

# Heterometallic Clusters as Catalyst Precursors. Synergism Arising from the Facile Generation of a Reactive Fragment

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The homogeneous rhodium-catalyzed hydroformylation of 3,3-dimethylbut-1-ene has been studied at 293 K, 2.0 MPa of hydrogen, and 2.0 MPa of carbon monoxide in *n*-hexane as solvent, using  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoRh}(\text{CO})_7$ , and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors. The time-dependent concentrations of  $\text{RCORh}(\text{CO})_4$  ( $\text{R} = -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ), the one and only observable rhodium intermediate, and of the organic product 4,4-dimethylpentanal (44DMP) were measured in situ using high-pressure infrared spectroscopy. Maximum yields for the transformation of the above precursors to  $\text{RCORh}(\text{CO})_4$  were approximately 0.56, 0.62, 0.56, 0.35, 0.97, and 1.00 respectively. Definitions for precursor conversion, precursor selectivity to intermediates, and intermediate yields are introduced. The reactions were carried out to 17% conversion of 3,3-dimethylbut-1-ene, corresponding to a turnover number (TON) of 80, at a nominal rhodium concentration of  $5 \times 10^{-5}$  mole fraction. The induction periods were less than 10 min starting with the heterometallic carbonyl clusters  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  and 6–12 h starting with the homometallic carbonyl clusters  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$ . It is shown (i) that the activities of all the systems can be expressed as  $(d[44\text{DMP}]/dt)_t = \text{TOF} \cdot [\text{RCORh}(\text{CO})_4]_t$ , and (ii) that the turnover frequency has the value  $\text{TOF} = 0.138 \pm 0.028 \text{ min}^{-1}$  for all systems. As a consequence, it is concluded that the "synergism" observed in this study, starting with  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors, arises exclusively from their facile fragmentation under reaction conditions, and the rapid and selective formation of  $\text{RCORh}(\text{CO})_4$ . The synergism does not arise either from cluster catalysis or from a catalytic binuclear elimination reaction.

## Introduction

Enhanced selectivities and/or enhanced activities have been observed, for the transformation of reagents to products, using numerous heterometallic homogeneous catalytic systems. Such heterometallic systems can be obtained from mixtures of homometallic complexes or directly from heterometallic complexes. This combined application of more than one metal and the observation of regioselective, chemoselective, and/or kinetic results which differ significantly from the use of either metal alone, has been collectively called "synergism".<sup>1</sup> At the mechanistic level, both cluster catalysis<sup>2</sup> and catalytic binuclear elimination<sup>3,4</sup> have been repeatedly invoked to explain synergistic effects.<sup>5,6</sup>

The unmodified homogeneous hydroformylation reaction is usually carried out starting with either cobalt carbonyls or rhodium carbonyls as precursors.<sup>7-9</sup> However, the combined application of cobalt and rhodium leads to a variety of synergistic effects. These include the observation of (I) enhanced regioselectivities at elevated temperatures<sup>10,11</sup> and (II) enhanced reaction rates at low temperatures. Concerning the latter, the heterometallic cluster  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  has been shown to rapidly transform unfunctionalized alkenes to aldehydes at  $P_{\text{H}_2} = 0.05 \text{ MPa}$ ,

(6) Examples of chemical transformations which are believed to proceed via a catalytic binuclear elimination reaction can be found in the references: (a) Beletskaya, I. P.; Madomedov, G. K. I.; Voskoboinikov, A. Z. *J. Organomet. Chem.* 1990, 385, 289. (b) Jenner, G. *J. Organometal. Chem.* 1988, 346, 237.

(7) (a) The term *catalyst precursor* or simply *precursor*, will be adopted to describe a metal complex which under reaction conditions gives rise to a closed sequence(s) of organometallic intermediates and thereby effects the catalyzed transformation of reagents to products. (b) This usage is consistent with that found in: Muetterties, E. L.; Krause, M. *J. Angew. Chem., Int. Ed. Engl.* 1983, 22, 135.

(8) The complexes  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_4(\text{CO})_{12}$  are typically employed as catalyst precursors under the reaction conditions  $P_{\text{H}_2, \text{CO}} \geq 10.0 \text{ MPa}$  and  $T \geq 393 \text{ K}$ . See: Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls Vol. II*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977.

(9) The complexes  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  are typically employed as catalyst precursors under the reaction conditions  $P_{\text{H}_2, \text{CO}} \geq 5.0 \text{ MPa}$  and  $T \geq 343 \text{ K}$ . See: (a) Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; Reidel: Dordrecht, 1986. (b) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer: Berlin, 1980. (c) Markó, L. In *Aspects of Homogeneous Catalysis Vol II*; Ugo, R., Ed.; Reidel: Dordrecht, 1974.

(10) Changes in the regioselective hydrocarbonylation of diketene have been observed starting with mixtures of  $\text{Co}_2(\text{CO})_8$  and  $\text{Rh}_4(\text{CO})_{12}$  at 353–398 K. Pino, P.; von Bézard, D. A. Ger. Offen 2 807 251, 1978.

(11) Changes in the regioselective hydroformylation of  $\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$  at 353–398 K have been observed starting with mixtures of  $\text{Co}_2(\text{CO})_8$  and  $\text{Rh}_4(\text{CO})_{12}$  or with  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ . Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horváth, I. T. *J. Am. Chem. Soc.* 1988, 110, 150.

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(1) Adams, R. D. *Polyhedron* 1988, 7, 2251.

(2) (a) Cluster catalysis can be defined to be the catalytic transformation of reagents to products via a unicyclic sequence of organometallic intermediates, all having one and the same nuclearity ( $m \geq 2$ ). (b) For general discussions of "cluster catalysis" see: (c) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* 1975, 44, 43. (d) Muetterties, E. L. *Bull. Soc. Chim. Belg.* 1975, 84, 959. (e) Ugo, R. *Catal. Rev.* 1975, 11, 225. (f) Muetterties, E. L. *Bull. Soc. Chim. Belg.* 1976, 85, 451.

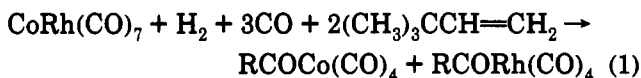
(3) (a) The stoichiometric binuclear elimination reaction between two mononuclear organometallic complexes can be written  $\text{RML}_m + \text{R}^*\text{M}^*\text{L}_n \rightarrow \text{RR}^* + \text{MM}^*\text{L}_{m+n}$ . This reaction need not be elementary. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* 1979, 101, 5447.

(4) The catalytic binuclear elimination reaction can be defined to be the catalytic transformation of reagents to products via a closed bicyclic reaction scheme of mononuclear and dinuclear organometallic intermediates, possessing a stoichiometric binuclear elimination sequence  $\text{RML}_m + \text{R}^*\text{M}^*\text{L}_n \rightarrow \text{RR}^* + \text{MM}^*\text{L}_{m+n}$ .

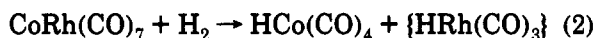
(5) Examples of chemical transformations which are strongly believed to proceed by cluster catalysis can be found in the references: (a) Lausarot, P. M.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta.* 1979, 36, 213. (b) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* 1976, 98, 1056. (c) Pittman, C. U.; Ryan, R. C.; McGee, J.; O'Connor, J. P. *J. Organomet. Chem.* 1979, 178, C43.

$P_{\text{CO}} = 0.05$  MPa, and 298 K.<sup>12</sup> The species  $\text{CoRh}(\text{CO})_7$  also hydroformylates alkenes at pressures and temperatures as low as  $P_{\text{H}_2} = 0.2$  MPa,  $P_{\text{CO}} = 0.1$  MPa, and 255 K.<sup>13</sup> At low CO pressures, both heterometallic systems show a very high initial rate of hydroformylation, followed by deactivation. In contrast, long induction periods are the rule rather than the exception when starting with homometallic clusters.

