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$Rh_4(CO)_{12}$-Catalyzed Hydroformylation of Cyclopentene Promoted with $HMn(CO)_5$. Another Example of $Rh_4(CO)_{12}$/$HMn(CO)_5$ Bimetallic Catalytic Binuclear Elimination

Chuanzhao Li, Effendi Widjaja, and Marc Garland*

Department of Chemical and Biomolecular Engineering, 4 Engineering Drive 4,
National University of Singapore, Singapore 119260

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A detailed in situ high-pressure FTIR spectroscopic study was performed to investigate the bimetallic origins of catalytic synergism in homogeneous catalysis. The reaction chosen was the homogeneous catalyzed hydroformylation of cyclopentene to cyclopentanecarboxaldehyde, starting with unmodified rhodium and manganese carbonyls as catalyst precursors in *n*-hexane as solvent. The spectra were analyzed by an advanced signal processing and statistical technique. Only four organometallic spectra could be found. These were $RCORh(CO)_4$, $Rh_4(CO)_{12}$, $HMn(CO)_5$, and $Mn_2(CO)_{10}$. A very significant increase in aldehyde formation was observed in the experiments when both rhodium carbonyl and manganese carbonyl complexes were used simultaneously. The kinetics of product formation shows a distinct linear−bilinear form in observable organometallics; $k_1[RCORh(CO)_4][H_2][CO]^{-1} + k_2[RCORh(CO)_4][HMn(CO)_5][CO]^{-1.6}$. The determined activation parameters for the bilinear term were $\Delta H^{\ddagger} = 47 \pm 8$ kJ/mol and $\Delta S^{\ddagger} = -88 \pm 28$ J/(mol K). The results, particularly the bilinear term and the negative entropy of activation, suggest that the origin of synergism is the presence of bimetallic catalytic binuclear elimination: namely, the hydride attack on the acyl species. The present results are consistent with observations and conclusions reached for a previously studied $Rh_4(CO)_{12}$/$HMn(CO)_5$/3,3-dimethylbut-1-ene hydroformylation system.

Introduction

Stoichiometric binuclear elimination is the term used to describe the reaction between two organometallic complexes yielding a higher nuclear complex and an organic product. Thus, in the case of two substituted mononuclear complexes $R^1M^1L_n$ and $R^2M^2L'_n$, the dinuclear complex $M^1M^2L_nL'_n$ and product R^1R^2 result. When M^1 and M^2 are the same element, the stoichiometric binuclear elimination is homometallic. In perhaps the first known case, Heck and Breslow identified such a reaction pathway involving an intermolecular hydride transfer between $HCo(CO)_4$ and $CH_3COCo(CO)_3$ to eliminate the dinuclear complex $Co_2(CO)_8$ and aldehyde product.[1] Additonal examples of homometallic stoichiometric binuclear elimination have been identified.[2]

When M^1 and M^2 are the different elements, the stoichiometric binuclear elimination is heterobimetallic. Approximately 13 heterobimetallic stoichiometric binuclear eliminations are presently known. An extensive list is provided in Table 1.

The possible existence of heterobimetallic binuclear eliminations during bimetallic catalytic syntheses has been a subject of considerable interest. Indeed, the bimetallic catalytic binuclear elimination reaction would constitute a well-defined reaction topological basis for synergism. [7] In such a context, synergism refers to the combined application of more than one metal, leading to regio-, chemo-, and stereoselectivities and/or activities which differ significantly from a strictly additive effect.

Hidai and co-workers indicated that the synergistic effect for cobalt and ruthenium in the hydroformylations

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* To whom correspondence should be addressed. E-mail: chemvg@nus.edu.sg. Phone: +65-6-874-6617. Fax: +65-6-779-1936.

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Table 1. Bimetallic Stoichiometric Binuclear Elimination Reactions

no.	reacn	ref
1	$HMn(CO)_5 + CH_3AuPPh_3 \rightarrow Au(PPh_3)Mn(CO)_5 + CH_4$	3
2	$HOs(CO)_4Si(CH_3)_3 + CH_3AuPPh_3 \rightarrow Au(PPh_3)Os(CO)_4Si(CH_3)_3 + CH_4$	3
3	$Os(CO)_4(H)CH_3 + HRe(CO)_5 \rightarrow HOs(CO)_4Re(CO)_5 + CH_4$	2c
4	$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)^2 + (\eta^5\text{-}C_5H_5)Mo(CO)_3H \rightarrow (C_5H_5)_2CH_3ZrMo(C_5H_5)(CO)_3 + CH_4$	4
5	$EtRe(CO)_5 + HMn(CO)_5 \rightarrow EtCHO + Re(CO)_4Mn(CO)_5$	5
6	$EtRe(CO)_5 + HW(CO)_3CpEtCHO + Re(CO)_5W(CO)_3Cp$	5
7	$(\eta^5\text{-}C_5H_5)MoH_2 + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)(CO)Mo(\eta^5{:}\eta^1\text{-}C_5H_4)Mn(CO)_4 + H_2 + CH_4$	6
8	$(\eta^5\text{-}C_5H_5)WH_2 + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)(CO)W(\eta^5{:}\eta^1\text{-}C_5H_4)Mn(CO)_4 + H_2 + CH_4$	6
9	$(\eta^5\text{-}C_5H_5)ReH + CH_3Mn(CO)_5 \rightarrow (\eta^5\text{-}C_5H_5)(H)Re(\eta^5{:}\eta^1\text{-}C_5H_4)Mn(CO)_4 + CO + CH_4$	6
10	$HMn(CO)_5 + EtOC(O)Co(CO)_4 \rightarrow EtOC(O)H + MnCo(CO)_9$	2m
11	$HMn(CO)_5 + EtOC(O)CH_2Co(CO)_4 \rightarrow EtOC(O)CH_3 + MnCo(CO)_9$	2m
12	$HCo(CO)_4 + EtOC(O)Mn(CO)_5 \rightarrow EtOC(O)H + MnCo(CO)_9$	2m
13	$HCo(CO)_4 + EtOC(O)CH_2Mn(CO)_5 \rightarrow EtOC(O)CH_3 + MnCo(CO)_9$	2m

of cyclohexene, 1-hexene, and styrene might be explained by such a dinuclear elimination between a cobalt acyl and a ruthenium hydride.[8] In addition, the cobalt–ytterbium-meditated syntheses of aldehydes by the Russian group of Beletskaya deserve special attention. It was shown that lanthanum hydrides react in a stoichiometric manner with acyl cobalt tetracarbonyls to give aldehyde.[9] Furthermore, under catalytic reaction conditions a large increase in activity is observed. This observation was interpreted to mean that the bimolecular reaction of acyl cobalt carbonyl $RCOCo(CO)_x$ with the ytterbium hydride $HYb(C_5H_5)_y$ represents the largest single contribution to aldehyde formation. However, in situ spectroscopic and kinetic information was not available.

