

## The Characterization of $\text{HRh}(\text{CO})_2\text{I}_3^-$ and $\text{EtCORh}(\text{CO})_2\text{I}_3^-$ : Two Key Intermediates in Rhodium-Catalyzed Carbonylation of Ethylene

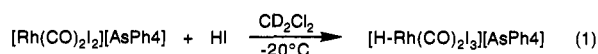
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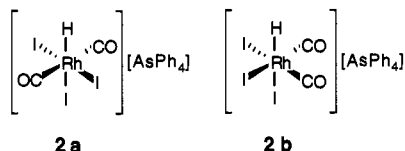
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The rhodium-catalyzed HI-promoted carbonylation of methanol to acetic acid (Monsanto process) is not limited to methanol, as higher alcohols such as ethanol or propanol and olefins such as ethylene and propene are also converted into  $\text{C}_3$  and  $\text{C}_4$  monocarboxylic acids, respectively. On a molecular level, there are two mechanisms proposed to account for the formation of carboxylic acids from olefins. One involves the formation of alkyl iodides as described in the literature for methanol carbonylation.<sup>1</sup> The other involves an olefin/rhodium hydride pathway. The first alternative has been thoroughly investigated, and the mechanism for the oxidative addition of methyl iodide to  $\text{Rh}(\text{CO})_2\text{I}_2^-$  is widely accepted.<sup>2</sup> In contrast, a mechanism involving rhodium hydrides and olefins in the carbonylation of olefins and higher alcohols has not yet been established even though it has been proposed.<sup>3</sup> Herein we report the characterization of  $[\text{HRh}(\text{CO})_2\text{I}_3][\text{AsPh}_4]$  (**2**) and its reactivity with ethylene to elucidate the mechanism of ethylene carbonylation.

The reaction of  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]$  (**3**) with 1 equiv of HI in dichloromethane solution was monitored by  $^1\text{H}$  NMR spectroscopy. At  $-20^\circ\text{C}$ , the  $^1\text{H}$  NMR spectrum shows a doublet at  $\delta(^1\text{H}) = -10.45$  ppm [ $^1J(^{103}\text{Rh}-^1\text{H}) = 4.2$  Hz], which vanishes on warming the solution to  $25^\circ\text{C}$  and is replaced by a singlet at  $\delta(^1\text{H}) = 4.7$  ppm appropriate for dihydrogen. The presence of a high-field proton resonance in the cold solution can be attributed to the hydride **2** formed by reaction of **3** with HI as shown in eq 1.



Further spectroscopic evidence of the formation of **2** was obtained from the reaction of  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]$  with HI at  $-20^\circ\text{C}$ .  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]$  ( $\delta(^{13}\text{C}) = 182.8$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 72.3$  Hz]) reacts quantitatively with 1 equiv of HI to give  $[\text{HRh}(\text{CO})_2\text{I}_3][\text{AsPh}_4]$  ( $\delta(^{13}\text{C}) = 177.9$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 50.5$  Hz,  $^1J(^{13}\text{C}-^1\text{H}) = 3.8$  Hz],  $\delta(^1\text{H}) = -10.45$  ppm, [ $^1J(^{13}\text{C}-^1\text{H}) = 3.8$  Hz,  $^1J(^{103}\text{Rh}-^1\text{H}) = 3.4$  Hz]). The NMR data is consistent with structures **2a** and **2b** where the two CO ligands are equivalent. Infrared analysis of **2** at  $-10^\circ\text{C}$  shows



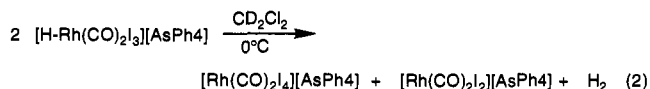
only one CO stretching frequency at  $2080\text{ cm}^{-1}$ , which rules out

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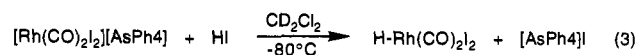
(2) Haynes, A.; Mann, B. E.; Gulliver, D. J.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 8567. Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 4093.

