The Rh$_4$(CO)$_{12}$-Catalyzed Hydroformylation of 3,3-Dimethylbut-1-ene Promoted with HMn(CO)$_5$. Bimetallic Catalytic Binuclear Elimination as an Origin for Synergism in Homogeneous Catalysis

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Abstract: The bimetallic origins of catalytic synergism were studied using unmodified rhodium and manganese carbonyls as catalyst precursors during the low-temperature hydroformylation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal in *n*-hexane solvent ($T \approx 298$ K, $P_{CO} = 1.0-4.0$ MPa, $P_{H_2} = 0.5-2.0$ MPa). A dramatic increase in the catalytic rate was observed in the experiments conducted when both metals were used simultaneously. Detailed in-situ FTIR measurements indicated the observable presence of only homometallic complexes during catalysis, e.g., RCORh(CO)$_4$, Rh$_4$(CO)$_{12}$, Rh$_6$(CO)$_{16}$, HMn(CO)$_5$, and Mn$_2$(CO)$_{10}$. The kinetics of product formation show a distinct linear-bilinear form in observables: k_1[RCORh(CO)$_4$][CO]$^{-1}$[H$_2$] + k_2[RCORh(CO)$_4$][HMn(CO)$_5$][CO]$^{-1.5}$. The first term represents the classic unicyclic rhodium catalysis, while the second indicates a hydride attack on an acyl species. These spectroscopic and kinetic results strongly suggest that the origin of synergism is the presence of bimetallic catalytic binuclear elimination and not cluster catalysis. This appears to be the first detailed evidence for such a catalytic mechanism, and its implications for selectivity and nonlinear catalytic activity are accordingly discussed.

Introduction

The combined application of more than one metal, leading to regio-, chemo-, and stereoselectivities and/or activities that differ significantly from a strictly additive effect, is often referred to as "synergism".[1,2] The observation of synergism in homogeneous catalysis is not entirely uncommon. However, due to the rather widespread lack of detailed in-situ experimental studies, the potentially diverse phenomenological origins of synergism remain to a considerable extent unproven. A leading candidate has been "cluster catalysis", a term coined by Muetterties.[3,4] In a synergetic context, the anomalous observations of activity and/or selectivity arise from the presence of dinuclear or polynuclear species possessing two or more metallic elements. Thus the catalytic system involves a closed sequence of elementary reactions where each intermediate has one and the same nuclearity. The unicyclic sequence of reactions, involving dinuclear or polynuclear organometallic intermediates, affects the overall organic transformation of reactants to products. Synergism arising from cluster catalysis has been invoked repeatedly to rationalize observations in bi- or multi-metallic homogeneous catalysis.[5] It is convenient to regard such

synergism via cluster catalysis as a *structural basis* for the anomalous observations.

Simple associative, dissociative, and interchange reactions play a significant role in mechanistic organometallic chemistry,[6] and much of this understanding has developed from the study of reactions between ligands and complexes. However, reactions between complexes, particularly mononuclear complexes, are also known. In this regard, the reactions between mononuclear complexes, leading to the coupling of two ligands, the formation of a dinuclear complex, and simultaneous elimination of an organic product is particularly interesting.[7] The first example of such a reaction was apparently observed by Heck and Breslow,[8] and the name "binuclear elimination reaction" has become associated with such mechanisms.

$$HCo(CO)_4 + RCOCo(CO)_4 \rightarrow RCHO + Co_2(CO)_8 \quad (1)$$
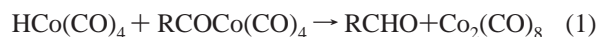
About 20 well-defined binuclear elimination reactions between mononuclear complexes are presently known. Some of these occur between complexes possessing different metallic elements.[9-15] The latter reactions produce organic products

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ranging from molecular hydrogen, to methane, and even aldehydes. All the above-mentioned reactions between mononuclear complexes are *stoichiometric*; thus 1 equiv of product is formed.

The possible existence of *catalytic* binuclear elimination reactions (CBER) is particularly exciting. In such systems, a mechanism would exist whereby the dinuclear complex further reacts with additional reactants to give the original mononuclear complexes, and binuclear elimination reoccurs. This repeated product formation and dinuclear complex degradation in the presence of excess organic reactants makes the system catalytic. The active system in a catalytic binuclear elimination reaction would consist of a nontrivial reaction topology which simultaneously possesses both mononuclear and dinuclear organometallic intermediates. If two metallic elements are present, then the physical system would involve two sets of distinct mononuclear species and one set of bimetallic dinuclear complexes. The bimetallic catalytic binuclear elimination reaction would constitute a well-defined *reaction topological basis* for synergism.[16]

The most convincing evidence to date for such a phenomenolgical basis for catalytic synergism appears to come from the Russian group of Beletskaya. They were able to show that lanthanum hydrides react in a stoichiometric manner with acyl cobalt tetracarbonyls to give aldehyde.[17] They were also able to show that catalytic production of aldehydes, well beyond that achievable from simple cobalt catalysis, can occur in the presence of excess alkene, hydrogen, and carbon monoxide when lanthanum hydrides and cobalt carbonyl are added together.[18] However, in-situ spectroscopic and kinetic information was not available. In addition, there exist a few known and/or anticipated complicating factors related to the interpretation of the results, most notably the tendency for monomeric lanthanium hydride cyclopentadienyl complexes to dimerize and form dinuclear lanthanium complexes[19] and the omnipresence of cobalt hydride tetracarbonyl under hydroformylation conditions.[20−23]