Recently, the $Rh_4(CO)_{12}/HMn(CO)_5$ bimetallic catalyzed hydroformylation of 3,3-dimethylbut-1-ene (33DMB) was studied systematically.[10] The spectroscopic and kinetic analyses provided evidence for the existence of bimetallic CBER. The present contribution extends our understanding of the $Rh_4(CO)_{12}/HMn(CO)_5$ bimetallic system by application to the homogeneous catalyzed hydroformylation of cyclopentene. New details about the mechanism have been obtained, and support for a second example of bimetallic CBER is presented.

Experimental Section

General Information. All solution preparations and transfers were carried out under a purified argon (99.9995%, Saxol, Singapore) atmosphere using standard Schlenk techniques.[11] The argon was further purified before use by passing it through deoxy and zeolite columns. Purified carbon monoxide (research grade, 99.97%, Saxol, Singapore) and purified hydrogen (99.9995%, Saxol, Singapore) were also further purified through deoxy and zeolite columns before they were used in the hydroformylation experiments. Purified nitrogen (99.9995%, Saxol, Singapore) was used to purge the Perkin-Elmer FT-IR spectrometer system.

$Rh_4(CO)_{12}$ (98%) was purchased from Strem Chemicals (Newport, MA) and was used as obtained. $Mn_2(CO)_{10}$ (98%) was also purchased from Strem Chemicals and was used without further purification.

$HMn(CO)_5$ was prepared using a modified literature preparation.[12] The reaction involves the interaction of H_2 with $Mn_2(CO)_{10}$ according to eq 1.

$$Mn_2(CO)_{10} + H_2 + h\nu \rightarrow 2HMn(CO)_5 \qquad (1)$$

The standard procedure is as follows. A 100 mg portion of $Mn_2(CO)_{10}$ was dissolved in 50 mL of *n*-hexane in a Schlenk tube. The solution was first saturated with H_2 and a small amount of CO for ca. 15 min at room temperature and then irradiated with an immersion lamp (450 W mercury-vapor lamp, Model 7825-34, ACE Glass, Vineland, NJ). Trace CO was needed during photoirradiation in order to prevent total decomposition of the manganese carbonyl and hydride. After ca. 10 min, infrared spectroscopy indicated the formation of $HMn(CO)_5$ (ν_{CO} 2014, 2007 cm^{-1}). Under our experimental conditions, it was found that the maximum yield (ca. 25%) of $HMn(CO)_5$ appeared around 70 min and further irradiation would give some yellow precipitate. It was also found that the reproducibility of this photoreaction was not ideal; therefore, the $HMn(CO)_5$ concentrations for each experiment are somewhat different from run to run. (Note that this has no detrimental effect on the quality of the catalytic data or their analysis, since all concentrations can be measured in situ.) Since the $HMn(CO)_5$ is very unstable, the $HMn(CO)_5$ solution was immediately transferred under CO/argon to the autoclave after photoirradiation.

The puriss quality cyclopentene (Fluka AG) obtained for this study had a purity of 98.5%. To remove the possible trace of dienes in it, the cyclopentene was first refluxed with 2 equiv of maleic anhydride (99%, Fluka AG) for 2 h. The distilled cyclopentene was repeatedly washed with distilled water, passed over 4-A molecular sieves, distilled from calcium hydride (95%, Merck), and stored under argon at −20 °C. The resulting purity of the cyclopentene was 99.99%, as determined by GC analysis (HP6890; HP-1 methylsiloxane capillary column, 100 °C; FID, 250 °C). The puriss quality *n*-hexane (99.6%, Fluka AG) was distilled from sodium−potassium under argon for ca. 5 h to remove the trace water and oxygen.

Apparatus. The apparatus used in this study was identical with that used in our previous study of the Rh−Mn-catalyzed hydroformylation of 3,3-dimethylbut-1-ene.[10]

In Situ Spectroscopic and Kinetic Studies. The general procedures used are that same as those used in ref 10. The experimental design of the experiments involved 300 mL of solvent and the intervals 281.5−308.9 K, $P_{H_2} = 1.0-4.0$ MPa, $P_{CO} = 1.0-4.0$ MPa, initial alkene 2−10 mL, initial $Rh_4(CO)_{12}$ 24.05−106.47 mg, and initial $Mn_2(CO)_{10}$ 25.0−229.0 mg. The detailed experimental design for this study is shown in Table 2.

All hydroformylation experiments exhibited product formation rates belonging to infinitely slow reaction compared to

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Table 2. Experiment Design for the Bimetallic $Rh_4(CO)_{12}$/$HMn(CO)_5$-Catalyzed Hydroformylation of Cyclopentene

expt	amt of $Mn_2(CO)_{10}$, mg	amt of CO, MPa	amt of H_2, MPa	amt of CP, mL	amt of $Rh_4(CO)_{12}$, mg	temp, K
standard	117.36	2.0	2.0	5	51.60	289.7
blank	0	2.0	2.0	5	0	289.7
pure Rh	0	2.0	2.0	5	51.89	289.7
pure Mn	122.0	2.0	2.0	5	0	289.7
CO variation	103.07	1.0	2.0	5	53.73	289.7
	108.45	3.0	2.0	5	54.32	289.7
	108.97	4.0	1.0	5	52.58	289.7
H_2 variation	106.30	2.0	1.0	5	49.46	289.7
	101.86	2.0	3.0	5	52.48	289.7
	104.57	2.0	4.0	5	47.74	289.7
cyclopentene	100.37	2.0	2.0	2	49.53	289.7
variation	109.36	2.0	2.0	10	50.63	289.7
$Mn_2(CO)_{10}$	25.00	2.0	2.0	5	51.04	289.7
variation	50.00	2.0	2.0	5	49.80	289.7
	150.25	2.0	2.0	5	51.84	289.7
	229.00	2.0	2.0	5	50.63	289.7
temp	104.79	2.0	2.0	5	48.12	281.5
variation	108.28	2.0	2.0	5	49.00	293.7
	104.50	2.0	2.0	5	52.05	299.4
	103.11	2.0	2.0	5	50.07	308.9
$Rh_4(CO)_{12}$	103.29	2.0	2.0	5	24.05	289.7
variation	103.68	2.0	2.0	5	82.11	289.7
	100.30	2.0	2.0	5	106.47	289.7

gas−liquid mass transfer (category H of the Hatta classifications).[13] Since the maximum rate of the hydroformylation in this study was 10^{-6} mol/s, gas−liquid mass transfer control can be ignored in all the experiments.

