HYDROGENOLYSIS OF ACYLCOBALT CARBONYL WITH METAL CARBONYL HYDRIDES¹⁾

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Investigation of dinuclear reductive elimination reactions between hexanoylcobalt tetracarbonyl and various ruthenium and cobalt metal carbonyl hydrides showed that $[HRu(CO)_4]$ reacts much faster to form hexanal than HCo(CO)₄. Other hydrides such as $[HRu_3(CO)_{11}]^-$, $[H_2Ru_4(CO)_{12}]^{2-}$, $HRuCo_3(CO)_{12}$ and $HFeCo_3(CO)_{12}$ are less reactive compared with the above hydrides.

The hydrogenolysis step of a metal acyl intermediate forming an aldehyde is now the subject of controversy in the mechanism for the hydroformylation reaction of olefins. Recently several papers suggested the dinuclear reductive elimination of aldehydes from metal acyls and metal hydrides in the cobalt- and rhodium-catalyzed hydroformylation.²⁾ In a previous paper, we found remarkable synergistic effect of cobalt and ruthenium on the hydroformylation of cyclohexene catalyzed by a mixture of $\text{Co}_2(\text{CO})_8$ and $\text{Ru}_3(\text{CO})_{12}$.³⁾ This finding has led us to investigate the reaction of acylcobalt with ruthenium hydrides. We describe here the kinetic results of the dinuclear reductive elimination of hexanal from hexanoylcobalt tetracarbonyl and several kinds of metal carbonyl hydrides.

All reactions were performed in NMR tubes under CO and the initial rates were determined by measuring the intensity of the aldehyde proton signal by JNM GX-400 NMR Spectrometer with a variable temperature probe. In a typical experiment, a solution of a metal hydride in dry CD_2Cl_2 was syringed into an NMR tube under CO which contained a CD_2Cl_2 solution of the nearly equimolar acylcobalt with naphthalene as an internal standard. The mixture was stirred quickly at room temperature and measured periodically by the spectrometer. In the reactions with HCO(CO)₄ or [HRu(CO)₄]⁻, the mixtures were prepared at -78 °C and warmed up to 20 °C or 0 °C in the NMR probe just before the measurement. A typical stacked plot of the ¹H NMR



Fig. 1. Stacked plot of ¹H NMR spectra taken during the reaction of hexanoylcobalt tetracarbonyl with HCo(CO)₄ at 20 °C (Table 1, run 1). The peak marked 'b' is uncharacterized. The peaks of naphthalene, solvent and THF are omitted here for clarity.

spectra taken during the reaction with HCo(CO) 4 at 20 °C is shown in Fig. 1.

Table 1 shows the initial rates of hexanal formation and the rate constants calculated by assuming that the reactions proceed with first-order in each reactant. It is noteworthy that the hydrido complex $[HRu(CO)_4]^-$ which shows hydridic character reacts much faster with the acylcobalt to form hexanal than $HCo(CO)_4$ which is a strong acid.⁵⁾ Other hydrides such as $[HRu_3(CO)_{11}]^-$, $[H_2Ru_4(CO)_{12}]^{2-}$, $HRuCo_3(CO)_{12}$ and $HFeCo_3(CO)_{12}$ were less reactive compared with $[HRu(CO)_4]^-$ and $HCo(CO)_4$. Though the pKa value of $HFeCo_3(CO)_{12}$ is ca. 2.0⁶⁾ which is close to that of $HCo(CO)_4$ (ca.