As a point of contrast and in the interest of completeness, the I/Ru/Ir system for the carbonylation of methanol to acetic acid should be mentioned.[24] In this process, mononuclear ruthenium carbonyl, mononuclear iridium carbonyl, and bimetallic ruthenium−iridium carbonyl complexes are simultaneously present and responsible for the observed activity of the system. Detailed in-situ spectroscopic studies have convincingly

revealed that the role of ruthenium is to promote the abstraction of iodine from iridium, and it is not involved in any product elimination step.[25,26] Such a bimetallic synergism arising from promotion of a ligand exchange/abstraction is fundamentally different from the mechanism underlying the activity of a bimetallic CBER.

In the present contribution, we present in-situ spectroscopic and kinetic experimental evidence for the existence of the bimetallic catalytic binuclear elimination reaction in a well-defined system at ca. 298 K. The overall organic reaction is the hydroformylation of 3,3-dimethylbut-1-ene with molecular hydrogen and carbon monoxide. The reaction is very regioselective, yielding the aldehyde 4,4-dimethylpentanal in more than 95% selectivity. The catalytic system is initiated with the use of $Rh_4(CO)_{12}$ and $Mn_2(CO)_{10}/HMn(CO)_5$ as co-precursors. Rhodium is by far the most active metal for the homogeneous-catalyzed hydroformylation of alkenes.[27] Both homoleptic carbonyl clusters and phosphine complexes are extensively used. The unmodified system was discovered in the early 1950s[28] and the subject of considerable study.[29] Catalytic hydroformylation is one of the largest volume homogeneous processes.[30]

Results

Spectroscopic Aspects. The in-situ spectroscopic data were subjected to band-target entropy minimization (BTEM),[31−33] an advanced and totally blind deconvolution technique based on Shannon entropy criteria.[34] Although it was possible to account for more than 98.4% of the total integrated signal arising from the 21 experiments represented here, only five organometallic spectra could be found. These pure component spectra corresponded to (a) $RCORh(CO)_4$, (b) $Rh_4(CO)_{12}$, (c) $Rh_6(CO)_{16}$, (d) $HMn(CO)_5$, and (e) $Mn_2(CO)_{10}$. Their average concentrations, from the entire experimental study, were ca. 70, 11, 1.5, 16, and 95×10^{-6} mole fraction, respectively.

Notable vectors from the singular value decomposition of the matrix $A_{713 \times 2951}$ are shown in Figure 1, and the recovered pure component organometallic spectra obtained from the BTEM analysis are shown in Figure 2. From a spectroscopic/observable viewpoint, the reactive system is very well defined. The signal-to-noise level is very high. Although BTEM has been previously and successfully used to recover unknown pure component spectra, with less than 0.07% of the total signal intensity, no further observable species could be identified in the present experimental study.

Hydroformylation of 33DMB with only $Mn_2(CO)_{10}/HMn(CO)_5$. In stark contrast to rhodium, manganese is nearly

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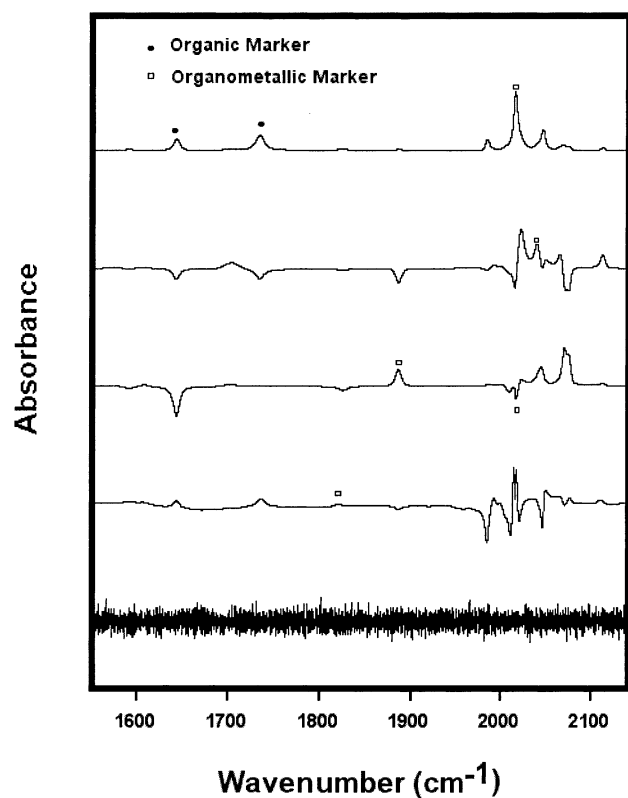(34) Shannon, C. E. *Bell Syst. Technol. J.* **1948**, *27*, 379−423.