Blank experiments, in the presence of organic reactants but without added complexes, were performed throughout the study. A very small residual activity of the cleaned reactor with blank experiments was occasionally observed.

The in situ spectra were taken every 10 min during the each 6 h experiment in the range of 1000−2500 cm^{-1} with a resolution of 4 cm^{-1}. A total of 1461 spectra were obtained for the further spectroscopic and kinetic analyses.

The appropriateness of various finite difference schemes for the evaluation of in situ homogeneous catalytic rate data and TOF evaluation has been carefully evaluated.[14] The rates of the product formation of cyclopentanecarboxaldehyde were calculated in terms of turnover frequency (TOF) by using a finite difference equation:

$$\mathrm{TOF}_t = \frac{\mathrm{d[aldehyde]}_t/\mathrm{d}t}{[\mathrm{RCORh(CO)_4}]_t} \tag{2}$$

This central difference expression provides a numerical value for the reaction rate at time t, based on the measured in situ concentrations of the aldehyde at time $t - 1$ and $t + 1$. The time interval between t and $t + 1$ or $t - 1$ was 20 min.

Computational Section

Spectroscopic Aspects. The newly developed algorithm for algebraic system identification was employed to analyze the in situ IR spectra.[15] Since no special features were observed in the wavenumber range from 1000 to 1550 cm^{-1}, all experimental spectroscopic data were accordingly truncated. The consolidated data gave rise to an absorbance matrix with the following size: rows, 1461 vectors (spectra); columns, 4751 channels (wavenumber range is 1550−2500 cm^{-1} and data interval 0.2 cm^{-1}). Discussion of the mathematical procedures used are discussed in detail in ref 15.

Kinetics and Activation Parameters. Mole fraction concentrations were used throughout for all species including dissolved gases. Rate expressions were developed using only the mole fractions as concentrations.

Arrhenius and Eyring type activation parameters were determined for the rate constants obtained as a function of temperature. Accordingly, the rate constants were modeled as either

$$k_{\mathrm{i}} = A \exp(-\Delta \mathrm{Ea_i}/RT) \tag{3}$$

or

$$k_{\mathrm{i}} = \kappa T/h \exp(-\Delta H_{\mathrm{i}}^{\ddagger}/RT + \Delta S_{\mathrm{i}}^{\ddagger}/R) \tag{4}$$

where κ is Boltzmann's constant, h is Planck's constant, A is the Arrhenius preexponential factor, Ea is the apparent activation energy, $\Delta H^{\ddagger}$ is the standard enthalpy of activation, and $\Delta S^{\ddagger}$ is the standard entropy of activation.

Results

Spectroscopic Aspects. The in situ spectroscopic data were subjected to band-target entropy minimization (BTEM).[15] BTEM is an advanced and totally blind deconvolution technique based on Shannon entropy criteria.[16] Hydroformylation of alkene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures.[17]

In the present $Rh_4(CO)_{12}$/$HMn(CO)_5$ bimetallic catalyzed hydroformylation of cyclopentene (CP), the chemometric analysis of the in situ infrared spectra of the reaction recovered the following: the precursors $Rh_4(CO)_{12}$, $HMn(CO)_5$, and $Mn_2(CO)_{10}$, the organic reagent cyclopentene, the rhodium intermediate $RCORh(CO)_4$, and the organic product cyclopentanecarboxaldehyde. Similar to the results of the $Rh_4(CO)_{12}$/$HMn(CO)_5$-catalyzed hydroformylation of 33DMB,[10] no Rh−Mn complex analogous to $MnCo(CO)_9$[2m] was observed in $Rh_4(CO)_{12}$/$HMn(CO)_5$-catalyzed hydroformylation of the cyclopentene system. Furthermore, GC analysis (HP6890; HP-1 methyl siloxane capillary column, 90 °C; FID, 250 °C) did not find the possible hydrogenation product cyclopentane in the reaction mixture.

A total of 1461 in situ FTIR spectra were acquired in this experimental study, over the spectral interval 1550−2500 cm^{-1} with data intervals of 0.2 cm^{-1}. Notable vectors from the singular value decomposition of the spectroscopic matrix $\mathbf{A}_{1461\times4751}$ are shown in Figure 1, and the recovered pure component spectra obtained from the BTEM analysis are shown in Figure 2 (solvent hexane, atmospheric moisture, CO_2, and dissolved CO are omitted). From a spectroscopic/observable viewpoint, the reactive system is very well defined and the signal-to-noise level is very high. No further

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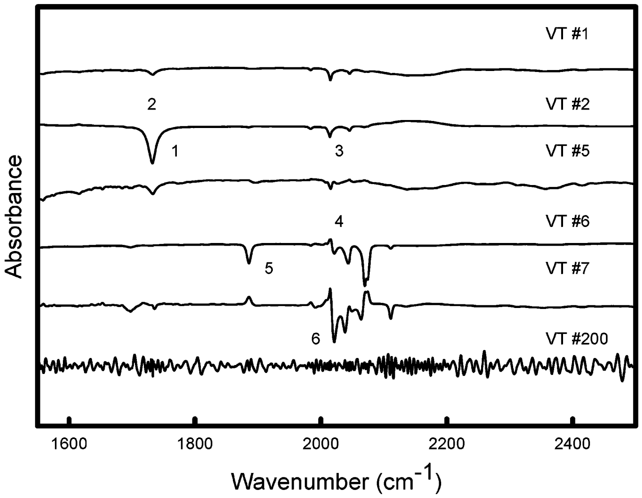

Figure 1. Singular value decomposition of the preconditioned in situ spectroscopic data showing the 1st, 2nd, 5th, 6th, and 7th significant vectors and the 200th vector. The marked extrema are those which were used to recover the organometallic pure component spectra as well as alkene and aldehyde by BTEM.