In situ spectroscopic studies of the hydroformylation of 3,3-dimethylbut-1-ene at 293 K and starting with  $\text{CoRh}(\text{CO})_7$  in *n*-hexane as solvent have shown the presence of both  $\text{RCOC}(\text{CO})_4$  and  $\text{RCORh}(\text{CO})_4$  ( $R = -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ) in the active systems.<sup>13,14</sup> At low CO partial pressures  $P_{\text{CO}} \leq 0.5$  MPa, the system readily deactivates to give as final organometallic products  $\text{RCOC}(\text{CO})_4$  and  $\text{Rh}_4(\text{CO})_{12}$ . At higher CO partial pressures  $P_{\text{CO}} \geq 2.0$  MPa, the concentration of  $\text{RCORh}(\text{CO})_4$  remains constant, and deactivation does not occur.<sup>13</sup>



The heterometallic carbonyls also undergo a wide variety of stoichiometric transformations.<sup>15</sup> In the present context, the rapid reaction of  $\text{CoRh}(\text{CO})_7$  with molecular hydrogen under CO to give  $\text{HCo}(\text{CO})_4$  and  $\text{Rh}_4(\text{CO})_{12}$  is particularly important.<sup>16</sup> At  $P_{\text{CO}} = 0.2$  MPa,  $P_{\text{H}_2} = 0.2$  MPa, and 293 K the half-life for the reaction is approximately 3 min. The simple form of the rate expression, i.e.  $k[\text{CoRh}(\text{CO})_7][\text{H}_2][\text{CO}]^0$ , indicates the oxidative addition of  $\text{H}_2$  to  $\text{CoRh}(\text{CO})_7$  as a rate-limiting step followed by rapid metal-metal bond cleavage to give mononuclear metal carbonyl hydrides.<sup>17</sup>



Taken together, the above observations strongly suggest that the "synergism" exhibited by  $\text{CoRh}(\text{CO})_7$  in the hydroformylation reaction at low temperatures is due to rapid hydrogen activation to give  $\{\text{HRh}(\text{CO})_3\}$ , followed by the subsequent formation of  $\text{RCORh}(\text{CO})_4$ . In other words, one can postulate that  $\text{CoRh}(\text{CO})_7$  is simply a very good precursor for low-temperature rhodium-catalyzed hydroformylation. The use of  $\text{CoRh}(\text{CO})_7$  reduces, by orders of magnitude, the induction period leading to the fully developed catalytic system.<sup>18</sup> Cluster catalysis is not occurring, and a significant contribution to the overall rate from a catalytic binuclear elimination reaction is doubtful.

In order to test the aforementioned postulate, a wide variety of rhodium-containing homometallic and heter-

ometallic complexes, namely  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoRh}(\text{CO})_7$ , and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ , were examined as catalyst precursors. The unmodified hydroformylation of 3,3-dimethylbut-1-ene was carried out at 293 K, in an apolar solvent (*n*-hexane), and under very low nominal metal concentrations. The time-dependent concentrations of the intermediate  $\text{RCORh}(\text{CO})_4$  and the product 4,4-dimethylpentanal are reported for the systems starting with each precursor, and the corresponding turnover frequencies (TOF) are evaluated.

## Experimental Section

**General Information.** All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern, Switzerland) atmosphere using standard Schlenk techniques.<sup>19</sup>  $\text{Rh}_4(\text{CO})_{12}$  (Strem Chemicals Inc., Bismarck France),  $\text{Rh}_6(\text{CO})_{16}$  (Fluka AG, Buchs, Switzerland), and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$  (Johnson Matthey, England) were used as obtained.  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ ,  $\text{CoRh}(\text{CO})_7$ , and  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  were synthesized by literature methods.<sup>15a,20</sup> Elemental analysis of recrystallized  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  gave 21.7% carbon and 31.1% rhodium (courtesy of CIBA-GEIGY AG, Basel, Switzerland). The calculated values for  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  are 21.8% carbon and 31.2% rhodium. "Puriss" quality *n*-hexane (Fluka AG) was refluxed from sodium potassium alloy under nitrogen. 3,3-Dimethylbut-1-ene (Fluka AG) was degassed and stored over molecular sieves. Reactions were carried out with carbon monoxide 99.997% (Messer Griesheim GmbH Duisburg, Germany) and hydrogen 99.999% (Pan Gas).

Kinetic studies were performed in a 1.5-L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) which was connected to a high-pressure infrared cell. The autoclave ( $P_{\text{max}} = 22.5$  MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineer, Erie PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK30, Orlita AG, Germany) with a maximum rating of 32.5 MPa and 3-L/h flow rate was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via a jacketed 1/8-in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, autoclave, transfer lines, and infrared cell, were cooled using a Lauda RX20 (Germany) cryostat and could be maintained isothermally ( $\Delta T \approx 0.5$  °C) in the range -20 to +40 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with Pt-100 thermoresistors. The necessary connections to vacuum and gases were made with 1/4-in. (SS316) high-pressure tubing (Autoclave Engineers), and 5.00-, 10.00-, and 20.00-MPa piezocrystals were used for pressure measurements (Keller AG, Winterthur, Switzerland). The piezocrystals were periodically calibrated on a Haenni PDG 022 calibration bench (Stuttgart, Germany). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Z of SS316 steel and could be heated or cooled. The  $\text{CaF}_2$  single-crystal windows (Korth Monokristalle, Kiel, Germany) had dimensions of 40-mm diameter by 15-mm thickness. Two sets of Viton and silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow-through cell<sup>21a</sup> is a variation on a design due to Noack<sup>21b</sup> and

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(16) Horváth, I. T.; Garland, M.; Bor, G.; Pino, P. *J. Organomet. Chem.* 1988, 358, C17.

(17) Garland, M.; Pino, P. *Organometallics* 1990, 9, 1943.

(18) A further distinction can be made between (I) enhanced initial catalytic reaction rates due to a reduction in the induction period and (II) enhanced (psuedo) steady-state catalytic reaction rates. Type I enhancement is associated with the precatalytic transformation of precursor to intermediates, and Type II enhancement is associated with intrinsic changes in the catalytic mechanism(s). The latter can be expected to result in changes in the measured turnover frequency (TOF).

differs in some respects from other high-pressure infrared cells described in the literature (for a review see Whyman<sup>21a</sup>). The high-pressure cell was situated in a Perkin-Elmer PE983 infrared spectrophotometer equipped with a Model 3600G data station. Details of the equipment and IR cell can be found elsewhere.<sup>13</sup>

**Calibrations.** The mononuclear intermediate  $\text{RCORh}(\text{CO})_4$  ( $\text{R} = -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ) has absorbance maxima at 2111, 2065, 2039, 2020, and 1698  $\text{cm}^{-1}$ .<sup>14</sup> Calibrations for the determination of  $\epsilon_{2111}$  were made starting with  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursor. In these experiments, 100% conversion of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  has occurred before 105 min of reaction (first spectrum) and little or no  $\text{Rh}_6(\text{CO})_{16}$  can be identified. This suggests that the yield of  $\text{RCORh}(\text{CO})_4$  is  $y_{\text{max}} = 1.00$  and that the corresponding selectivity is  $s_{\text{max}} = 1.00$ . The extinction coefficient at 2111  $\text{cm}^{-1}$  was  $\epsilon_{2111} = 1570 \text{ L}/(\text{mol cm})$ . Using this result, further calibrations for the band at 2020  $\text{cm}^{-1}$  were made with both  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  as catalyst precursors. The resulting extinction coefficient at 2020  $\text{cm}^{-1}$  was  $\epsilon_{2020} = 4150 \pm 340 \text{ L}/(\text{mol cm})$ .

The extinction coefficient of *n*-hexane at 1246  $\text{cm}^{-1}$  ( $\text{CH}_2$  wagging mode)<sup>22a</sup> is  $\epsilon_{1246} = 1.339 \text{ L}/(\text{mol cm})$ . 3,3-Dimethylbut-1-ene and 4,4-dimethylpentanal have absorbance maxima at 1642  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  stretching mode)<sup>22b</sup> and 1734  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching mode),<sup>22c</sup> respectively, and the corresponding extinction coefficients are  $\epsilon_{1642} = 80 \text{ L}/(\text{mol cm})$  and  $\epsilon_{1734} = 360 \text{ L}/(\text{mol cm})$ .