Figure 1. Singular value decomposition of the preconditioned in-situ spectroscopic data showing the 1st, 4th, 5th, and 7th significant vectors and the 713th vector. The marked extrema are those that were used to recover the organometallic pure component spectra as well as alkene and aldehyde by BTEM. Atmospheric moisture and CO_2, hexane, and dissolved CO were removed from the experimental data during preconditioning.
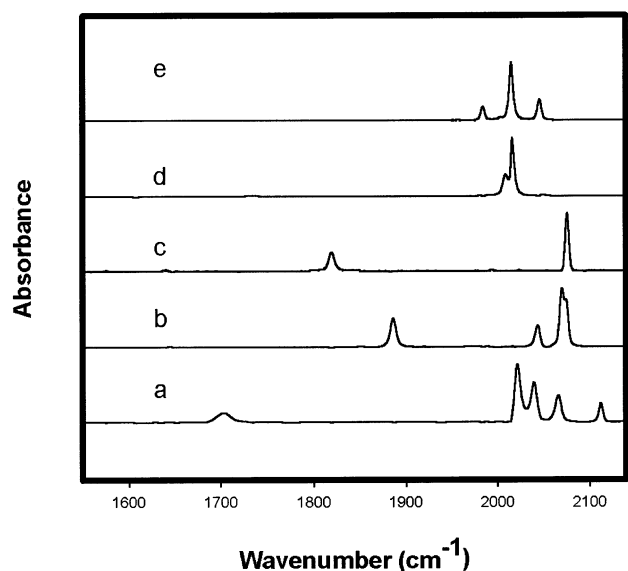

Figure 2. Recovered pure component spectra of the organometallic species using BTEM: (a) $RCORh(CO)_4$, (b) $Rh_4(CO)_{12}$, (c) $Rh_6(CO)_{16}$, (d) $HMn(CO)_5$, and (e) $Mn_2(CO)_{10}$.

inert toward transformations of alkenes. In particular, neither $Mn_2(CO)_{10}$ nor $HMn(CO)_5$ shows reactivity toward alkenes at ambient conditions. In addition, manganese is essentially inert toward the hydroformylation reaction, although one reference exists to support minimal activity at the severe conditions of ca. 500 K and hundreds of bar total pressure.[35]
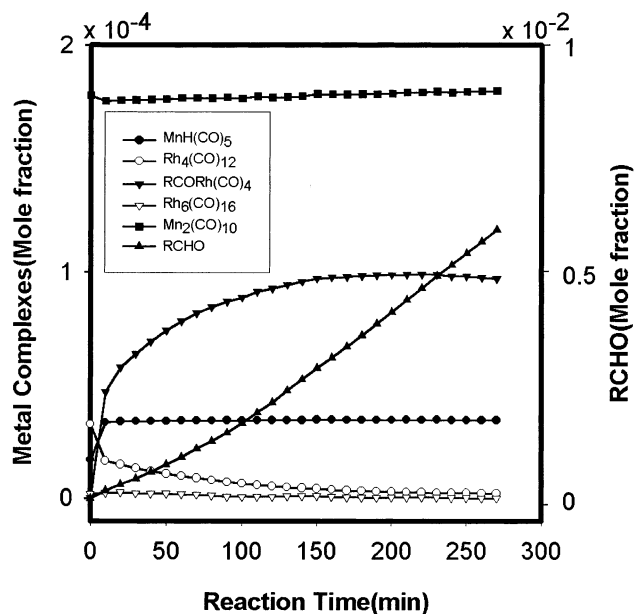
Figure 3. Representative example of the concentration profiles of the organometallic species and the product aldehyde. This experiment was performed with 300 mL of *n*-hexane at 298 K with 2.0 MPa CO and 1.0 MPa H_2. The initial conditions of the remaining reagents were 5.0 mL of 3,3-dimethylbut-1-ene, 54.1 mg of $Rh_4(CO)_{12}$, and 210.0 mg of $Mn_2(CO)_{10}$.

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 CO, 1.0 MPa H_2, 298 K).

Hydroformylation of 33DMB with $Rh_4(CO)_{12}$ and $HMn(CO)_5$. 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 declined in all experiments and the concentration of $RCORh(CO)_4$ monotonically increased in all experiments. The asymptotic mass balance limits were reached within ca. 5 h. The concentrations of $HMn(CO)_5$ and $Mn_2(CO)_{10}$ also monotonically changed, but the direction depended on the experimental conditions used. The concentrations of $HMn(CO)_5$ never approached zero in any 5 h experiment. Production of aldehyde could be identified within the first few minutes. A representative example of the concentration profiles of the organometallic species and the product aldehyde are shown in Figure 3. It should be noted that even under reaction conditions of ca. 4.0 MPa, the spectroscopic measurements of concentration are exceptionally accurate: very low fluctuation between sequential measurements can be observed, even at these low concentrations. Net loss of organometallic complexes during reaction was negligible. The mass balances over the soluble rhodium and manganese remained constant.