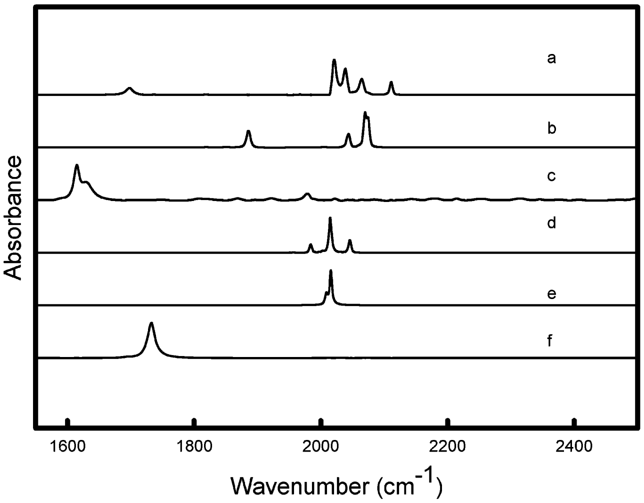

Figure 2. Recovered pure component spectra of the organic and organometallic species using BTEM: (a) $RCORh(CO)_4$; (b) $Rh_4(CO)_{12}$; (c) cyclopentene (CP); (d) $Mn_2(CO)_{10}$; (e) $HMn(CO)_5$; (f) cyclopentanecarboxaldehyde.

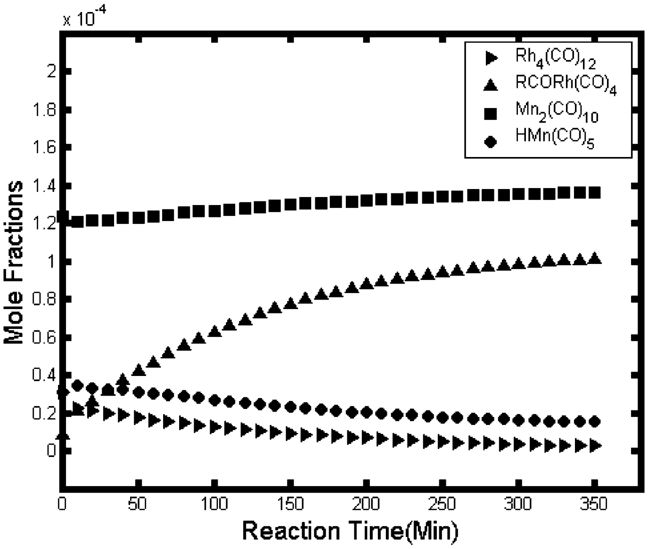

Figure 3. Time-dependent mole fractions of the four observable organometallics $Rh_4(CO)_{12}$, $RCORh(CO)_4$, $Mn_2(CO)_{10}$, and $HMn(CO)_5$ during a 350 min hydroformylation of cyclopentene at ca. 2.0 MPa of CO, 2.0 MPa of H_2, and 289.7 K with 350 mL of hexane and 5 mL of cyclopentene.

observable species could be identified in the present experimental study.

Hydroformylation of Cyclopentene with Only $Mn_2(CO)_{10}$/$HMn(CO)_5$. To determine the activities of $Mn_2(CO)_{10}$/$HMn(CO)_5$, a blank experiment with only $Mn_2(CO)_{10}$/$HMn(CO)_5$ as the precursor was carried out. The 6 h experiment showed there was no observable reaction under our reaction conditions (2.0 MPa of CO, 2.0 MPa of H_2, 289.7 K). This is consistent with the inert behavior of manganese toward transformations of alkenes under mild conditions.[18]

Hydroformylation of Cyclopentene with $Rh_4(CO)_{12}$ and $HMn(CO)_5$. Initial Reaction Times. The typical time-dependent concentrations of the precursors $Rh_4(CO)_{12}$, $HMn(CO)_5$, and $Mn_2(CO)_{10}$ and the only observable intermediate, $RCORh(CO)_4$, during an active hydroformylation of cyclopentene are shown in Figure 3.

It can be noted that after the simultaneous addition of the manganese carbonyls $HMn(CO)_5$ and $Mn_2(CO)_{10}$ and hydrogen to the systems initially containing $Rh_4(CO)_{12}$, alkene, hexane, and CO, the concentrations of $Rh_4(CO)_{12}$ monotonically decreased and the concentration of $RCORh(CO)_4$ monotonically increased for the first 6 h. However, the data presented in Figure 3 indicate that the decrease of $Rh_4(CO)_{12}$ and increase of $RCORh(CO)_4$ are not simple monotonic functions at initial reaction times. Indeed, upon addition of $Mn_2(CO)_{10}$, $HMn(CO)_5$, and H_2, a rapid decline in the catalyst precursor concentration and a corresponding increase in acyl complex concentration occur.

The data from all 23 experimental runs suggest that the concentration of $HMn(CO)_5$ has a big effect on the transformation of $Rh_4(CO)_{12}$. Generally speaking, the higher the concentration of $HMn(CO)_5$, the faster the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$. Moreover, the half-life for $Rh_4(CO)_{12}$ in the mixed $Rh_4(CO)_{12}$/$HMn(CO)_5$ system is ca. 60 min when 150.25 mg of $Mn_2(CO)_{10}$ was used, whereas a half-life under similar reaction conditions for pure Rh systems is ca. 2 h. This atypical initial time behavior is indicative of the existence of a second parallel precatalytic pathway for the transformation of $Rh_4(CO)_{12}$ to $RCORh(CO)_4$ in the presence of manganese carbonyls: namely, the hydride-facilitated degradation of the cluster $Rh_4(CO)_{12}$. It should be mentioned that the effects observed in the present study were also observed in the $Rh_4(CO)_{12}$/$HMn(CO)_5$/3,3-dimethylbut-1-ene system.[10]

In addition, Figure 3 contains a new piece of information which was unavailable in our previous study.[10] In the present study, $HMn(CO)_5$ was added and a short period (5 min) was allowed to transpire before molecular hydrogen was added to the system and the spectral acquisition started. As seen from the first data point in Figure 3, the concentration of the rhodium acyl complex is nonzero; therefore, the species is present in the first

