sequently, but results so far establish that rectification can be achieved with a relatively small assembly of molecular materials.

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Supplementary Material Available: A scheme and experimental details for the synthesis of I, II, and IV and ^{1}H NMR data (4 pages). Ordering information is given on any current masthead page.

C-H vs. O-H Reductive Elimination of Methanol from a Metal Complex. Which Is a More Likely Process?

David Milstein

Contribution No. 3999
Central Research & Development Department
E. I. du Pont de Nemours & Company
Experimental Station, Wilmington, Delaware 19898

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Elimination of methanol from a metal complex, which constitutes the product-forming step in CO hydrogenation to this product, may, in principle, involve C-H reductive elimination of a hydroxymethyl hydride complex or O-H reductive elimination of a methoxy hydride intermediate[1] (eq 1). Although intramo-

$$\text{H-M-CH}_2\text{OH} \xrightarrow{\text{I}} \text{CH}_3\text{OH} \xleftarrow{\text{II}} \text{H-M-OCH}_3 \qquad (1)$$

lecular C-H reductive elimination is now well documented,[2] examples for processes of the type I or II are exceedingly scarce. *cis*-$[\text{HIr(PMe}_3)_4\text{CH}_2\text{OH}]^+$ does not eliminate methanol[3] whereas methanol is formed on reaction of Rh(OEP)(CH_2OH) with Rh(OEP)H[4] and hydrogenation of $(\text{CO})_4\text{MnCH}_2\text{OR}$ (R = Et, COCMe_3) yields CH_3OR.[5] Protonation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr(OCH}_3)\text{H}$ yields methanol[6] and $\eta^5\text{-C}_5\text{Me}_5\text{Ir(OEt)(PPh}_3)\text{H}$ photochemically eliminates ethanol.[7] Hydroxyplatinum hydride complexes undergo reductive elmination of water[8] and decomposition of methoxyplatinum complexes leads to methanol via postulated intermediacy of a methoxy hydride complex.[9]

Ideally, for the best possible comparison of processes I and II, complexes containing the same metal, ligands, and stereochemical arrangement have to be employed. Here we describe such a study, leading to the conclusion that under identical conditions, methanol production via process II is preferred.

We have previously described[10] the preparation and preliminary decomposition data of the hydroxyacetyl complex **1**. The structural isomer of **1**, the carbomethoxy complex **2**, is obtained in 79% yield by addition of excess methyl formate to a toluene solution of $\text{Rh(PMe}_3)_3\text{Cl}$ at 25 °C followed by removal of the solvent in vacuo and crystallization of the resulting solid from toluene/pentane. **2**, obtained as yellow crystals, is unambiguously characterized by ^{1}H NMR, ^{31}P NMR, IR, and elemental analysis.[11]

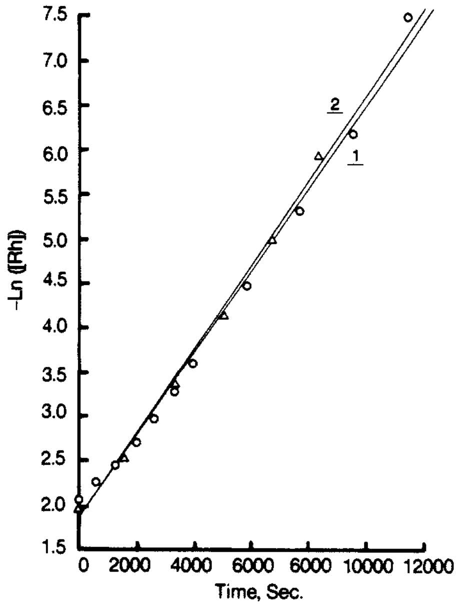
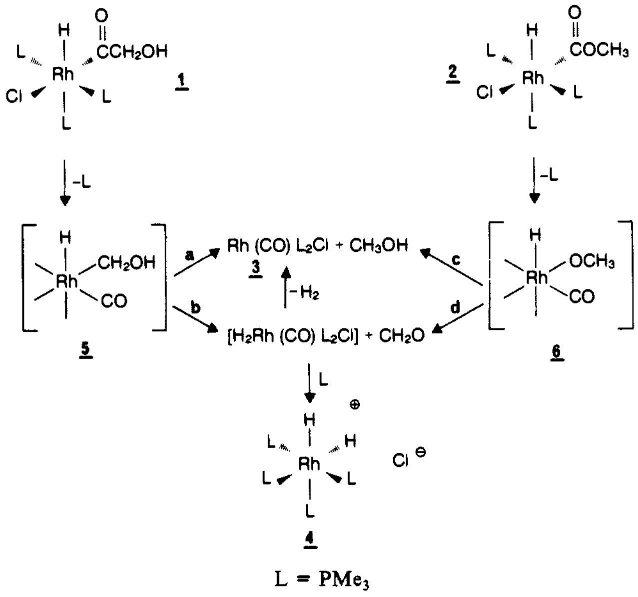


Figure 1. First-order plot for the decomposition of **1** and **2** in dioxane at 70 °C.