**Kinetic Studies.** In each experiment, catalyst precursor (corresponding to  $5 \times 10^{-5}$  mol of rhodium) was dissolved/suspended in 200 mL of *n*-hexane (1.51 mol) in a Schlenk tube under a nitrogen atmosphere, and 5 mL (0.039 mol) 3,3-dimethylbut-1-ene was added. Further, in the case of  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$  as catalyst precursors, 0.2 mL ( $1.4 \times 10^{-3}$  mol) and 0.5 mL ( $3.5 \times 10^{-3}$  mol) of  $\text{Et}_3\text{N}$ , respectively, were also added as a halide scavenger. The solutions were then transferred into the evacuated and thermostated autoclave. At 293 K, the total pressure in the autoclave was  $P_T = 0.01\text{--}0.03$  MPa, the vapor pressure of *n*-hexane plus a low partial pressure of nitrogen. With stirring (200 RPM), carbon monoxide (2.0 MPa) was added to the system. The high-pressure membrane pump continuously circulated the *n*-hexane solution from the autoclave to the high-pressure infrared cell and back to the autoclave. At a time  $t = 0$ , a program was executed to record spectra every 105 min. Initial in situ infrared spectra were then taken from 2200–1600  $\text{cm}^{-1}$  ( $\nu_{\text{CO}}$  range) and from 1300–1100  $\text{cm}^{-1}$  (hexane). Little to no additional noise could be identified in the in situ spectra as the solution was pumped (10 cm/s) through the high-pressure infrared cell. After the initial spectra were recorded, hydrogen (2.0 MPa) was added to the system. The spectra were analyzed off-line after the end of the experiments.

Two kinetic experiments under identical reaction conditions were conducted with each catalyst precursor. In any single experiment, less than 0.01-mol conversion of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal occurred. Therefore, the partial pressures of hydrogen and carbon monoxide in the closed-batch autoclave decreased by less than 1% during each of the experiments. This partial pressure change was considered negligible, and the liquid-phase concentrations of the two gaseous components were treated as constants for the duration of each experiment. Blank experiments, conducted at the standard experimental conditions, but in the absence of catalyst precursor, showed less than 0.3% ( $2 \times 10^{-4}$  mol) conversion of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal after 36 h of reaction.

3,3-Dimethylbut-1-ene is a sterically hindered alkene, and hydroformylation gives almost exclusively 4,4-dimethylpentanal (regioselectivity  $\geq 97\%$ ). Further, at these reaction conditions, hydrogenation to 2,2-dimethylbutane is very low (chemoselectivity  $\leq 2\%$ ).

The present hydroformylation reactions were performed under negligible gas-liquid mass-transfer resistance. The experimentally measured overall mass-transfer coefficients  $K_1a$  for hydrogen

and carbon monoxide into *n*-hexane at 200 RPM were approximately 0.1 and 0.06  $\text{s}^{-1}$ , respectively, as determined using the method of Deimling.<sup>23a</sup> Since the maximum observed rate of hydroformylation in this study was  $1.2 \times 10^{-7} \text{ mol s}^{-1}$ , all experiments belong to the category of infinitely slow reaction with respect to gas-liquid mass transfer (the kinetic regime).<sup>23b</sup> The liquid phase of each experiment became essentially saturated with dissolved CO and  $\text{H}_2$  in the first 60 s. Mass-transfer effects are known to severely complicate the interpretation of kinetic data from hydroformylation reactions.<sup>23c</sup>

## Calculations

**Reactant Concentrations.** The time-dependent in situ concentrations of the intermediate  $\text{RCORh}(\text{CO})_4$  and the organic product 4,4-dimethylpentanal (44DMP) were calculated using the characteristic infrared maxima at 2111 or 2020  $\text{cm}^{-1}$ , and 1734  $\text{cm}^{-1}$ , respectively. At the end of each hydroformylation experiment, a program was executed to subtract the hexane absorbance from each spectrum (2200–1600  $\text{cm}^{-1}$ ) and to calculate the concentration of the above components. In the dimensionless Lambert-Beer equation (eq 3),<sup>24</sup>  $x_i$  are mole fractions in the liquid phase,  $A_i$  are measured in situ absorbance, and  $\epsilon_i$  are extinction coefficients.

$$x_i = x_{\text{hex}}(A_i \epsilon_{1246}) / (A_{1246} \epsilon_i) \quad (3)$$

$$x_{\text{hex}} = n_{\text{hex}} / (n_{\text{hex}} + n_{33\text{DMP}} + n_{\text{CO}} + n_{\text{H}_2} + n_{44\text{DMP}}) \quad (4)$$

In situ measurements of both the *i*th component absorbance as well as the absorbance of *n*-hexane (1246  $\text{cm}^{-1}$ ) were needed for the calculation of liquid-phase concentrations. The numerical value of  $x_{\text{hex}}$  was 0.93 in all experiments. Since  $(n_{33\text{DMP}})_0 = (n_{33\text{DMP}})_t + (n_{44\text{DMP}})_t$ , the parameter  $x_{\text{hex}}$  was calculated from the initial reaction conditions for each experiment and remained constant for the duration of each experiment. The solubility of hydrogen at 2.0 MPa and 293 K in *n*-hexane is 0.018 mole fraction,<sup>25</sup> and the solubility of carbon monoxide at 2.0 MPa and 293 K in *n*-hexane is 0.033 mole fraction.<sup>26</sup>

In the present experimental system, the concentration of  $\text{RCORh}(\text{CO})_4$  could be measured with an accuracy greater than  $2 \times 10^{-6}$  mole fraction. The "noise" in a typical spectrum was less than 0.01 absorbance unit, and the signal to noise ratio of  $[\text{RCORh}(\text{CO})_4]_{\text{max}}$  was usually better than 20:1.

**Reaction Rates.** The reaction rates, for the transformation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal, were calculated using the finite difference eq 5. This expression provides a numerical value for the rate of

$$(d[44\text{DMP}]/dt)_t = ([44\text{DMP}]_{t+1} - [44\text{DMP}]_{t-1}) / 2\Delta t \quad (5)$$

hydroformylation at a time  $t$ , based on the measured in situ concentrations of 4,4-dimethylpentanal at times  $t - 1$  and  $t + 1$ . The time interval between  $t$  and  $t - 1$  or  $t + 1$  was 105 min, the interval between spectra. This central

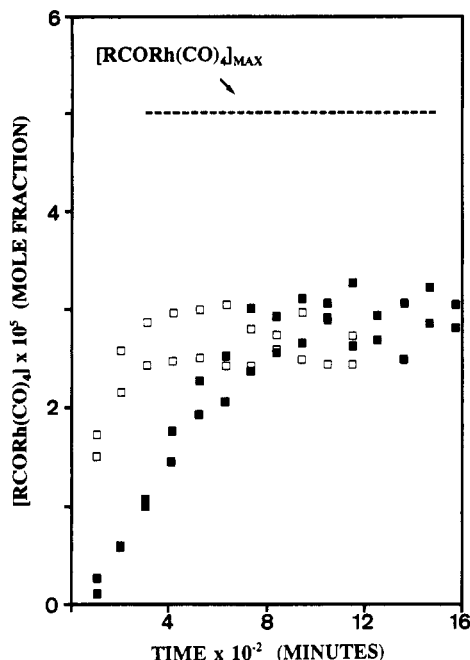
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**Figure 1.** Concentration of the intermediate  $\text{RCORh}(\text{CO})_4$  as a function of reaction time starting with the homometallic carbonyl clusters  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  as catalyst precursors: ( $\square$ )  $\text{Rh}_4(\text{CO})_{12}$ ; ( $\blacksquare$ )  $\text{Rh}_6(\text{CO})_{16}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.