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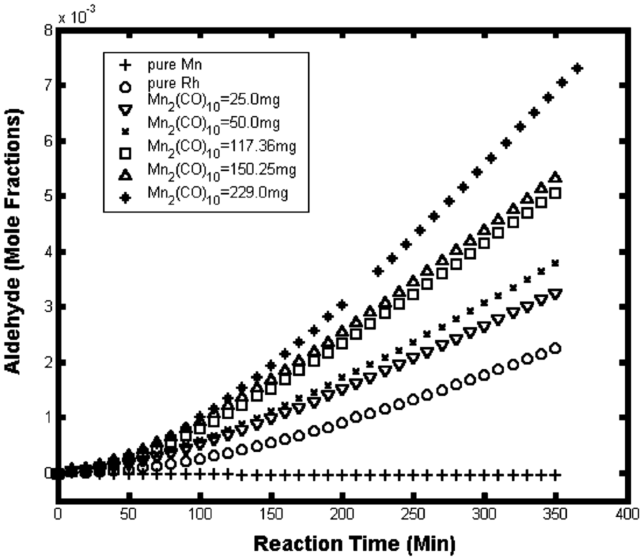

Figure 4. Time-dependent mole fractions of the product aldehyde during 350 min hydroformylations conducted with different manganese loadings. Typical reaction conditions during a 350 min hydroformylation of cyclopentene are ca. 2.0 MPa of CO, 2.0 MPa of H_2, and 289.7 K with 350 mL of hexane and 5 mL of cyclopentene. (The missing data at ca. 220 min for 229 mg of $Mn_2(CO)_{10}$ represent a data acquisition interruption.)

spectrum taken. This is rather compelling evidence for the $HMn(CO)_5$ attack on $Rh_4(CO)_{12}$ in the presence of substrate to produce $RCORh(CO)_4$. This provides an independent confirmation of the manganese hydride facilitated $Rh_4(CO)_{12}$ fragmentation.

Product Formation. The concentration profiles of the product aldehyde as a function of increasing manganese loadings are shown in Figure 4. The concentrations of the product aldehyde monotonically increase in all six experiments. The production of aldehyde could be identified within the first few minutes when $HMn(CO)_5/Mn_2(CO)_{10}$ were added simultaneously.

As shown in Figure 4, a very significant increase in aldehyde formation was observed in the experiments when both rhodium carbonyl and manganese carbonyl complexes were used. Increased concentrations of $HMn(CO)_5$ lead to increased hydroformylation rates. After the first 100 min, the rates of product formation are more or less constant. The rates are ca. 8.2×10^{-6}, 1.1×10^{-5}, 1.3×10^{-5}, 1.6×10^{-5}, 1.8×10^{-5}, and 2.3×10^{-5} (mol fraction)/min when $Mn_2(CO)_{10}$ amounts are 0, 25.0, 50.0, 117.36, 150.25, and 229.0 mg, respectively. When 229.0 mg of $Mn_2(CO)_{10}$ was used with $Rh_4(CO)_{12}$, the rate of hydroformylation was 300% of the rate anticipated from the rhodium loading alone. Since $HMn(CO)_5/Mn_2(CO)_{10}$ is nearly inert toward transformations of alkenes under the present reaction conditions, it implies that $HMn(CO)_5/Mn_2(CO)_{10}$ is involved in the rhodium catalytic pathway to produce aldehyde. This is consistent with the observations in the $Rh_4(CO)_{12}$/$HMn(CO)_5$/3,3-dimethylbut-1-ene system.[10]

TOF Analyses. The effect of $HMn(CO)_5/Mn_2(CO)_{10}$ loading on the TOF is shown in Figure 5. The turnover frequencies (TOF) based on rhodium and defined in the Experimental Section were 0.12 ± 0.01, 0.15 ± 0.01, 0.20 ± 0.02, 0.23 ± 0.002, 0.21 ± 0.02, and 0.28 ± 0.02 min^{-1} when initial $Mn_2(CO)_{10}$ amounts were 0, 25.0, 50.0, 117.36, 150.25, and 229.0 mg, respectively. The errors are listed as twice the standard deviation: i.e., the 95% confidence limit.

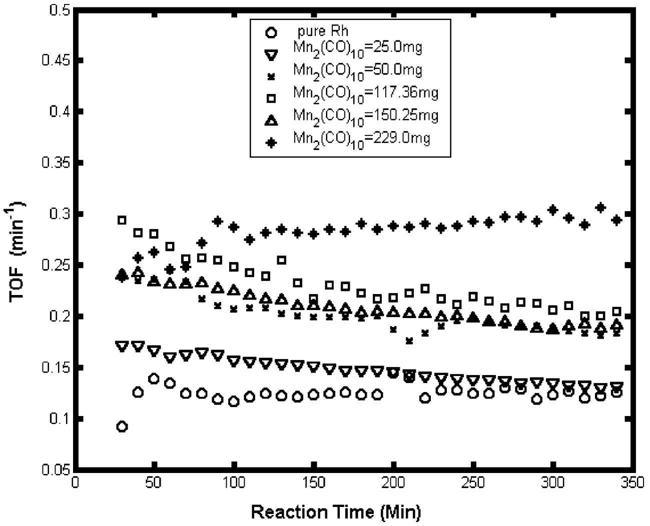

Figure 5. Effect of manganese loading on the turnover frequency of the rhodium-catalyzed hydroformylation of cyclopentene at ca. 2.0 MPa of CO, 2.0 MPa of H_2 and 289.7 K with 350 mL of hexane and 5 mL of cyclopentene.

The TOF values further demonstrate that manganese promotes rhodium-catalyzed hydroformylation of cyclopentene. In previous hydroformylations of 33DMB, cyclohexene, and styrene with pure unmodified rhodium carbonyl, it has been repeatedly shown that turnover frequencies (based on instantaneous concentration of rhodium intermediates) are only dependent on the temperature, hydrogen pressure, and carbon monoxide pressure. Our present results clearly show that TOFs increase with the increased manganese loadings. When the initial loading of $Mn_2(CO)_{10}$ was 229.0 mg, the TOF is 230% of that anticipated from pure rhodium-catalyzed hydroformylation.

Moreover, it should be noted that the TOF with 150.25 mg of $Mn_2(CO)_{10}$ is quite close to that of 50.0 mg of $Mn_2(CO)_{10}$ and even smaller than the TOF with 117.36 mg of $Mn_2(CO)_{10}$. This can be traced to the $HMn(CO)_5$ concentration profiles shown in Figure 6. Indeed, the average $HMn(CO)_5$ concentrations of the experiments with 50.0 and 150.25 mg of $Mn_2(CO)_{10}$ are quite similar, while the average $HMn(CO)_5$ concentrations with 117.36 mg of $Mn_2(CO)_{10}$ are higher. This suggests that $HMn(CO)_5$ and not $Mn_2(CO)_{10}$ is associated with the high activities in the $Rh_4(CO)_{12}/HMn(CO)_5$ bimetallic system. The higher the $HMn(CO)_5$ concentration in an experiment, the higher the TOF.