Effects of $HMn(CO)_5/Mn_2(CO)_{10}$. The initial concentration of the precursor $HMn(CO)_5$ was systematically varied in five hydroformylations. Five kinetic experiments were performed at 298 K, 2.0 MPa CO, and 1.0 MPa H_2 to investigate the effect of $HMn(CO)_5$ on the unmodified rhodium-catalyzed hydroformylation. The initial loadings of $Mn_2(CO)_{10}$ were 0, 50.8,

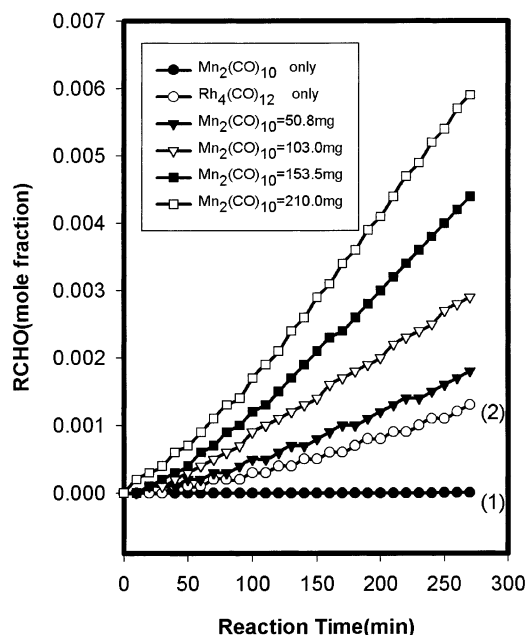(35) Weil, T. A.; Metlin, S.; Wender, I. *J. Organomet. Chem.* **1973**, *49* (1), 227−232.

Figure 4. Effect of manganese loading on the hydroformylation reaction rate. The monometallic base case experiments were (1) 0.0 mg of $Rh_4(CO)_{12}$ and 105.0 mg of $Mn_2(CO)_{10}$ and (2) 49.0 mg of $Rh_4(CO)_{12}$ and 0.0 mg of $Mn_2(CO)_{10}$. The remaining bimetallic experiments had initial conditions 51.0−55.5 mg of $Rh_4(CO)_{12}$ and 50.8−210.0 mg of $Mn_2(CO)_{10}$. These experiments were performed with 300 mL of *n*-hexane at 298 K with 5.0 mL of 3,3-dimethylbut-1-ene, 2.0 MPa CO and 1.0 MPa H_2.

103.0, 153.5, and 210.0 mg. Accordingly, after UV irradiation the initial reactor concentrations of $HMn(CO)_5$ in mole fraction were $X_{HMn(CO)5} = 0, 3 \times 10^{-7}, 2.5 \times 10^{-5}, 3.0 \times 10^{-5}$, and 3.3×10^{-5}, respectively.

A very significant increase in aldehyde formation was observed in the experiments when both rhodium carbonyl and manganese carbonyl complexes were used simultaneously. Rates of hydroformylation as great as 500% that which would be anticipated from the rhodium loading alone were observed. A stark visual impression of the effect of manganese on the hydroformylation reaction is shown in Figure 4. Increased concentrations of $HMn(CO)_5$ lead to increased hydroformylation rates. Indeed the final conversions of 33DMB after 280 min were 9.55%, 12.1%, 19.4%, 26.4%, and 31.6% in the experiments starting with $X_{HMn(CO)5}$ of $0, 3 \times 10^{-7}, 2.5 \times 10^{-5}, 3.0 \times 10^{-5}$, and 3.3×10^{-5}, respectively. The turnover frequencies (TOF) based on rhodium and defined in the Experimental Section were $0.079 \pm 0.016, 0.076 \pm 0.016, 0.131 \pm 0.036, 0.198 \pm 0.038$, and 0.206 ± 0.044 min^{-1}, respectively. The monometallic rhodium TOF value obtained in this study is consistent with our previous studies.[36,37] The TOF values provide clear-cut quantitative confirmation that the bimetallic system with $HMn(CO)_5$ and $Rh_4(CO)_{12}$ is very active for the hydroformylation of 33DMB.

Catalysis and Kinetics. Twenty-one kinetic experiments in six subseries were performed for the kinetic studies. In each set, one experimental parameter was systematically varied, while the remaining variables were held essentially constant. The complete experimental design is documented in the Experimental Section.

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The aldehyde product formation was modeled in terms of the instantaneous mole fractions of all observable species. The temperature and pressure dependence of hydrogen solubility in *n*-hexane was fully taken into account in all calculations.[38]

Hydroformylation of 3,3-dimethylbut-1-ene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures.[36] Detailed in-situ FTIR spectroscopic studies have shown the presence of only four observable organometallics, namely, the known species $RCORh(CO)_4$,[39] $Rh_2(CO)_8$,[40] $Rh_4(CO)_{12}$,[41] and $Rh_6(CO)_{16}$,[42] where the latter normally exists at the ppm or sub-ppm level under most catalytic conditions. No evidence for observable quantities of the known rhodium hydride species[33,43,44] could be obtained in the presence of the very reactive organic reagent 3,3-dimethylbut-1-ene. Analysis of the spectroscopic measurements provides very clean kinetics, where the rate of aldehyde formation is

$$r = k[RCORh(CO)_4][CO]^{-1}[H_2][alkene]^0 \qquad (2)$$

The rate expression is consistent with the equilibrium generation of a coordinatively unsaturated intermediate $RCORh(CO)_3$ followed by the subsequent activation of molecular hydrogen. The kinetics supports the widely accepted unicyclic catalytic reaction mechanism where all intermediates are mononuclear.[45] The reactions and kinetics are very reproducible. 3,3-Dimethylbut-1-ene has been used in other hydroformylation experiments starting with different unmodified rhodium carbonyl complexes, and similar turnover frequencies have been observed.[36] Detailed kinetic studies using cyclohexene and styrene as substrate have also shown a functional form of $[RCORh(CO)_4][CO]^{-1}[H_2][alkene]^0$ during the rhodium-catalyzed hydroformylation.[38,46]

In principle, the bimolecular reaction of $[RCORh(CO)_3]$ with molecular hydrogen is not the only mechanism available for the hydrogenolysis of $RCORh(CO)_4$. In addition, there is the possibility that some aldehyde formation occurs via a bimolecular elimination reaction.