(3) Dekleva, T. W.; Forster, D. *J. Mol. Catal.* **1985**, *33*, 269; *J. Am. Chem. Soc.* **1985**, *107*, 3565, 3568.

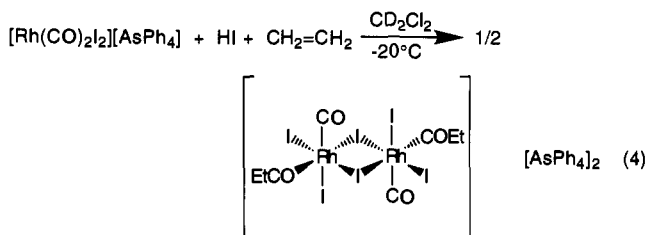
structure **2b**.<sup>4</sup> The Rh-H stretching frequency was not located. **2** is stable if kept at low temperatures ( $-30^\circ\text{C}$  or below) but disproportionates at higher temperatures ( $t_{1/2}$  at  $-20^\circ\text{C} = 7$  h) to **3**,  $[\text{Rh}(\text{CO})_2\text{I}_4][\text{AsPh}_4]$  (**4**), and dihydrogen (eq 2).



The formation of **2** does not occur in one step. We found, by monitoring the reaction of  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]$  with HI from  $-80^\circ\text{C}$  to  $-20^\circ\text{C}$ , that prior to formation of **2** there appears a new complex suggesting an intermediate in the pathway to **2**. This intermediate exhibits ( $-80^\circ\text{C}$ ) a broad resonance centered at  $\delta(^1\text{H}) = -8.40$  ppm in the  $^1\text{H}$  NMR spectrum and a doublet at  $173.83$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 60.3$  Hz] ( $^1\text{H}-^{13}\text{C}$  coupling was not observed) in the  $^{13}\text{C}$  NMR spectrum.  $^1\text{H}-^{103}\text{Rh}$  coupling (6.2 Hz) was observed at  $-100^\circ\text{C}$ . The presence of a hydride-like resonance and the clean conversion to **2** suggest the structure  $\text{HRh}(\text{CO})_2\text{I}_2$  (**1**) as an intermediate in the formation of **2** (eq 3).  $\text{HRh}(\text{CO})_2\text{I}_2$  would be the initial product of a two-step oxidative addition of HI to **3**.

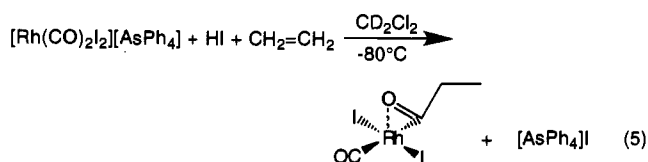


The participation of **1** and **2** in catalytic reactions was also examined. As a simple example of the chemistry of these two hydrido compounds, we studied their reactivity toward ethylene. Reaction of **3** with HI in the presence of ethylene gives  $[\text{Et}(\text{CO})\text{Rh}(\text{CO})\text{I}_3][\text{AsPh}_4]_2$  (**5**) quantitatively at  $-20^\circ\text{C}$ .<sup>5</sup> In contrast to this fast transformation, reaction of **3** with ethyl iodide failed to give **5** under the same or more forcing conditions ( $60^\circ\text{C}$ , 24 h). The structure of **5** is analogous to that of  $[\text{Me}(\text{CO})\text{Rh}(\text{CO})\text{I}_3][\text{AsPh}_4]_2$ <sup>4</sup> as judged from the  $^{13}\text{C}$  NMR spectrum of  $[\text{Et}(\text{CO})\text{Rh}(\text{CO})\text{I}_3][\text{AsPh}_4]_2$  in dichloromethane where the presence of two isomers ( $214.8$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 21.6$  Hz],  $182.7$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 70.8$  Hz], and  $208.5$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 23.1$  Hz],  $182.4$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 66.7$  Hz]) is observed.  $^{13}\text{C}$  NMR magnetization transfer experiments indicate that both isomers are exchanging at a rate of about  $1.5\text{ s}^{-1}$ . It is very likely that the interconversion between the isomers involves dissociation to a five-coordinate intermediate,  $[\text{Et}(\text{CO})\text{Rh}(\text{CO})\text{I}_3][\text{AsPh}_4]$ , that can re-form **5** or deinsert carbon monoxide to give **3** and **4** along with ethylene and hydrogen. **5** is easily converted into  $[\text{Et}(\text{CO})\text{Rh}(\text{CO})_2\text{I}_3][\text{AsPh}_4]$  (**6**) in the presence of CO, and in the absence of CO **5** is regenerated cleanly.