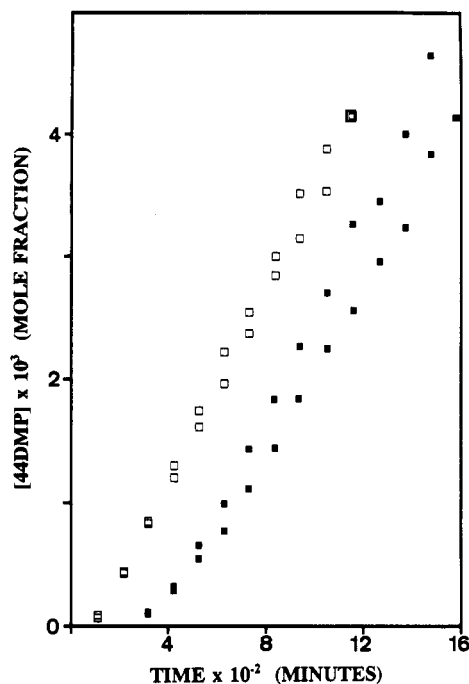
difference expression was chosen since it provides an accurate approximation of derivatives from sets of smooth monotonically increasing or decreasing experimental data.<sup>27</sup>

## Results

### $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ as Catalyst Precursors.

The samples of  $\text{Rh}_4(\text{CO})_{12}$  used were entirely soluble in the 205-mL solution of *n*-hexane and 3,3-dimethylbut-1-ene. The  $\nu_{\text{CO}}$  range of the in situ spectra under 2.0 MPa of CO showed only the characteristic band structure of  $\text{Rh}_4(\text{CO})_{12}$  at 2074, 2068, 2061, 2043, and 1885  $\text{cm}^{-1}$ ,<sup>28</sup> free from the common impurity  $\text{Rh}_6(\text{CO})_{16}$ .<sup>29</sup> No transformation of  $\text{Rh}_4(\text{CO})_{12}$  was observed to occur before the addition of hydrogen.

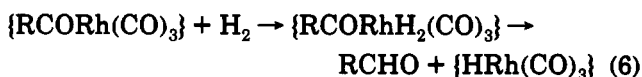
After addition of 2.0 MPa of hydrogen, and over the next 500 min (8 h), the smooth monotonic decrease of  $\text{Rh}_4(\text{CO})_{12}$  and the smooth monotonic increase of  $\text{RCORh}(\text{CO})_4$  (Figure 1) were observed until essentially 100% conversion of  $\text{Rh}_4(\text{CO})_{12}$  was achieved, as evidenced by the disappearance of the band at 1885  $\text{cm}^{-1}$ . In addition to the characteristic IR bands of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{RCORh}(\text{CO})_4$ ,  $\nu_{\text{CO}}$  vibrations at 2073 and 1808  $\text{cm}^{-1}$  arising from  $\text{Rh}_6(\text{CO})_{16}$  were also observed. During the initial 500 min of reaction, the rate of formation of 4,4-dimethylpentanal was observed to steadily increase until a constant max-



**Figure 2.** Concentration of the product 4,4-dimethylpentanal as a function of reaction time starting with the homometallic catalyst precursors  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$ : ( $\square$ )  $\text{Rh}_4(\text{CO})_{12}$ ; ( $\blacksquare$ )  $\text{Rh}_6(\text{CO})_{16}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.

imum rate was achieved (Figure 2). The maximum yield and maximum selectivity for the transformation of  $\text{Rh}_4(\text{CO})_{12}$  to the intermediate  $\text{RCORh}(\text{CO})_4$  were  $y_{\text{max}} = s_{\text{max}} = 0.56$ , and a turnover number of 80 was achieved after 1100 min (18 h).<sup>30</sup>

It is known that the loss of  $\text{Rh}_4(\text{CO})_{12}$  and formation of  $\text{RCORh}(\text{CO})_4$  involves the precatalytic<sup>31</sup> reaction sequence  $\{\text{Rh}_4(\text{CO})_{12} \rightleftharpoons \text{Rh}_4(\text{CO})_{14} \dots \text{RCORh}(\text{CO})_4\}$ , and the rate expression is  $d[\text{Rh}_4(\text{CO})_{12}]/dt = -k[\text{Rh}_4(\text{CO})_{12}][\text{CO}]^{1.8}[\text{H}_2]^{0.7}[\text{33DMP}]^{0.1}$ .<sup>32</sup> Further, there exists a *one-to-one* relationship between  $[\text{RCORh}(\text{CO})_4]_t$  and the rate of aldehyde formation  $(d[44\text{DMP}]/dt)_t = k[\text{RCORh}(\text{CO})_4]_t[\text{CO}]^{-1}[\text{H}_2]$ .<sup>32</sup> Since there were no higher order terms in rhodium for the rate of hydroformylation, a measurable contribution from a binuclear elimination of the form  $\text{RCORh}(\text{CO})_x + \text{HRh}(\text{CO})_y \rightarrow \text{RCHO} + \text{Rh}_2(\text{CO})_{x+y}$  could be excluded. The activity of the system is due to the simple bimolecular reaction of molecular hydrogen with an unsaturated acylrhodium tricarbonyl.



The samples of  $\text{Rh}_6(\text{CO})_{16}$  used in this study were essentially insoluble in the 205-mL solution of *n*-hexane and 3,3-dimethylbut-1-ene. This was due in part to the low solubility of this complex but more importantly to the large crystal size of the samples used. Therefore, the dissolution kinetics played a substantial role. The initial

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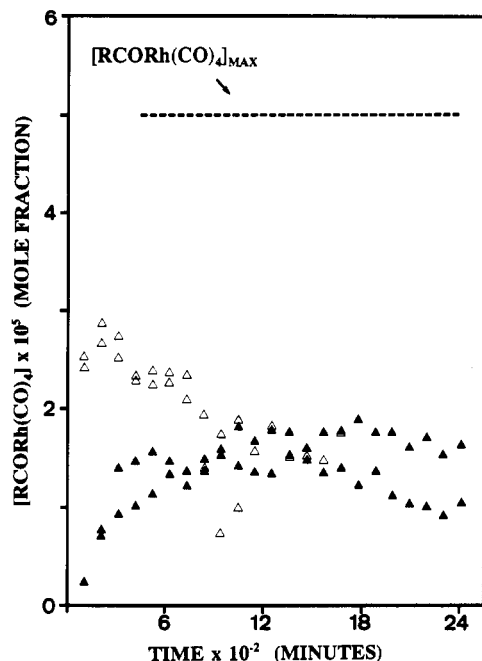
(28) (a) Beck, W.; Lottes, K. *Chem. Ber.* 1961, 94, 2578. (b) Bor, G.; Sbrignadello, G.; Noack, K. *Helv. Chim. Acta* 1975, 58, 815.

(29) The IR maxima in Nujol occur at (a) 2105, 2070 (s), 2047, 2040, 2022, 2020, 1833, 1793 (s)  $\text{cm}^{-1}$  (Chini, P. *J. Chem. Soc., Chem. Commun.* 1967, 440) and (b) 2075 (s), 2025 (m), 1800 (s)  $\text{cm}^{-1}$  (James, B. R.; Remple, G. L.; Teo, W. K. *Inorg. Synth.* 1976, 16, 49).

(30) Turnover numbers in the present study are defined as  $\text{TON}(t) = [44\text{DMP}]_t/[\text{Rh}]_0$ . This provides an alternate measure of system activity.

(31) The term *precatalytic* sequence has appeared previously. Parshall, G. *Homogenous Catalysis*; Wiley: New York, 1980; p 17.

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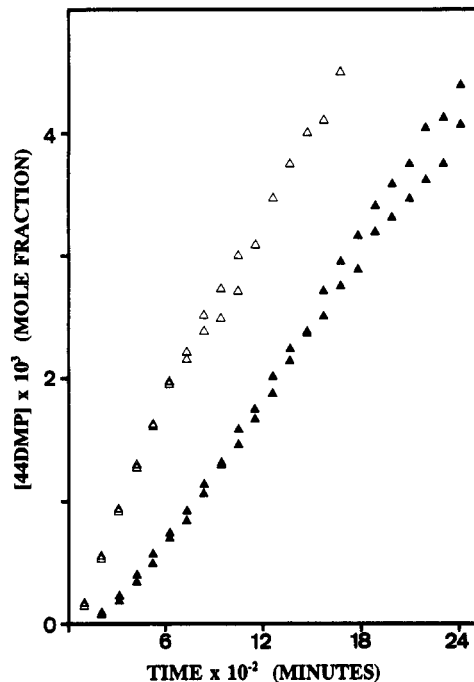


**Figure 3.** Concentration of the intermediate  $\text{RCORh}(\text{CO})_4$  as a function of reaction time starting with the halide-containing catalyst precursors  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ : ( $\Delta$ )  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ; ( $\blacktriangle$ )  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.

in situ infrared spectra under 2.0 MPa of CO showed virtually no absorption from  $\text{Rh}_6(\text{CO})_{16}$ .