| Run | Metal carbonyl hydride (H-M) | [H-M] 10 ² M | $\frac{[\text{RCOCo}(\text{CO})_4]}{10^2 \text{M}}$ | Rate Ms ⁻¹ | к ^{b)} м ⁻¹ s ⁻¹ |
|-----------------|--|----------------------------|---|------------------------------|--|
| | | | | | |
| 2 | $[(PPh_3)_2N][HRu(CO)_4]$ | 2.07 | 1.87 | 3.0×10^{-5} | 7.8×10^{-2} |
| 3 ^{d)} | нсо (со) ₄ | 2.11 | 2.08 | 1.4×10^{-7} | 3.1×10^{-4} |
| 4 ^{d)} | $[(PPh_3)_2N][HRu(CO)_4]$ | 2.55 | 2.49 | 5.8×10^{-6} | 9.2×10^{-3} |
| 5 | [Et ₄ N] [HRu ₃ (CO) ₁₁] | 2.81 | 3.03 | 1.4×10^{-7} | 1.6×10^{-4} |
| 6 ^{e)} | [Et ₄ N] [HRu ₃ (CO) ₁₁] | 3.48 | 2.71 | 2.9×10^{-7} | 3.1×10^{-4} |
| 7 | $[PPh_4]_2 [H_2Ru_4 (CO)_{12}]$ | 2.56 | 2.68 | 2.9×10^{-7} | 4.2×10^{-4} |
| 8 | $HRuCo_3(CO)_{12}$ | 1.49 | 1.60 | 1.8×10^{-8} | 7.4×10^{-5} |
| 9 | HFeCo ₃ (CO) ₁₂ | 1.72 | 2.20 | 2.9×10^{-8} | 7.8×10^{-5} |

Table 1. Initial rates of hexanal formation and the rate constants in the reactions of $CH_3(CH_2)_4COCo(CO)_4$ with various metal carbonyl hydrides^{a)}

a) Reactions were carried out in dry CD_2Cl_2 under CO (1 atm). Reaction temperature was kept between 19 °C and 21 °C. b) $k = Rate/[RCOCO(CO)_4][H-M]$. c) The NMR tube was sealed off at -196 °C in vacuo. d) At 0 °C. e) Under N₂ 1 atm.

1.0),⁵⁾ the reactivity of the hydride toward the acylcobalt is extremely lower than that of HCo(CO)₄. In the reaction with [HRu(CO)₄]⁻, the hydrides $[H_2Ru_4(CO)_{12}]^{2-}$ and $[HRu_3(CO)_{11}]^-$ were formed together with hexanal. The rates of the formation of those hydrides were similar to that of the aldehyde. A possible overall equation of this reaction is described as follows on the basis of the ¹H NMR data.

$$7 \text{RCOCo}(\text{CO})_{4} + 10 [\text{HRu}(\text{CO})_{4}]^{-} \longrightarrow 7 \text{ RCHO} + 7 [\text{Co}(\text{CO})_{4}]^{-} + \text{Ru}_{3}(\text{CO})_{12} + [\text{HRu}_{3}(\text{CO})_{11}]^{-} + [\text{H}_{2}\text{Ru}_{4}(\text{CO})_{12}]^{2-} + 5\text{CO}$$

The hexanal formation from the reaction between $[HRu_3(CO)_{11}]^-$ and the acylcobalt was accelerated under N₂, indicating that the slow step of the reaction may be the formation of coordinatively unsaturated acylcobalt species (runs 5 and 6). The reaction gives both hexanal and two kinds of hydrides which exhibit the hydride resonances at $\delta = -13.9$ and -18.8, respectively, in the ¹H NMR spectra. When the reaction is carried out under CO, $\operatorname{Ru}_3(\operatorname{CO})_{12}$ and a metal hydride which shows the hydride resonance at $\delta = -13.9$ are formed together with hexanal. The reaction with $\left[\operatorname{H}_2\operatorname{Ru}_4(\operatorname{CO})_{12}\right]^{2-}$ under CO gives $\left[\operatorname{HRu}_3(\operatorname{CO})_{11}\right]^{-}$ and several metal carbonyl hydrides in addition to hexanal. However, in the reactions, the rates of the formation of those metal carbonyl hydrides were rather slower than those of the aldehyde.

The above results indicate that the remarkable rate increase in the hydroformylation with cobalt/ruthenium bimetallic systems is probably caused by dinuclear reductive elimination of aldehydes from acylcobalt carbonyls and ruthenium hydrides such as $[HRu(CO)_{4}]^{-}$.

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