Scheme I



Isomers **1** and **2** are stable at 25 °C in the solid state but slowly decompose in solution. Upon heating 0.1 M solutions of the complexes in acetone or dioxane at 70 °C in sealed tubes for 12 h under identical conditions, **1** and **2** undergo complete decomposition, leading to formation of the same products but in very different amounts. **1** yields formaldehyde as the major organic product[10] (87% yield based on **1**) in addition to methanol (13%), $\text{Rh(CO)(PMe}_3)_2\text{Cl}$ (**3**) (61%), and $\text{H}_2\text{Rh(PMe}_3)_4{}^+\text{Cl}^-$ [12] (39%),

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(1) See, for example: (a) Dombek, B. D. *ACS Symp. Ser.* **1981**, *No. 152*, 213. (b) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (c) Feder, H. M.; Rathke, J. W.; Chen, J. M.; Curtiss, L. A. *ACS Symp. Ser., 1981, 152*, 19. (d) Keim, W. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Dordrecht, Netherlands, 1983; p 89.

(2) For recent reviews, see: (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

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(5) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466.

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(11) IR (film) 1960 cm^{-1} (m, $\nu_{\text{Rh-H}}$), 1630 (s, $\nu_{\text{C=O}}$), 1035 (s, $\nu_{\text{C-O}}$); ^{1}H NMR (C_6D_6) δ 1.24 (d, J = 7.3 Hz, 9 H, PMe_3), 1.39 (t, J = 3.3 Hz, 18H, 2PMe_3), 3.41 (s, 3H, OCH_3), -8.93 (d of q, $J_{\text{H-P}}$(trans) = 200.5, $J_{\text{H-P}}$(cis) = 15.7, $J_{\text{H-Rh}}$ = 15.8 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -5.21 (d of d, $J_{\text{Rh-P}}$ = 105.2, $J_{\text{P-P}}$ = 27.6 Hz, 2 P), -24.16 (d of t, $J_{\text{Rh-P}}$ = 86.2, $J_{\text{P-P}}$ = 27.6 Hz, 1 P).

(12) This complex is reported in: Jones, R. A.; Mayor, Real, F.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans* **1980**, 511.

whereas methanol (93%) is the major organic product obtained from **2**, followed by formaldehyde (7%), **3** (96%), and **4** (4%).[13] Scheme I outlines a mechanistic interpretation of these results. Both **1** and **2** undergo PMe_3 dissociation followed by deinsertion leading to intermediate hydroxymethyl hydride **5** and methoxy hydride **6**. These intermediates then undergo competing reductive elimination leading to methanol and **3** and β-hydride elminination forming formaldehyde and $H_2R(PMe_3)_2COCl$. The latter, which was not observed, undoubtedly reacts with PMe_3 to yield the isolated complex **4**, but it can also reductively eliminate hydrogen to form **3**. Indeed, when **4** is treated with 1 atm of CO at 25 °C in acetone, immediate H_2 elimination takes place to yield **3**. Since two modes for formation of **3** are operative, the relative importance of processes a and b as well as c and d is determined by the ratio of methanol to formaldehyde rather than **3** to **4**. Both the reductive elimination and the β-elimination processes are irreversible: **3** does not react with methanol and **4** does not react with formaldehyde (in the presence or absence of CO).

The disappearance of **1** and **2** in dioxane-d_8 at 70 °C was followed by ^1H NMR. In both cases, first-order dependence was observed for at least 3 half-lives. Significantly, almost the same rate constants are observed (Figure 1): for **1**, $k_{obsd} = 4.74 \times 10^{-4}$ s^{-1}, and for **2**, $k_{obsd} = 4.85 \times 10^{-4}$ s^{-1}. This is most likely a result of both processes having the same rate-determining step. Various elimination modes of octahedral *cis*-acylrhodium hydride–PMe_3 complexes[2b,14] as well as reductive elimination from *cis*-alkylrhodium hydride–PMe_3 complexes[2b,15] were shown to proceed via an unsaturated five-coordinate intermediate formed by a rate-determining PMe_3 dissociation from the position trans to the hydride. This is also most likely the case for the hydroxyacetyl complex **1** and thus also for **2**. Although careful rate measurements in the presence of added PMe_3 have not been carried out yet, retardation of the decomposition rate of both **1** and **2** upon addition of PMe_3 has been observed. It is thus possible to conclude that PMe_3 dissociation from **1** and **2**, required to allow for the migration process, is rate-determining. This tends to exclude a mechanism for methanol formation from **2** by deprotonation involving a methoxide anion generated from the carbomethoxy ligand. Additional support for this exclusion is obtained by partial decomposition of **2** in the presence of CD_3OD. At 50% decomposition, no incorporation of deuterium into **2** was observed. It is noteworthy that these results indicate, by microscopic reversibility, a concerted migratory mechanism for CO "insertion" into Rh-OCH_3, in agreement with results obtained for Pt(dppe)(OCH_3)CH_3.[16] Carbonylation of $Ir(PPh_3)_2(CO)(OR)$, however, is thought to proceed via an ionic mechanism.[17]