The present results are entirely consistent with those of the $Rh_4(CO)_{12}$/ $HMn(CO)_5$ bimetallic catalyzed hydroformylation of 33DMB.[10] Specifically, the activity of the systems appears correlated with the $HMn(CO)_5$ concentrations and not the $Mn_2(CO)_{10}$ concentrations. $HMn(CO)_5$ appears necessary for the final product formation and is therefore involved in at least one step of the catalytic cycle of the hydroformylation.

Catalysis and Kinetics. A total of 23 kinetic experiments in six subseries were performed for the kinetic study. In each set, one experimental parameter was systematically varied while the remaining variables were held essentially constant. The complete experi-

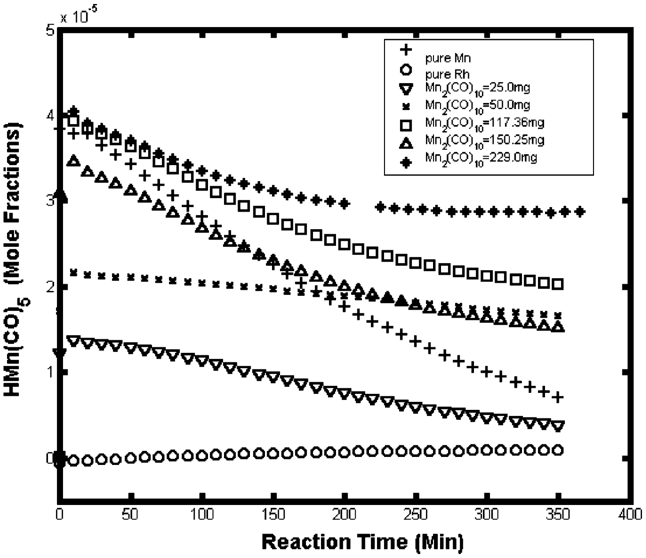

Figure 6. Actual time-dependent concentrations of HMn(CO)$_5$ in experiments with different nominal manganese loadings at ca. 2.0 MPa of CO, 2.0 MPa of H_2, and 289.7 K with 350 mL of hexane and 5 mL of cyclopentene.

mental design is documented in the Experimental Section. The strong effect of HMn(CO)$_5$ on the product formation rate and TOF was elucidated.

As observed in the $Rh_4(CO)_{12}$-catalyzed hydroformylation of 33DMB promoted with HMn(CO)$_5$/$Mn_2(CO)_{10}$,[10] the following two-term linear−bilinear form in organometallic species provided an excellent fit for the observable kinetics of the aldehyde formation:

$$r_{\text{total}} = k_1[\text{RCORh(CO)}_4][\text{H}_2][\text{CO}]^{-1} + k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^x \quad (5)$$

Approximately 1200 sets of mole fraction data were used in the regression. The activity of the system (rate of product formation) did not correlate with the presence of any other observables.

Using the nonlinear regression program “nonlinfit” in Matlab, the regressed numerical values of the rate constants at 289.7 K were $k_1 = 0.314 \pm 0.08$ min^{-1}, $k_2 = 37 \pm 15$ min^{-1}, and $x = -1.6 \pm 0.01$. The errors are listed as twice the standard deviation: i.e., the 95% confidence limit. The rate constant k_1 is consistent with the previous studies. The rate constants and the exponent for CO are in agreement with the results of the $Rh_4(CO)_{12}$-catalyzed hydroformylation of 33DMB promoted with HMn(CO)$_5$/$Mn_2(CO)_{10}$, where $k_1 = 0.446 \pm 0.018$ min^{-1} and $k_2 = 44.5 \pm 14$ min^{-1} at 298 K and the exponent was $x = -1.5 \pm 0.1$.[10] In a broader context, the hydroformylation rate differences between the cyclic alkene (cyclopentene) and the branched alkene (33DMB) are small. This result is consistent with the extensive rate studies by Marko,[19] as well as in situ studies [17d] using unmodified rhodium carbonyl and many different alkenes.

The contributions of these two terms under the reference reaction conditions of this experimental study were ca. 1:1. In particular, at 289.7 K, 2.0 MPa of CO, 2.0 MPa of H_2, 5 mL of cyclopentene, ca. 50 mg of $Rh_4(CO)_{12}$, and 229.0 mg of $Mn_2(CO)_{10}$ ($X_{\text{MnH(CO)}_5} = 4 \times 10^{-5}$) the contribution of CBER to the final product formation is 51%.

Table 3. Regressed *k* Values at Different Temperatures

expt no.	temp (K)	k_1 (L/min)	k_2 (L/min)
T-1	281.5	0.095	21
T-2	289.7	0.314	37
T-3	293.7	0.524	44
T-4	299.4	0.995	71
T-5	308.9	3.02	137

Rearrangement of the two terms $k_1[\text{CO}]^{-1}/k_2[\text{CO}]^{-1.6}$ leads to the conclusion that under 2.0 MPa of CO, HMn(CO)$_5$ is ca. 520 times more efficient than H_2, for reaction with the acyl−rhodium bond, on a mole-to-mole basis. The exponent $x = -1.6 \pm 0.01$ suggests that coordinative unsaturation may occur in both metal carbonyl complexes.

The temperature was systematically varied in five unmodified rhodium-catalyzed hydroformylations of cyclopentene promoted with HMn(CO)$_5$ at 2.0 MPa of CO and 2.0 MPa of H_2 to regress the reaction activation parameters. The five temperatures and the corresponding regressed rate constants k_1 and k_2 at different reaction temperatures are shown in Table 3.

Regression of the rate constants as a function of temperature provided acceptable estimates of the activation parameters ΔE_a, $\Delta H^\ddagger$, and $\Delta S^\ddagger$. For k_1 the parameters were $\Delta E_a = 91 \pm 6$ kJ/mol, $\Delta H^\ddagger = 88 \pm 6$ kJ/mol, and $\Delta S^\ddagger = 15 \pm 20$ J/(mol K). For k_2 the parameters are $\Delta E_a = 49 \pm 8$ kJ/mol, $\Delta H^\ddagger = 47 \pm 8$ kJ/mol, and $\Delta S^\ddagger = -88 \pm 28$ J/(mol K). The errors are listed as twice the standard deviation: i.e., the 95% confidence limit.

