₂⁻.⁵ (OC)₂Mn(H)(OH)⁻ failed to react with H₂O ($k < 10^{-13}$ cm³ molecule⁻¹ s⁻¹) under these same reaction conditions.⁵

(8) McDonald, R. N.; Jones, M. T. *J. Am. Chem. Soc.* 1986, 108, 8097.