Regardless of the exact mechanism by which the intermediates **3** and **4** eliminate methanol and formaldehyde, we conclude that in our system methanol formation via an alkoxy hydride intermediate is preferred over methanol elimination from an hydroxymethyl hydride complex, which favors β-hydride elimination to yield formaldehyde.[18,19] This conclusion is relevant not only to CO hydrogenation mechanism but also to the mechanism of aldehyde hydrogenation[20,21] and formaldehyde hydroformylation[22] favoring alcohol formation by O–H rather than C–H reductive elimination.

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(13) The total amount of formaldehyde and products derived from it (trioxane, hemiformal) was determined colorimetrically by the chromotropic acid method, as described in: Walker, J. F. *Formaldehyde*, 3rd ed.; Reinhold: New York, 1964; p 469. Methanol was quantitatively determined by GC and NMR.

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(18) It is instructive to consider the thermodynamics of these reactions. Since the order of thermodyanic stability is $CH_2O + H_2 < CH_3OH$ and apparently $H_2Rh(CO)(PMe_3)_2Cl < Rh(CO)(PMe_3)_2Cl+H_2$ (since $H_2Rh(CO)(PMe_3)_2Cl$ apparently undergoes spontaneous reductive elimination of hydrogen), it follows that formation of $H_2Rh(CO)(PMe_3)_2Cl + CH_2O$ is thermodynamically less favored than $Rh(CO)(PMe_3)_2Cl + CH_3OH$. Thus, prevalence of the β-elimination process for **5** is probably kinetic in nature.

(19) Ru–OCH_3 intermediacy is postulated in the clean Ru-catalyzed CO hydrogenation to methanol.[1a] The reported formation of glycols in this system upon addition of carboxylic acids may be a result of trapping of a hydroxymethyl intermediate by esterification which prevents the β-elimination process.

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An Unusual Methoxy Group Migration: Synthesis of *cis*-CH_3OSF_4NCO and *cis*-$CH_3OSF_4NHC(O)OCH_3$

Joseph S. Thrasher,*[1a] Jon L. Howell,[1b,c] Matthew Clark,[1a] and Alan F. Clifford[1b]

Department of Chemistry, The University of Alabama
University, Alabama 35486
Department of Chemistry, Virginia Polytechnic
Institute and State University
Blacksburg, Virginia 24061

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In 1977 we reported the synthesis of $SF_4{=}NC(O)N(C_2H_5)_2$ from the reaction of pentafluorosulfanyl isocyanate with (diethylamino)trimethylsilane.[2] At that time the only other compound known to contain the $SF_4{=}N$ moiety was $SF_4{=}NCF_3$.[3] Since then several other $SF_4{=}NR$ derivatives have been prepared, where R = CH_3,[4] C_2H_5,[5] F,[6] C_2F_5,[7] and SF_5.[8] Shreeve and co-workers have also described a series of related $SF_3X{=}NR_f$[9] compounds. Recently, we have obtained additional spectroscopic data on $SF_4{=}NC(O)N(C_2H_5)_2$ and have prepared its dimethylamido analogue as well as the products $R_2NSF_3{=}NC(O)NR_2$ (R = CH_3, C_2H_5) which result from the addition of a second equivalent of the nucleophile.[10]

$$SF_5NCO + (C_2H_5)_2NSi(CH_3)_3 \rightarrow SF_4{=}NC(O)N(C_2H_5)_2 + (CH_3)_3SiF \quad (1)$$

In an attempt to synthesize further compounds containing the $SF_4{=}N$ moiety, we carried out the reaction of SF_5NCO with trimethylmethoxysilane. Initially, stoichiometric amounts of reactants were used, and since the isocyanate moiety did not disappear as expected, the reaction mixture was heated to 60 °C. The unexpected isolation of *cis*-methoxytetrafluorosulfanyl iso-

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(1) (a) The University of Alabama. (b) Virginia Polytechnic Institute and State University. (c) Current address: E. I. du Pont de Nemours & Co., Chemical and Pigments Dept., Wilmington, DE 19898.

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