After addition of 2.0 MPa of hydrogen, the concentration of soluble  $\text{Rh}_6(\text{CO})_{16}$ , as determined by the band at 2073  $\text{cm}^{-1}$ , increased slowly with time. The concentration of  $\text{RCORh}(\text{CO})_4$  achieved its maximum value after approximately 800 min (13 h) of reaction (Figure 1). At this point, the rate of formation of 4,4-dimethylpentanal achieved a maximum constant value (Figure 2). Only  $\nu_{\text{CO}}$  vibrations corresponding to the species  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{RCORh}(\text{CO})_4$  were observed, and the maximum yield of  $\text{RCORh}(\text{CO})_4$  was  $y_{\text{max}} = 0.62$ . A turnover number of 80 was achieved after 1500 min (25 h).

**$\text{Rh}_2(\text{CO})_4\text{Cl}_2$  and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$  as Catalyst Precursors.** The complex  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  was entirely soluble in the 205-mL solution of *n*-hexane, 3,3-dimethylbut-1-ene, and  $\text{Et}_3\text{N}$ . The in situ spectra under 2.0 MPa of CO showed bands at 2083 (s), 2073 (s), 2068 (s), 2042 (m), 2000 (vs), and 1885 (m)  $\text{cm}^{-1}$ , and no IR bands characteristic of  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  at 2107, 2091, 2080, 2052, and 2036  $\text{cm}^{-1}$  nor  $\text{Rh}(\text{CO})_3\text{Cl}$  at 2098 and 2052  $\text{cm}^{-1}$ .<sup>33</sup> After addition of 2.0 MPa of hydrogen, the rapid formation of  $\text{RCORh}(\text{CO})_4$  with a maximum yield and maximum selectivity of  $y_{\text{max}} = s_{\text{max}} = 0.56$  was observed (Figure 3). Subsequently, the concentration of the intermediate monotonically decreased with time. This loss of intermediate was accompanied by an increase in the intensity of a number of other IR absorbance maxima. In Figure 4, the deactivation of the catalytic system due to the loss of  $\text{RCORh}(\text{CO})_4$  is clearly seen in the decreasing slope of the curves of 4,4-dimethylpentanal versus time. Though the mechanism for the loss of  $\text{RCORh}(\text{CO})_4$  is unknown, it is certainly connected



**Figure 4.** Concentration of the product 4,4-dimethylpentanal as a function of reaction time starting with the halide-containing catalyst precursors  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ : ( $\Delta$ )  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ; ( $\blacktriangle$ )  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.

with the excess  $\text{Et}_3\text{N}$  used as halide scavenger. A turnover number of 80 was achieved after 1500 min (25 h).

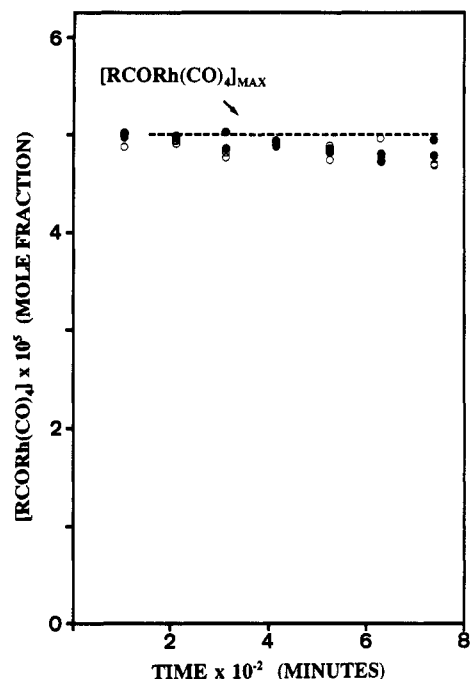
The finely ground inorganic catalyst precursor  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$  was completely insoluble in the 205-mL reaction solution consisting of *n*-hexane, 3,3-dimethylbut-1-ene, and  $\text{Et}_3\text{N}$ . After addition of 2.0 MPa of CO and 2.0 MPa of hydrogen and over the next 1500 min (25 h), the very slow formation of both  $\text{RCORh}(\text{CO})_4$  and  $\text{Rh}_6(\text{CO})_{16}$  only are observed (Figure 3). The formation of  $\text{Rh}_6(\text{CO})_{16}$  as a deactivation product has been noted in previous studies and was attributed to the presence of nucleophiles, including trace quantities of molecular oxygen.<sup>34</sup> Assuming 100% conversion of  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ , maximum yield and maximum selectivity to the intermediate  $\text{RCORh}(\text{CO})_4$  were  $y_{\text{max}} = s_{\text{max}} = 0.35$ . An induction period is clearly visible in the time-dependent curves for  $[\text{44DMP}]_t$  in the first 1500 min of reaction (Figure 4). A turnover number of 80 was achieved after 2200 min (36 h) of reaction.

**$\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as Catalyst Precursors.** The complex  $\text{CoRh}(\text{CO})_7$ , a very labile homoleptic metal carbonyl, was first identified, synthesized, and used as a catalyst precursor by Pino et al.<sup>15a,b</sup> Solutions containing 27 mg of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ , completely dissolved in 205 mL of *n*-hexane and 3,3-dimethylbut-1-ene, were transferred to the autoclave. After addition of 2.0 MPa of CO, and within minutes, the original samples of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  were quantitatively transformed to  $\text{CoRh}(\text{CO})_7$ .

(34) Kagan, Y. B.; Slivinskii, E. V.; Kurkin, V. L.; Korneeva, G. A.; Aranovich, R. A.; Fal'kov, I. G.; Rzhavskaya, N. N.; Loktev, S. M. *Neftekhimiya* 1985, 25, 791; *Chem. Abstr.* 1986, 104, 56974d.

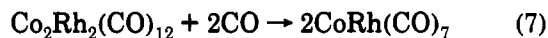
(35) Garland, M.; Pino, P. *Organometallics* 1991, 10, 2643.

(33) Morris, D. E.; Tinker, H. B. *J. Organomet. Chem.* 1973, 49, C53.



**Figure 5.** Concentration of the intermediate  $\text{RCORh}(\text{CO})_4$  as a function of reaction time starting with the mixed-metal carbonyls  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors: (○)  $\text{CoRh}(\text{CO})_7$ ; (●)  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.

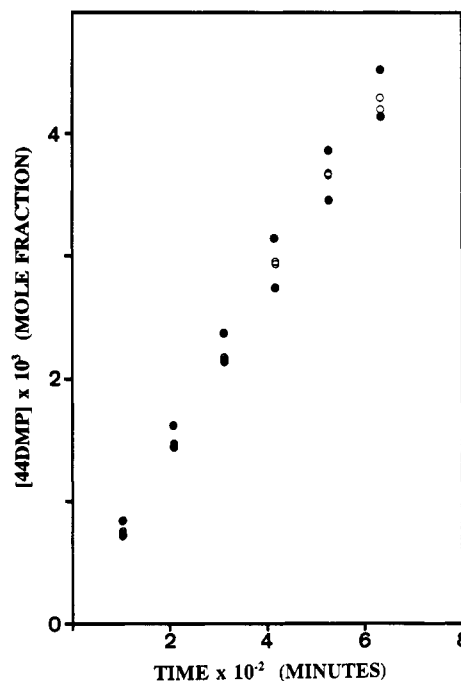
These results are consistent with the known kinetics,<sup>35</sup> and thermodynamics,<sup>36</sup> of the transformation



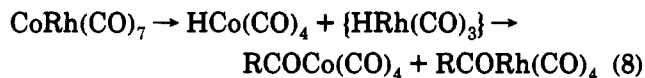
The in situ spectra under 2.0 MPa of CO showed the characteristic bands for  $\text{CoRh}(\text{CO})_7$  at 2134, 2064, 2058, 2049, 2006, 1977, and 1955  $\text{cm}^{-1}$ .<sup>15b</sup> No transformation of  $\text{CoRh}(\text{CO})_7$  was observed to occur in the presence of alkene and in the absence of hydrogen.