Under the present experimental conditions, there may exist several active species, which could be involved in the product formation. These active species are $RCORh(CO)_3$, $RCORh(CO)_4$, $HMn(CO)_4$, and $HMn(CO)_5$. The two most probable binuclear reactions that could be involved in the product formation are listed below.

$$HMn(CO)_4 + RCORh(CO)_3 \rightarrow RCHO + RhMn(CO)_7 \quad (3)$$

$$HMn(CO)_5 + RCORh(CO)_3 \rightarrow RCHO + RhMn(CO)_8 \quad (4)$$
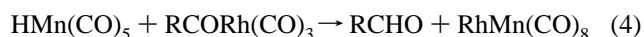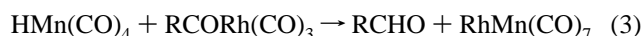
Substituting for the pseudo-equilibrium concentration of $HMn(CO)_x$ in terms of $HMn(CO)_5$ and $RCORh(CO)_y$ in terms of $RCORh(CO)_4$, the corresponding formation rates of aldehyde

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by CBER are expressed as follows.

$$r = k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^{-1} \quad (5)$$

$$r = k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^{-2} \quad (6)$$

The reaction rate with the unicyclic hydroformylation mechanism is well documented. Assuming that both unicyclic hydroformylation and CBER hydroformylation occur simultaneously and the two mechanisms are independent, the overall product formation rate can be written as eq 7.

$$r_{\text{Total}} = k_1[\text{RCORh(CO)}_4][\text{H}_2][\text{CO}]^{-1} + \\ k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^x \quad (7)$$

With respect to the catalysis or product formation, the above two-term linear-bilinear form in organometallic species provided an excellent fit for the observable kinetics of the aldehyde formation. About 700 sets of mole fraction data were used in the regression (see Computational Section). The activity of the system (rate of product formation) did not correlate with the presence of any other observables. In most experiments, the second term was significantly larger than the first, and the contributions of these two terms at the reference reaction conditions of this experimental study were ca. 1:1.

The numerical values of the rate constants were $k_1 = 0.446 \pm 0.018$ and $k_2 = 44.5 \pm 14$ min^{-1} at 298 K, and the exponent was $x = -1.5 \pm 0.1$. The rate constant k_1 is consistent with our previous studies.[36,37] The first term corresponds to a turnover frequency of ca. 0.11 min^{-1} at the mean conditions, again consistent with our previous studies. Rearrangement of the two terms leads to the conclusion that HMn(CO)$_5$ is ca. 170 times more efficient than H$_2$, for the hydrogenolysis of the acyl–rhodium bond, on a mole-to-mole basis. The exponent $x = -1.5 \pm 0.1$ suggests that coordinative unsaturation may occur in both metal carbonyl complexes.

Discussion

Evidence for Existence of CBER. The kinetic results strongly suggest the simultaneous existence of a unicyclic catalytic topology and at least one bimetallic catalytic elimination reaction. The unicyclic catalysis occurs exclusively on mononuclear rhodium intermediates, and the bimetallic CBER occurs on a set of rhodium, manganese, and rhodium–manganese intermediates.

RCORh(CO)$_4$ has repeatedly been 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 an acyl complex RCORh(CO)$_3$ is the rate-limiting step in the unicyclic rhodium catalysis, and attack of (a) HMn(CO)$_5$ on RCORh(CO)$_3$ and (b) HMn(CO)$_4$ on RCORh(CO)$_3$ are the rate-limiting steps in the bimetallic CBER. The exponent $x = -1.5 \pm 0.1$ arises from this later competing situation.

The attack of HMn(CO)$_5$ on RCORh(CO)$_3$ or HMn(CO)$_4$ on RCORh(CO)$_3$ with elimination of aldehyde implies the existence of a transient bimetallic rhodium manganese dinuclear complex with probable stoichiometry RhMn(CO)$_8$ (or possibly RhMn(CO)$_7$). The fact that such a species (or its coordinatively saturated analogue) was unobservable in these experiments

attests 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,[47] is known to occur exceptionally rapidly, even at low temperatures, on heterometallic dinuclear carbonyl complexes, where CoRh(CO)$_7$ is perhaps the best example.[48]

The proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh–Mn CBER hydroformylation reactions is shown in Scheme 1. All intermolecular transformations in the unicyclic topology are first-order in the 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 that 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$_2$RhMn(CO)$_8$. The β step is the binuclear elimination step. The steps $-\alpha$ and β are bimolecular in metal complexes. The binuclear elimination step has been drawn as if the process proceeds through a concerted four-center transition state for convenience. This *is not a crucial assumption* for the existence of the bimetallic CBER. If the elimination does not proceed through a four-center transition state, but instead through two or more simple transition states, additional intermediates exist on the reaction pathway.