(4) In contrast to  $\text{R}-\text{Ir}(\text{CO})_2\text{I}_3^-$  complexes where the thermodynamically stable isomer is the fac, cis isomer ( $\text{R} = \text{H}$ ,  $2102$ ,  $2050\text{ cm}^{-1}$ ;  $\text{R} = \text{Me}$ ,  $2098$ ,  $2045\text{ cm}^{-1}$ ;  $\text{R} = \text{COMe}$ ,  $2110$ ,  $2061\text{ cm}^{-1}$ ),  $\text{R}-\text{Rh}(\text{CO})_2\text{I}_3^-$  complexes that have been isolated exist as the mer, trans isomer with only one CO stretching band ( $\text{R} = \text{COMe}$ ,  $2083\text{ cm}^{-1}$ ;  $\text{R} = \text{COEt}$ ,  $2085\text{ cm}^{-1}$ ). The fac, cis isomers can be detected at low temperature reacting  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]$  with  $\text{RCOI}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ), but they isomerize quickly at  $-40^\circ\text{C}$  to the mer, trans isomer. It seems that for the Rh system the mer, trans isomer is the thermodynamically stable isomer and the fac, cis isomer the kinetic product.

When  $[\text{Rh}(\text{}^{13}\text{CO})_2\text{I}_2][\text{AsPh}_4]$  is treated with HI in the presence of ethylene at  $-80^\circ\text{C}$  and the reaction is monitored by  $^{13}\text{C}$  NMR, a signal at  $\delta(^{13}\text{C}) = 296.2$  ppm [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 28.9$  Hz] is observed. Increasing the temperature from  $-80^\circ\text{C}$  to  $-20^\circ\text{C}$  resulted in a gradual decrease in intensity of the low-field resonance and a concomitant increase in resonances corresponding to  $[(\text{CH}_3\text{-CH}_2\text{}^{13}\text{CO})\text{Rh}(\text{}^{13}\text{CO})\text{I}_3]_2[\text{AsPh}_4]_2$ . The detection of a low-field resonance in the reaction of ethylene with  $\text{HRh}(\text{CO})_2\text{I}_2$  suggests that the first intermediate formed may be a complex of structure  $\eta^2\text{-CH}_3\text{CH}_2\text{CO-Rh}(\text{CO})\text{I}_2$  with an  $\eta^2$ -acyl group (eq 5). To