After addition of 2.0 MPa of hydrogen, and within approximately 10 min,<sup>13</sup> the quantitative conversion of  $\text{CoRh}(\text{CO})_7$  to  $\text{RCOC}(\text{CO})_4$  ( $\text{R} = -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ) (2104, 2044, 2022, 2003  $\text{cm}^{-1}$ )<sup>37</sup> and  $\text{RCORh}(\text{CO})_4$  occurred. The concentrations of  $\text{RCOC}(\text{CO})_4$  remained constant with time. The very slow loss of  $\text{RCORh}(\text{CO})_4$  with the formation of  $\text{Rh}_6(\text{CO})_{16}$  as a function of time was observed (Figure 5). The time-dependent concentrations of 4,4-dimethylpentanal are shown in Figure 6, where there is an essentially constant rate of hydroformylation. Conversion of  $\text{CoRh}(\text{CO})_7$  was 100%, and the maximum yield and maximum selectivity to the intermediate  $\text{RCORh}(\text{CO})_4$  were  $y_{\text{max}} = s_{\text{max}} = 0.97$ . A turnover number of 80 was achieved after 525 min (9 h).

All available experimental evidence suggests that the catalyst precursor  $\text{CoRh}(\text{CO})_7$  disappears according to the precatalytic reaction sequence eq 8, where the rate-determining step is hydrogen activation. Accordingly, alkene activation proceeds via a hydride rather than



**Figure 6.** Concentration of the product 4,4-dimethylpentanal as a function of reaction time starting with the mixed-metal carbonyls  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors: (○)  $\text{CoRh}(\text{CO})_7$ ; (●)  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. Two experiments were carried out with each precursor.



unsaturated route, i.e., the former involving alkene coordination to a hydride complex.<sup>38</sup> At 2.0 MPa of hydrogen and 293 K, the half-life for the disappearance of  $\text{CoRh}(\text{CO})_7$  is 20 s.<sup>17</sup> The species  $\text{HCo}(\text{CO})_4$  has been spectroscopically identified in the initial 10 min of the hydroformylation reaction.<sup>13</sup>

The cluster  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  was first synthesized by Chini et al.,<sup>39</sup> and as previously mentioned, it shows considerable activity as a low-pressure and low-temperature catalyst precursor for hydroformylation ( $T = 298$  K,  $P_{\text{CO},\text{H}_2} \leq 0.1$  MPa).<sup>12</sup> The 27-mg samples used in this study were entirely soluble in the 205-mL solution of *n*-hexane and 3,3-dimethylbut-1-ene and showed characteristic infrared maxima at 2074, 2064, 2059, 2038, 2030, 1920, 1910, 1885, 1871, and 1858  $\text{cm}^{-1}$ .<sup>39</sup> No reaction was observed to occur before the simultaneous addition of carbon monoxide and hydrogen.

After addition of 2.0 MPa of CO and 2.0 MPa of hydrogen and within minutes, there was complete conversion of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ . Even though  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  shows hydrogen activation activity in the absence of CO,<sup>40</sup> the primary mode in the presence of CO involves the initial transfor-

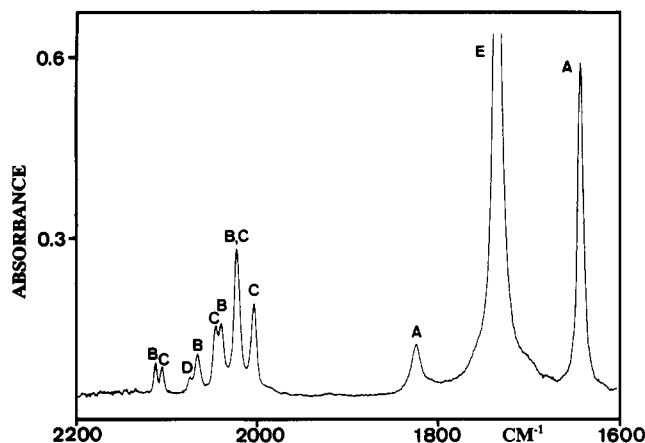
(36) Garland, M.; Horváth, I. T.; Bor, G.; Pino, P. *Organometallics* 1991, 10, 559.

(37) (a) Markó, L.; Bor, G.; Almasy, G.; Szabo, P. *Brennst.-Chem.* 1963, 44, 184. (b) Whyman, R. *J. Organomet. Chem.* 1974, 66, C23. (c) *Ibid.* 1974, 81, 97.

(38) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973; p 400.

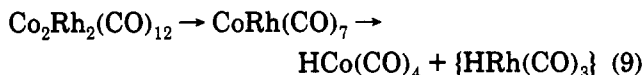
(39) Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F. *J. Organomet. Chem.* 1973, 59, 379.

(40) Garland, M.; Pino, P. *J. Organomet. Chem.* 1991, 417, 121.



**Figure 7.** In situ spectrum of an active hydroformylation reaction, starting with  $\text{CoRh}(\text{CO})_7$  as catalyst precursor, after 525 min of reaction: (A) 3,3-dimethylbut-1-ene; (B)  $\text{RCORh}(\text{CO})_4$ ; (C)  $\text{RCOC}(\text{CO})_4$ ; (D)  $\text{Rh}_6(\text{CO})_{16}$ ; (E) 4,4-dimethylpentanal. (Spectra starting from  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  are virtually identical.) Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium.

mation of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  to  $\text{CoRh}(\text{CO})_7$  and then hydrogen activation.<sup>16</sup>



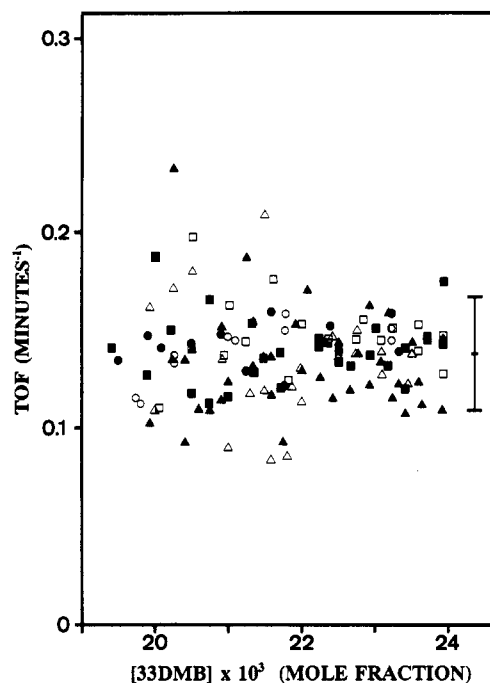
Again, the concentration of  $\text{RCOC}(\text{CO})_4$  remained constant and the concentration of  $\text{RCORh}(\text{CO})_4$  decreased slowly with time, accompanied by the formation of  $\text{Rh}_6(\text{CO})_{16}$  (Figure 5).<sup>41</sup> The resulting time-dependent concentrations of 4,4-dimethylpentanal are shown in Figure 6. It should be noted that the trajectories of  $[\text{44DMP}]_t$  starting with both  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors appear to coincide. This is not the least surprising since, at 2.0 MPa of CO and at 293 K, the half-life for the fragmentation of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  to  $\text{CoRh}(\text{CO})_7$  is less than 30 s.<sup>35</sup> The maximum yield and maximum selectivity to the intermediate  $\text{RCORh}(\text{CO})_4$  were  $y_{\text{max}} \equiv s_{\text{max}} \equiv 1.00$ . A turnover number of 80 was achieved after 525 min (9 h).

**Spectra.** The complexes  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{RCORh}(\text{CO})_4$  were identified as products in the homometallic systems, starting with  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ , and  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$  as catalyst precursors. Spectra of the intermediate  $\text{RCORh}(\text{CO})_4$  and an analysis of its band structure can be found in the literature.<sup>14</sup> Hydroformylations starting with  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors gave rise to both  $\text{RCOC}(\text{CO})_4$  and  $\text{RCORh}(\text{CO})_4$ . A typical in situ spectrum for these latter systems is shown in Figure 7.