Concerning other details in Scheme 1, the stereochemistry of the intermediates or even the multiplicity of intermediates with different geometries are not the emphasis of this diagram. Accordingly, we have assumed the most common geometry for five-coordinate rhodium structures, namely, axially substituted trigonal bipyramid geometries.

The interconnected topology of a unicyclic mechanism and a CBER mechanism as shown in Scheme 1 gives rise to the complex linear-bilinear form of the observed kinetics of product formation.

Initial Reaction Times and Precatalytic Steps. In the classic unmodified rhodium-catalyzed reaction, the catalyst precursor Rh$_4$(CO)$_{12}$ decomposes in the presence of the organic reactants to give the observable intermediate RCORh(CO)$_4$ in a highly reproducible fashion with first-order kinetics for the cluster.[36–38] 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 very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occur. The half-life for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system is ca. 10 min, whereas a half-life under similar reaction conditions for pure Rh systems is ca. 2 h.[36,37] 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)$_{12}$. Mononuclear hydride attack and subsequent opening of metal clusters is well documented in the literature.[49] In the present case, and in the presence of numerous organic

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

reactants, a sequence of steps leading to the rapid formation of $RCORh(CO)_4$ results.

With respect to the acyl formation, the following two-term equation provided a good fit for the observable kinetics of the acyl formation. The numerical values of the rate constants were $k_1' = (7.02 \pm 0.7) \times 10^1$ min^{-1} and $k_2' = (1.53 \pm 0.4) \times 10^5$ min^{-1} at 298 K. The rate constant k_1' is consistent with our previous studies.[36,37]

$$d[RCORh(CO)_4]/dt = k_1'[Rh_4(CO)_{12}][CO]^2[H_2] +$$
$$k_2'[Rh_4(CO)_{12}][CO]^2[HMn(CO)_5] \quad (8)$$

The functional form used for the first term is that which was previously shown to arise in simple monometallic rhodium hydroformylations. Different integer values of the exponent for CO in the second term were tested, but an exponent equal to two gave the best results. The common factor $[Rh_4(CO)_{12}][CO]^2$ suggests a rate-limiting step involving a preequilibrated open polyhedron intermediate $\{Rh_4(CO)_{14}\}$. Kinetic evidence for open polyhedron clusters as intermediates in cluster fragmentation reactions is readily available.[50] The second term dominates under manganese concentrations far lower than the dissolved hydrogen concentrations. In conclusion, it appears that the pronounced and accelerated rate of cluster fragmentation in the presence of $HMn(CO)_5$ is due to its efficient attack on $\{Rh_4(CO)_{14}\}$.

In addition, redistribution of manganese carbonyl complexes also occurs at initial reaction times. In the particular experiment shown in Figure 3, the $Mn_2(CO)_{10}$ concentration declines

somewhat from its initial value at $t = 0$ and the $HMn(CO)_5$ concentration increases from its nonzero initial value. The manganese carbonyl concentrations then remain essentially constant for the remainder of the experiment. Redistribution will occur for many reasons, including hydrogen activation on $Mn_2(CO)_{10}$, reaction of $HMn(CO)_5$ with the trace impurities (note that the hydride is extremely sensitive to trace moisture and/or oxygen) in the ca. 300 mL reaction autoclave solution, and reactions involving rhodium complexes, manganese complexes, and mixed rhodium−manganese species.

Deactivation. Loss of catalytic activity as a function of reaction time is frequently observed in homogeneous catalysis, and the unmodified rhodium-catalyzed hydroformylation reaction is no exception. The typical mechanism for deactivation is clusterification to the more thermodynamically stable $Rh_6(CO)_{16}$.[51] This becomes accelerated as the concentration of substrate declines. Although the omnipresence of $Rh_6(CO)_{16}$ during active hydroformylations has been repeatedly observed by this group, its decline as a function of time during $Rh_4(CO)_{12}$-initiated syntheses is unusual. The present mixed Rh−Mn hydroformylation (i.e., Figure 3) exhibits a steady decline in $Rh_6(CO)_{16}$ despite declining substrate concentrations. Undoubtedly, this retardation of the deactivation phenomenon is again associated with hydride attack. $HMn(CO)_5$-facilitated cluster degradation of $Rh_6(CO)_{16}$ is consistent with the chemistries involved.

Implications for Future Catalytic Syntheses. The confirmation of bimetallic CBER impacts four important areas, namely, (1) a new well-grounded phenomenological basis for synergism,

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(2) alternative synthetic metal-mediated strategies, (3) nonlinear catalytic kinetics and higher efficiency (TOF), and (4) chemical selectivity.

The first area refers to bimetallic catalytic binuclear elimination as the only viable explanation for the observed synergism in the Rh−Mn hydroformylation system. The in-situ spectroscopy and kinetic determinations are inconsistent with cluster catalysis.