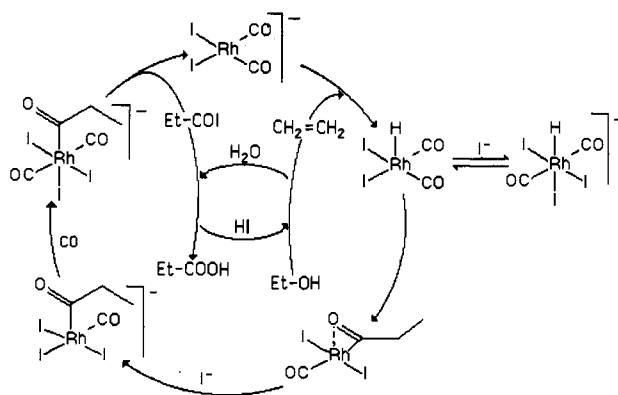


further substantiate this hypothesis,  $^{13}\text{CH}_2=^{13}\text{CH}_2$  was used instead of ethylene. In the presence of  $^{13}\text{C}$  ethylene the low-field doublet [ $\delta(^{13}\text{C}) = 296.2$  ppm] became a pseudotriplet with  $^{103}\text{Rh}-^{13}\text{C}$  coupling [ $^1J(^{103}\text{Rh}-^{13}\text{C}) = 28.9$  Hz] and  $^{13}\text{C}-^{13}\text{C}$  coupling [ $^1J(^{13}\text{C}-^{13}\text{C}) = 28.3$  Hz] indicating that the coupling of  $^{13}\text{C}$  ethylene with  $^{13}\text{CO}$  has already occurred. The driving force for the formation of this species is probably the coordinative unsaturation of the 14-electron intermediate, where coordination of a lone electron pair from oxygen renders the Rh center less unsaturated. This weak interaction can be replaced by further reaction with  $\text{I}^-$  to give 5.

The possibility of generating  $\text{HRh}(\text{CO})_2\text{I}_2$  or  $[\text{HRh}(\text{CO})_2\text{I}_3][\text{AsPh}_4]$  gives a unique opportunity to compare their reactivity toward ethylene. The half-life of 2 at  $-80^\circ\text{C}$  in the presence of ethylene is about 5 h; in contrast, the reaction of 1 with ethylene

(5) Anal. Calcd for  $\text{C}_{28}\text{H}_{25}\text{O}_2\text{I}_3\text{RhAs}$ : C, 35.32; H, 2.65; I, 39.99. Found: C, 35.14; H, 2.43; I, 41.27. IR ( $\text{CD}_2\text{Cl}_2$ ): 2059 (vs), 1768 (m), 1701 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 60 psi of CO, 360 MHz):  $\delta$  0.98 (t,  $J = 7.1$  Hz, 3H), 3.38 (q,  $J = 7.1$  Hz, 2H), 7.5–8.1 (m, 20H).

Scheme 1



to give 5 is almost instantaneous under identical conditions. This would suggest that  $\text{I}^-$  dissociation is required for olefin insertion and that the active catalyst is better represented by 1 than by 2.

The reverse reaction, the deinsertion of CO from  $[(\text{CH}_3\text{CH}_2\text{CO})\text{Rh}(\text{CO})\text{LI}_3][\text{AsPh}_4]$  ( $\text{L} = \text{CD}_3\text{CN}$ ) in  $\text{CD}_3\text{CN}$ , was monitored by  $^1\text{H}$  NMR to establish the participation of a  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]/\text{HI}/\text{CH}_2=\text{CH}_2$  or  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]/\text{EtI}$  pathway in the thermal decomposition. Within the limits of detection of NMR, only ethylene was observed, suggesting that  $[\text{HRh}(\text{CO})_2\text{I}_3][\text{AsPh}_4]$  is involved in this transformation. Analogously,  $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO})\text{Rh}(\text{CO})(\text{L})\text{I}_3][\text{AsPh}_4]$  was cleanly isomerized to  $[(\text{CH}_3)_2\text{CH}(\text{CO})\text{Rh}(\text{CO})(\text{L})\text{I}_3][\text{AsPh}_4]$  at  $40^\circ\text{C}$  and completely decarbonylated to  $[\text{Rh}(\text{CO})_2\text{I}_2][\text{AsPh}_4]/\text{HI}/\text{CH}_2=\text{CHCH}_3$  (*n*-propyl or isopropyl iodide was not detected) at  $80^\circ\text{C}$ .

The data presented allows us to propose a mechanism for the carbonylation of ethylene to propionic acid, where many of the proposed intermediates shown (Scheme 1) have been spectroscopically observed for the first time.

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