The present activation parameters for k_1, corresponding to the classic unicycle hydroformylation mechanism, are consistent with previous work (pure rhodium system[17] and HMn(CO)$_5$/$Mn_2(CO)_{10}$ bimetallic catalyzed hydroformylation of 33DMB[10]). As for k_2, the negative entropy clearly indicates that the degrees of freedom have decreased in the transition state.

Discussion

Evidence for Existence of CBER. Similar to the $Rh_4(CO)_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of 33DMB,[10] the present kinetic results for cyclopentene hydroformylation strongly suggest the simultaneous existence of a unicyclic catalytic topology and at least one bimetallic catalytic elimination reaction. Accordingly, the unicyclic catalysis occurs exclusively on mononuclear rhodium intermediates, and the bimetallic CBER occurs on a set of rhodium, manganese, and rhodium−manganese intermediates.

In pure rhodium carbonyl systems, RCORh(CO)$_4$ has been repeatedly shown to be the predominant coordinatively saturated rhodium intermediate under hydroformylation conditions and RCORh(CO)$_3$ is the equilibrated, coordinately unsaturated complex. Mechanistically, hydrogen activation on the acyl complex RCORh(CO)$_3$ is the rate-limiting step in the unicyclic rhodium catalysis. In the bimetallic CBER, the attack of (a) HMn(CO)$_5$ on RCORh(CO)$_3$ and/or (b) HMn(CO)$_4$ on RCORh(CO)$_3$ are the rate-limiting steps. The exponent $x = -1.6 \pm 0.1$ arises from this latter competing situation.

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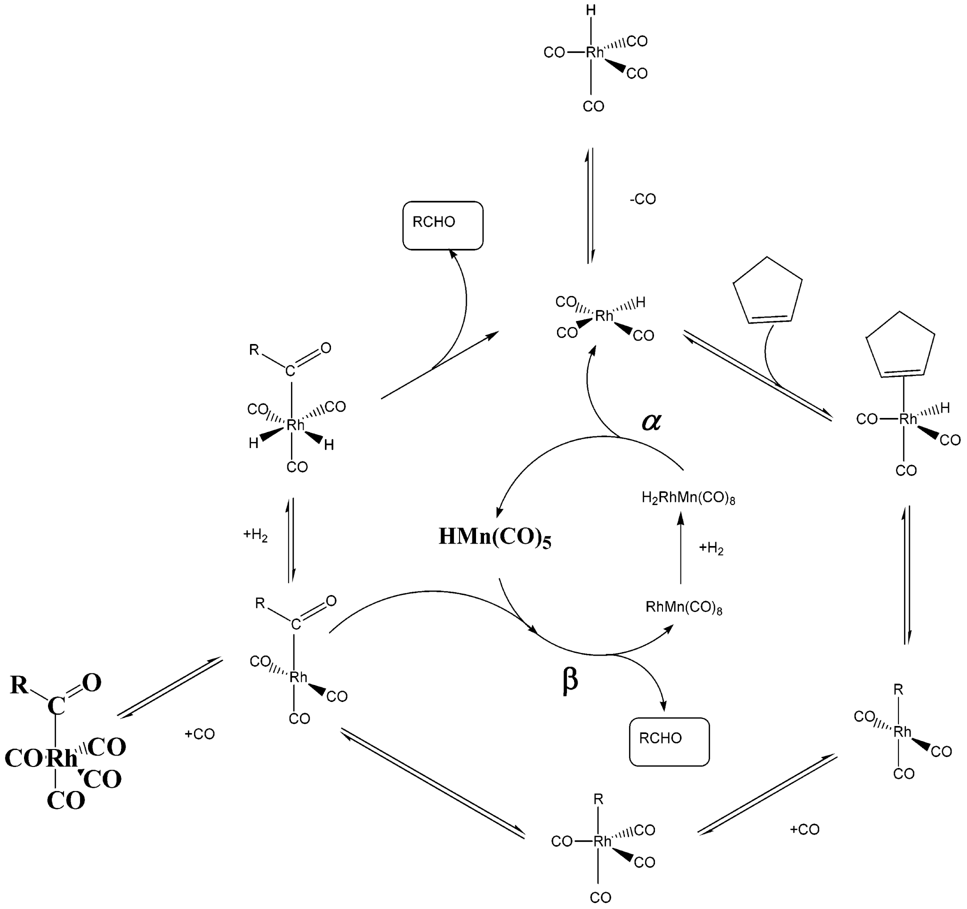
(19) Heil, B.; Marko, L. *Chem. Ber.* **1969**, *102*, 2238−2240.

Scheme 1. Proposed Reaction Topology for the Simultaneous Interconnected Unicyclic Rh and Bimetallic Rh−Mn CBER Cyclopentene Hydroformylation Reactions



In the bimetallic $Rh_4(CO)_{12}/HMn(CO)_5$ systems, the attack of $HMn(CO)_5$ on $RCORh(CO)_3$ or of $HMn(CO)_4$ on $RCORh(CO)_3$ with elimination of aldehyde implies the existence of a transient, coordinately unsaturated bimetallic rhodium manganese dinuclear complex with the probable stoichiometry $RhMn(CO)_8$ (or possibly $RhMn(CO)_7$). However, such a species (or its coordinatively saturated analog) was not observable in these experiments or in the $Rh_4(CO)_{12}/HMn(CO)_5$/33DMB system.[10] This inability to observe a dinuclear bimetallic complex is probably due to the very rapid activation of molecular hydrogen to regenerate $HRh(CO)_3$ and $HMn(CO)_5$. Hydrogen activation, which is normally very difficult to achieve, particularly under CO, is known to occur exceptionally rapidly, even at low temperatures, on heterometallic dinuclear carbonyl complexes.[20] Hydrogen activation on $CoRh(CO)_7$ is a good example.[21]

The simultaneous existence of a unicyclic Rh topology and a bimetallic Rh−Mn CBER for cyclopentene hydroformylation is represented in Scheme 1. All intermolecular transformations in the unicyclic topology are first order in the corresponding mononuclear metal complexes. Two elementary steps in Scheme 1 are highlighted by the labels α and β. These labels are used to identify the key mechanisms which give rise to the existence of the bimetallic CBER. The α step denotes the simultaneous generation of the crucial mononuclear hydrides $HRh(CO)_3$ and $HMn(CO)_5$ from the dinuclear complex $H_2RhMn(CO)_8$. The β step is the binuclear elimination step. The steps −α and β are bimolecular in metal complexes.