The second area refers to the two synthetic metal-mediated strategies, namely, stoichiometric use of metal reagents and transition metal homogeneous catalysis. Until now, the implicit working assumption for almost all homogeneous catalysis was its unicyclic topology. Synthetic chemists therefore usually consider variations on the metal used or ligand modifications to elicit the desired activity and/or selectivity patterns. Conclusive evidence for bimetallic CBER now significantly alters the implicit working assumption. A rationale for an entirely new direction in homogeneous catalysis arises since a plethora of $M^1L^1_y$ and $M^2L^2_z$ combinations are conceivable.

The third area refers to the turnover frequency (rate/[RCORh-$(CO)_4]_t$) of 0.11 min^{-1} in the rhodium-catalyzed system at the reference conditions and a turnover frequency of ca. 0.3 min^{-1} for the rhodium-catalyzed system spiked with ca. 1 equiv of manganese at the reference conditions. Unicyclic catalytic reactions possess a fixed turnover frequency at fixed organic concentrations (and constant T and P). The present bimetallic CBER has a turnover frequency that varies with the concentration of the second metal. Accordingly, the present bimetallic CBER is an example of intrinsic nonlinear catalytic kinetics. In the present case, the addition of a cheap second metal dramatically increases the utility of the expensive precious metal. The moles product achieved per mole rhodium per second is greatly enhanced.

A qualifier is required regarding the nonlinear kinetic effects in bimetallic CBERs; they are local effects and not global. The kinetic polynomial for a two-metal CBER has three limiting solutions, namely, regions where product formation is either linear in the first or second metal, and a third solution where product formation is proportional to the product of the two metals.[52] The observable kinetics of the present Rh−Mn CBER are defined by the latter. In the limits as Rh/Mn → ∞ or Mn/Rh → ∞, the kinetics would become first-order in one or the other metal. Of course, this multiplicity of mathematical solutions gives rise to an unsettling question, namely, is a bimetallic CBER catalytic system kinetically stable in time? Indeed, unicyclic homogeneous catalytic systems are intrinsically stable since they are first-order reaction networks in intermediates (CSTRs are the model configurations for this thought experiment). Accordingly, we have applied the Feinberg deficiency theorems[53] to generalized bimetallic CBER topologies and numerous permutations in Scheme 1.[54] These considerations suggest that bimetallic CBERs can be expected to be kinetically stable in time, hence useful synthetic tools.

Finally, the fourth and last area is chemical selectivity. Since all CBERs possess an elementary step involving the reaction between two mononuclear complexes, at least one elementary reaction step exists that requires an unusually large negative entropy of activation. This situation arises due to the bimolecular reaction between two structurally complex high molecular weight reactants. A large negative entropy of activation implies that a high degree of transition state order is required, and this leads immediately to issues of alternate reaction pathways and selectivity. If a regio-, chemo-, or stereodifferentiating situation can arise in a singular bimolecular context (isolated CBER), or its combinations (multiple simultaneous CBERs), then selectivity patterns can change. The most exciting prospect in this context is stereocontrol, particularly when either one or both metals can be chirally modified. Thus the combinations M^1L^{1*} & M^2L^2, M^1L^1 & M^2L^{2*}, and M^1L^{1*} & M^2L^{2*} represent some obvious permutations of chiral modification L* in a two-metal system. The organization in the respective transition states can be expected to vary greatly.

Other Rh−Mn Systems. Briefly we wish to note that the synergistic effects observed with $Rh_4(CO)_{12}$ and $HMn(CO)_5$ under hydroformylation conditions are not restricted to the use of 3,3-dimethylbut-1-ene alone. Preliminary experiments with other substrates, notably cyclopentene and styrene, indicate significant rate increases as well. Detailed studies with these substrates are in progress.

Conclusions

The addition of manganese carbonyl hydride to the unmodified rhodium-catalyzed hydroformylation of 3,3-dimethylbut-1-ene leads to a significant increase in system activity. Detailed in situ spectroscopic information indicates that this increase in the rate of product formation is due to the existence of bimetallic catalytic binuclear elimination. As secondary effects, manganese carbonyl hydride leads to a reduction in the induction period (promotes the precatalytic transformation of rhodium precursor to rhodium intermediates) and retards or even reverses deactivation due to cluster formation. The existence of bimetallic CBER leads to a number of rather important synthetic opportunities. These opportunities include a rationale for higher order catalysis and novel mechanistic avenues for the control of selectivity. From a reaction engineering/systems viewpoint, bimetallic CBERs appear to be viable synthetic methods since the topologies lead to stable kinetics in time.

Experimental Section

General Information. All solution preparations and transfers were carried out under purified argon (99.9995%, Saxol, Singapore) atmosphere using standard Schlenk techniques.[55] The argon was further purified before use by passing it through a deoxy and zeolite column. 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.

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HMn(CO)$_5$ was prepared using a modified literature preparation.[56] The Puriss 3,3-dimethylbut-1-ene (33DMB) was purchased from Fluka. The quoted purity is better than 99% and was used as obtained. 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. In-situ kinetic studies were performed in a 1.5 L stainless steel (SS316) autoclave (P_{max} = 22.5 MPa, Buchi-Uster, Swizerland) which was connected with a high-pressure infrared cell. The system was the same as that used previously.[38] The autoclave was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (autoclave Engineers, Erie, PA) and has a mantle for heating/cooling. The liquid-phase reaction mixture was circulated from the autoclave and to-and-fro the high-pressure IR cell with a high membrane pump (Model DMK 30, Orlita AG, Geissen, Germany) with a maximum rating of 32.5 MPa and a 3 L/h flow rate via jacketed 1/8 in. (SS316) high-pressure tubing (Autoclave Engineers).