## Discussion and Conclusions

**Turnover Frequencies.** Each of the complexes  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoRh}(\text{CO})_7$ , and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  proved successful as a catalyst precursor for the hydroformylation of 3,3-dimethylbut-

(41) As a secondary effect, the presence of cobalt may slow the formation of  $\text{Rh}_6(\text{CO})_{16}$ . Indeed, it is known that  $\text{HC}(\text{CO})_4$  reacts with  $\text{Rh}_4(\text{CO})_{12}$  according to  $4\text{HC}(\text{CO})_4 + \text{Rh}_4(\text{CO})_{12} = 2\text{H}_2 + 4\text{CoRh}(\text{CO})_7$ .<sup>16</sup> Since  $\text{HC}(\text{CO})_4$  is probably present at very low concentrations, then a mechanism may exist to slow deactivation due to cluster formation.



**Figure 8.** Turnover frequencies versus the concentration of 3,3-dimethylbut-1-ene for the experiments starting with  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoRh}(\text{CO})_7$ , and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  as catalyst precursors: (□)  $\text{Rh}_4(\text{CO})_{12}$ ; (■)  $\text{Rh}_6(\text{CO})_{16}$ ; (△)  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ; (▲)  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ; (○)  $\text{CoRh}(\text{CO})_7$ ; (●)  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ . Reaction conditions were 293 K, 0.018 mole fraction (2.0 MPa) hydrogen, 0.033 mole fraction (2.0 MPa) carbon monoxide, 0.024 mole fraction 3,3-dimethylbut-1-ene (initial), and  $5 \times 10^{-5}$  mole fraction rhodium. The error bar indicates the mean  $\pm$  one standard deviation based on all data points.  $\text{TOF} = 0.138 \pm 0.028 \text{ min}^{-1}$ .

1-ene at 293 K. Though the times required for the development of the active systems varied greatly, all complexes eventually gave rise to the formation of the intermediate  $\text{RCORh}(\text{CO})_4$  ( $\text{R} = -\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ), in observable concentrations (Figures 1, 3, and 5). Accompanying the appearance of  $\text{RCORh}(\text{CO})_4$ , the continuous formation of the organic product 4,4-dimethylpentanal was also observed, indicating the continuous hydrogenolysis of  $\text{RCORh}(\text{CO})_4$  under these relatively mild conditions (Figures 2, 4, and 6).

As a working hypothesis,  $\text{RCORh}(\text{CO})_4$  is assumed to be involved in the transformation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal in all the systems. Since the concentrations of all remaining mononuclear rhodium intermediates and reservoirs are very low (well below the present limits of spectroscopic detection), then  $[\text{RCORh}(\text{CO})_4]_t$  serves as a very good approximation to the total concentration of intermediates in the active systems, i.e.  $[\text{RCORh}(\text{CO})_4]_t \approx \sum [N_i]_t$ . The definition of the turnover frequency for the present hydroformylation experiments reduces to

$$\text{TOF}(x, T, P)_t \equiv (d[\text{RCHO}]/dt)_t / [\text{RCORh}(\text{CO})_4]_t \quad (10)$$

Since TOF is a function of the state of the systems  $(x, T, P)$  and is therefore not explicitly time dependent, it is instructive to consider a change of variable from  $t$  to  $[\text{33DMB}]_t$  and hence the mapping  $\text{TOF}(x, T, P)_t \rightarrow \text{TOF}(x, T, P)_{[\text{33DMB}]}$ .<sup>42</sup> Figure 8 presents the evaluated turnover

(42) An even more general change of variable is  $\text{TOF}(x, T, P)_t \rightarrow \text{TOF}(x, T, P)_\xi$ , where  $\xi$  is the extent of reaction.

frequencies for all the systems at all reaction times. These results suggest that there is little if any systematic variation of TOF as a function of the state variable [33DMB]. Further, since only low conversions of 3,3-dimethylbut-1-ene have occurred, it is convenient to consider the turnover frequencies to be constants, and to evaluate their numerical value in a small vicinity of [33DMB]<sub>0</sub>.<sup>43</sup> The corresponding average values of the turnover frequencies starting with each catalyst precursor were as follows: Rh<sub>4</sub>(CO)<sub>12</sub>, TOF = 0.147 ± 0.019 min<sup>-1</sup>; Rh<sub>6</sub>(CO)<sub>16</sub>, TOF = 0.139 ± 0.018 min<sup>-1</sup>; Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>; TOF = 0.133 ± 0.030 min<sup>-1</sup>; RhCl<sub>3</sub>·2H<sub>2</sub>O, TOF = 0.133 ± 0.027 min<sup>-1</sup>; CoRh(CO)<sub>7</sub>; TOF = 0.140 ± 0.014 min<sup>-1</sup>; Co<sub>2</sub>Rh<sub>2</sub>(CO)<sub>12</sub>, TOF = 0.143 ± 0.011 min<sup>-1</sup>.<sup>44</sup> It must be noted, that the differentiation of experimental concentration data typically leads to large standard deviations in the determined rate constants.<sup>45</sup> The evaluation of TOF in this study (eq 10) presents a similar situation.

Therefore, within experimental error, the same turnover frequencies are obtained for all the hydroformylation reactions in this study. There is a *one-to-one* relationship between the concentration of the intermediate RCORh(CO)<sub>4</sub> and the rate of formation of the product 44DMP regardless of whether a homometallic or heterometallic complex was used as catalyst precursor. It should also be noted that the presence of Cl, H<sub>2</sub>O, and Et<sub>3</sub>N did not effect the turnover frequencies to a statistically significant extent, in the hydroformylations starting with Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> and RhCl<sub>3</sub>·2H<sub>2</sub>O.

**CoRh(CO)<sub>7</sub> and Co<sub>2</sub>Rh<sub>2</sub>(CO)<sub>12</sub> as Precursors.** The in situ observation of both the complexes RCORh(CO)<sub>4</sub> and RCOC<sub>o</sub>(CO)<sub>4</sub>, starting with heterometallic complexes as catalyst precursors, strongly suggests the existence of not one but two catalytic sequences, namely a unicyclic sequence of mononuclear rhodium intermediates and a unicyclic sequence of mononuclear cobalt intermediates, in each system.<sup>46</sup> However, the kinetic results show that any contribution to the overall rate of hydroformylation from the hydrogenolysis of RCOC<sub>o</sub>(CO)<sub>4</sub> is negligible under the present reaction conditions (eq 11). This is entirely consistent with previous hydroformylation studies where it was concluded that cobalt is 2–4 orders of magnitude less active than rhodium under identical reaction conditions.<sup>47</sup>

$$\text{TOF}_{\text{Co}} / (\text{TOF}_{\text{Co}} + \text{TOF}_{\text{Rh}}) \approx 0 \quad (11)$$

The kinetic results also exclude a significant contribution

(43) It is known that the reaction order in 3,3-dimethylbut-1-ene for the unmodified rhodium-catalyzed hydroformylation approaches zero, specifically  $\alpha_{33\text{DMB}} = 0.1$ , under the present reaction conditions.<sup>32</sup>

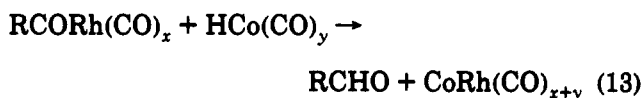
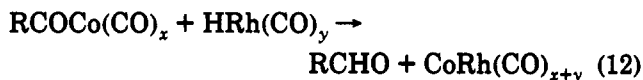
(44) (a) All turnover frequencies are reported as means and standard deviations. (b) In another study, the measured turnover frequency for the hydroformylation of 3,3-dimethylbut-1-ene starting with Rh<sub>4</sub>(CO)<sub>12</sub> as catalyst precursor was TOF = 0.131 ± 0.003 min<sup>-1</sup> at P<sub>CO</sub> = 2.0 MPa, P<sub>H<sub>2</sub></sub> = 2.0 MPa, and 20 °C.<sup>32</sup> Little or no Rh<sub>6</sub>(CO)<sub>16</sub> could be detected as a deactivation product, and the selectivity to RCORh(CO)<sub>4</sub> was *s* = 1.0. (c) The exact cause of Rh<sub>6</sub>(CO)<sub>16</sub> formation and subsequent deactivation in the present study remains unknown.