The possible existence of isomers of the intermediates is not the emphasis of Scheme 1, and accordingly, we have assumed the most common geometry for five-coordinate rhodium structures: namely, axially substituted trigonal-bipyramidal geometries. The interconnected topology of a unicyclic mechanism and a CBER mechanism as shown in Scheme 1 directly leads to the linear−bilinear mathematical form for the observed kinetics of product formation as shown in eq 5.

The binuclear elimination step β has been drawn as if the process proceeds through a concerted four-center transition state for convenience. If the elimination does not proceed through a four-center transition state but instead through two or more simpler transition states, additional intermediates exist on the reaction pathway. Although the assumption of a four-center transition state is not essential for the existence of the bimetallic CBER, it perhaps helps to explain the rate increase observed. In this regard, it is worthwhile to note that (1) the hydroformylation is being performed in an apolar solvent (*n*-hexane), (2) $HMn(CO)_5$ is acidic and hence quite polarized with partial positive charge on the hydrogen atom, and (3) $RCORh(CO)_4$ should be have a partial negative charge on the acyl carbon (the elec-

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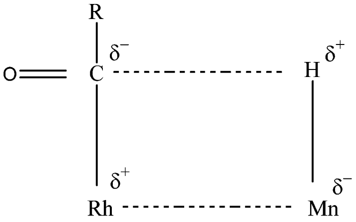
[20] James, B. R. In *Comprehensive Organometallic Chemistry*: The Synthesis, Reactions, and Structures of Organometallic Compounds; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 18.

[21] Garland, M.; Pino, P. *Organometallics* **1990**, *9*(6), 1943−1949.

Chart 1. Proposal for a Four-Center Transition State in the Binuclear Elimination Step, Highlighting the Partial Charges and Hence Preferred Alignment/Association of Manganese Hydride and Acyl−Rhodium Complexes



tronegativty of C is 2.55, and that of rhodium is 2.28). The polarized organometallics $HMn(CO)_5$ and $RCORh(CO)_4$ should not be randomly and uniformly distributed in solution. Instead, the molecules should have a nonnegligible tendency to associate and even align in solution. This situation is illustrated in Chart 1. In addition, there is the observation by Norton that metal hydrides should have an unusually good ability to fill vacant coordination sites.[2c] Taken together, these issues provide a working hypothesis in order to explain the significantly higher efficiency of $HMn(CO)_5$ over H_2 in the hydrogenolysis of the acyl−rhodium bond.

Initial Reaction Times and Precatalytic Steps. The observation of $RCORh(CO)_4$ formation upon addition of $HMn(CO)_5$ to $Rh_4(CO)_{12}$/alkene in the absence of added hydrogen suggests that two precatalytic mechanisms can be modeled. In the present $Rh_4(CO)_{12}/HMn(CO)_5$ bimetallic system, a two-term equation providing a good fit was again obtained from the 21 experiments at 289.7 K:

$$d[RCORh(CO)_4]/dt = k_1'[Rh_4(CO)_{12}][CO]^2[H_2] + k_2'[Rh_4(CO)_{12}][CO]^2[HMn(CO)_5] \quad (6)$$

The first term is that which was previously shown to arise in simple monometallic rhodium hydroformylations as well as during the $Rh_4(CO)_{12}/HMn(CO)_5$/33DMB hydroformylations.[10] The common factor $[Rh_4(CO)_{12}][CO]^2$ suggests a rate-limiting step involving the pre-equilibrated open polyhedral intermediate $\{Rh_4(CO)_{14}\}$. Kinetic evidence for open polyhedral clusters as intermediates in cluster fragmentation reactions is available.[22] The second term, which was also observed in the previous $Rh_4(CO)_{12}/HMn(CO)_5$/33DMB[10] study, dominates under manganese concentrations far lower than the dissolved hydrogen concentrations. Thus, the pronounced and accelerated rate of cluster fragmentation in the presence of $HMn(CO)_5$ is due to its efficient attack on $\{Rh_4(CO)_{14}\}$.

Redistribution of manganese carbonyl complexes also occurs at initial reaction times. In the particular experiments shown in Figure 3, the $HMn(CO)_5$ concentrations generally decrease from their nonzero initial values. However, the $HMn(CO)_5$ concentration never reached zero in any of the 6 h hydroformylations. This was also observed in the previous $Rh_4(CO)_{12}/HMn(CO)_5$/33DMB study.[10] Redistribution of $Mn_2(CO)_{10}$ and $HMn(CO)_5$ in the bimetallic system may occur due to hydrogen activation on $Mn_2(CO)_{10}$ and reaction of $HMn(CO)_5$ with the trace impurities in the 300 mL reaction autoclave solution. The manganese hydride is well-known to be acutely sensitive to trace moisture and oxygen. The redistribution of $Mn_2(CO)_{10}$ and $HMn(CO)_5$ may also occur due to other reactions involving rhodium complexes, manganese complexes, and mixed rhodium−manganese species.

Conclusions

Detailed, in situ spectroscopic and kinetic measurements have been performed for the homogeneous rhodium- and manganese-catalyzed hydroformylation of cyclopentene. A series of well-defined experiments were conducted to search for bimetallic catalytic binuclear elimination. The addition of manganese carbonyl hydride to the unmodified rhodium-catalyzed hydroformylation of cyclopentene leads to a significant increase in system activity. Regression of the kinetic data strongly suggests that there is a statistically significant contribution to aldehyde formation from the bimetallic catalytic binuclear elimination of manganese hydride complexes with acyl rhodium tetracarbonyl. As secondary effects, it was observed that manganese carbonyl hydride promotes the precatalytic transformation of rhodium precursor to acyl−rhodium. The present results are consistent with observations and conclusions reached for a previously studied $Rh_4(CO)_{12}/HMn(CO)_5$/3,3-dimethylbut-1-ene hydroformylation system. This study represents a second well-defined example of bimetallic catalytic binuclear elimination.

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[22] Bor, G.; Dietler, U. K.; Pino, P.; Poe, A. *J. Organomet. Chem.* **1978**, *154*, 301−315.