(45) (a) Hill, C. G. *Chemical Engineering Kinetics and Reactor Design*; Wiley: New York, 1977; p 44. (b) Butt, J. B. *Reaction Kinetics and Reactor Design*; Prentice-Hall: Englewood Cliffs, NJ, 1980; p 64.

(46) The unicyclic cobalt and rhodium hydroformylation sequences are believed to be {HM(CO)<sub>3</sub> → H(olefin)M(CO)<sub>3</sub> → RM(CO)<sub>3</sub> → RM(CO)<sub>4</sub> → RCOM(CO)<sub>3</sub> → RCOH<sub>2</sub>M(CO)<sub>3</sub> → HM(CO)<sub>3</sub>}, where the saturated species HM(CO)<sub>4</sub> and RCOM(CO)<sub>4</sub> are simply in equilibrium exchange with the corresponding tricarbonyls at steady state.<sup>3a</sup>

(47) (a) Imyanov, N. S.; Rudkovskii, D. M. *Neftekhimiya* 1963, 3, 198; *Chem. Abstr.* 1963, 59, 7396d. (b) Yamaguchi, M. *Shokubai* 1969, 11, 179; *Chem. Abstr.* 1970, 73, 137870. (c) Wakamatsu, H. *Nippon Kagaku Zasshi* 1964, 85, 227; *Chem. Abstr.* 1965, 33, 13173e. (d) Imyanov, N. S. *Hung. J. Ind. Chem.* 1975, 3, 331; *Chem. Abstr.* 1976, 83, 137395. (e) Heil, B.; Markó, L. *Chem. Ber.* 1968, 101, 2209.

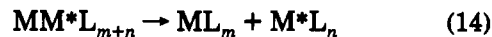
to the overall hydroformylation rate from a catalytic binuclear elimination reaction, at least at the very low nominal metal loadings used in these experiments. Indeed, the normalized hydroformylation activities TOF<sub>Rh</sub> for all experiments are the same regardless of the absence or presence of cobalt. These results do not exclude the existence *per se* of binuclear elimination reactions involving mononuclear species of cobalt and rhodium (eqs 12 and 13). Such a mechanism is analogous to the stoichiometric Heck–Breslow reaction between acylcobalt carbonyls and cobalt carbonyl hydrides.<sup>48</sup>



The present catalytic hydroformylations starting with CoRh(CO)<sub>7</sub> and Co<sub>2</sub>Rh<sub>2</sub>(CO)<sub>12</sub> as precursors, are examples of *synergism arising from the facile generation of a reactive fragment*. In other words, the observed activity of these heterometallic precursors is due to their unusually rapid transformation under the reaction conditions used, to give the transient species {HRh(CO)<sub>3</sub>} and subsequently RCORh(CO)<sub>4</sub>. In this study, the induction periods starting with the heterometallic complexes are 2–3 orders of magnitude shorter than the corresponding induction periods starting with the homometallic complexes Rh<sub>4</sub>(CO)<sub>12</sub> and Rh<sub>6</sub>(CO)<sub>16</sub>. Only one metal, namely rhodium, is responsible for the observed system activities.

At higher temperatures and especially at higher nominal metal concentrations, a binuclear elimination reaction could make a significant contribution to the overall rate of hydroformylation in mixed cobalt–rhodium systems. As a consequence, and depending on the alkene used, the regioselective outcome of the hydroformylation reaction may also change. Mechanisms such as eqs 12 and 13 may well explain the regioselective changes and hence synergistic effects observed by Pino and von Bézard<sup>10</sup> and Ojima et al.<sup>11</sup>

**Heterometallic Clusters and Synergism.** The facile fragmentation of heterometallic clusters to generate reactive fragments (eq 14) and subsequently to give rise to catalytic sequences involving just one metal (eq 15),



may represent a rather wide-spread phenomenon in homogeneous catalysis. Indeed, there are numerous examples of the facile fragmentation of heterometallic clusters—fragmentations which do not readily occur with the corresponding homometallic species.<sup>49</sup>

(48) (a) Breslow, D. S.; Heck, R. F. *Chem. Ind. (London)* 1960, 467. (b) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1961, 83, 4023. (c) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974. (d) Ungvary, F.; Markó, L. *Organometallics* 1982, 1, 1120. (e) Azran, J.; Orchin, M. *Organometallics* 1984, 3, 197. (f) Kovacs, I.; Ungvary, F.; Markó, L. *Organometallics* 1986, 5, 209.

(49) (a) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* 1980, 19, 2574. (b) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* 1982, 1, 1379. (c) Geoffroy, G. L.; Foley, H. C.; Fox, J. R.; Gladfelter, W. L. *ACS Symp. Ser.* 1981, 155, 111. (d) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, 18, 207.



The above phenomenon has potential applications for low-temperature fine-chemical synthesis. Since many fine-chemical syntheses involve multifunctional substrates, obtaining good chemoselectivities and yields is an ever present challenge. If a desired catalytic transformation can be initiated at a significantly lower temperature than would otherwise prevail, then the potential exists for obtaining new and possibly more favorable selectivity patterns.

**Selectivities and Effective Catalyst Precursors.** Consider two competitive and nonelementary transformations, namely (I) the transformation of a precursor to intermediates and (II) the transformation of a precursor to other metal complexes or metal. These overall reactions (eqs 16 and 17) lead to useful definitions of precursor conversion, precursor selectivity to intermediates, and intermediate yields.



Let  $[P]$  represent the moles of catalyst precursor and  $[N_i]$  represent the moles of the  $i$ th intermediate either on the catalytic cycle or in equilibrium exchange with the catalytic cycle as a reservoir. Further, let  $\phi$  be the ratio of nuclearities of the intermediates and precursor. Then the conversion of catalyst precursor (eq 18), the integral selectivity for precursor transformation to intermediates (eq 19), the differential selectivity for precursor transformation to intermediates (eq 20), and the yield of intermediates can be defined (eq 21).<sup>50,51</sup>

$$c_t \equiv ([P]_0 - [P]_t)/[P]_0 \quad (18)$$

$$s_t \equiv \phi \sum [N_i]_t / ([P]_0 - [P]_t) \quad (19)$$

$$ds_t \equiv \phi d \sum [N_i]_t / d[P]_t \quad (20)$$

$$y_t \equiv s_t c_t \quad (21)$$

The above definitions suggest that an effective catalyst precursor should (I) exhibit a high maximum conversion and a high selectivity for the transformation to intermediates and (II) possess the highly desirable property of rapid degradation kinetics under the reaction conditions. On the basis of both criteria, the complexes  $\text{CoRh}(\text{CO})_7$  and  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  are excellent catalyst precursors.

**Conclusions.** Two phenomenological aspects of homogeneous catalysis have been identified and addressed in this study. First, the synergism observed starting with some heteronuclear precursors  $\text{MM}^*\text{L}_{m+n}$  need not be due to cluster catalysis nor a binuclear elimination reaction. Instead, synergism (specifically high initial activities) may in fact arise due to the facile generation of a reactive fragment  $\text{M}^*\text{L}_n$  and the subsequent formation of a closed sequence of intermediates  $\{\text{M}^*\text{L}_i \rightarrow \dots \text{RM}^*\text{L}_j \rightarrow \dots \text{M}^*\text{L}_i\}$  involving just one metal, which is ultimately responsible for the observed system activity. Secondly, the transformation of a catalyst precursor to intermediates need not be highly selective, i.e.  $s(x, T, P) < 1$ . This latter phenomenon represents a loss of metal from the developing catalytic systems. Ultimately, such fundamental studies have relevance to maximizing the utilization of precious metal complexes in fine-chemical synthesis.

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(50) In terms of the transformation of reagents to products, integral and differential selectivities have been defined in heterogeneous catalytic systems. IUPAC Manual on Catalyst Characterization. *Pure Appl. Chem.* 1991, 63, 1227.

(51) Accordingly, maximum conversion, maximum selectivity, and maximum yield can be defined  $c_{\max} \equiv \max\{c_t\}$ ,  $s_{\max} \equiv \max\{s_t\}$  and  $y_{\max} \equiv \max\{y_t\}$ .