A Polyscience cryostat Model 9505 was used to keep the entire system, autoclave, transfer lines, and infrared cell isothermal ($\Delta T \leq$ 0.5 °C) for the range 293–308 K. Temperatures were measured at the cryostat and autoclave with PT-100 thermoresisters. The necessary connections to vacuum and gases were made with 1/4 in. (SS316) high-pressure tubing (Autoclave Engineers), and 1.0, 5.0, and 10.0 piezo-crystals were used for pressure measurements (Keller AG Winter, Switzerland). The entire system was gastight under vacuum as well as at 20.0 MPa.

The high-pressure infrared cell was constructed at ETH-Zurich using SS316 steel and could be heated and cooled. The 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 the necessary sealing, and Teflon spacers were used between the windows.[57] This high-pressure infrared cell was situated in a Perkin-Elmer SPECTRUM 2000 FT-IR spectrometer. The spectral resolution was 4 cm^{-1} at an interval of 0.2 cm^{-1} for the range 1000–2500 cm^{-1} in this study. A schematic diagram of the experimental setup can be found in ref 38.

In Situ Spectroscopic and Kinetic Studies. All the experiments were performed in a similar manner. First, single beam background spectra of the IR sample chamber were recorded. Then 150 mL of *n*-hexane was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, infrared spectra of the *n*-hexane in the high-pressure cell were recorded. The total system pressure was raised to 2.0 MPa CO, and the stirrer and high-pressure membrane pump were started. After equilibration, infrared spectra of the CO/*n*-hexane solution in the high-pressure cell were recorded. A solution of 5 mL of 3,3-dimethylbut-1-ene (33DMB) dissolved in 50 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. After equilibration, infrared spectra of the 33DMB/CO/*n*-hexane solution in the high-pressure cell were recorded. A solution of 50 mg of Rh$_4$(CO)$_{12}$ dissolved in 50 mL of *n*-hexane and a solution of 100 mg of Mn$_2$(CO)$_{10}$/HMn(CO)$_5$ were prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. After equilibration, infrared spectra of the Rh$_4$(CO)$_{12}$/Mn/33DMB/CO/*n*-hexane solution in the high-pressure cell were recorded. Then 1.0 MPa hydrogen was added to initiate the syntheses. The detailed experimental design for this study is shown in Table 1.

Spectra were recorded at 10 min intervals in the range 1000–2500 cm^{-1}. In every 5 h experiment, ca. 30 spectra were taken. This resulted in 713 spectra and 713 sets of concentrations (eight species are tracked). The eight evaluated liquid-phase species were hexane, alkene, aldehyde, RCORh(CO)$_4$, Rh$_4$(CO)$_{12}$, Rh$_6$(CO)$_{16}$, HMn(CO)$_5$, and Mn$_2$(CO)$_{10}$. The rate of product formation was evaluated by a finite difference scheme.

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Table 1. Experiment Design

experiment	Mn$_2$(CO)$_{10}$, mg	CO, MPa	H$_2$, MPa	33DMB, mL	Rh$_4$(CO)$_{12}$, mg	temperature, K
standard	103.0	2.0	1.0	5	51.0	298
blank	0	2.0	1.0	5	0	298
pure Rh	0	2.0	1.0	5	51.6	298
pure Mn	105.0	2.0	1.0	5	0	298
CO variation	108.0	1.0	1.0	5	54.0	298
	107.0	3.0	1.0	5	53.5	298
	109.0	4.0	1.0	5	51.0	298
H$_2$ variation	105.6	2.0	0.5	5	50.7	298
	106.0	2.0	1.5	5	51.0	298
	104.4	2.0	2.0	5	55.0	298
33DMB variation	108.0	2.0	1.0	2	52.0	298
	105.0	2.0	1.0	10	52.0	298
Rh$_4$(CO)$_{12}$ variation	105.0	2.0	1.0	5	26.0	298
	107.3	2.0	1.0	5	76.8	298
	106.0	2.0	1.0	5	103.0	298
temperature variation	106.0	2.0	1.0	5	52.0	293
	108.0	2.0	1.0	5	51.0	303
	108.0	2.0	1.0	5	52.0	308
Mn$_2$(CO)$_{10}$ variation	50.8	2.0	1.0	5	52.2	298
	153.5	2.0	1.0	5	52.4	298
	210.0	2.0	1.0	5	54.1	298

The appropriateness of various finite difference schemes for the evaluation of in-situ homogeneous catalytic rate data and TOF evaluation has been carefully examined.[58] The rates of the product formation of 44DMP were calculated in terms of turnover frequency (TOF).

$$\text{TOF}_t = \frac{d[44DMP]_t/dt}{[RCORh(CO)_4]_t} \tag{9}$$

A 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.

To a reasonable first approximation, the 5 h experiments correspond to initial rate data since rhodium-catalyzed hydroformylations are almost zero-order in alkene and since the average conversion of alkene was ca. 20% (8–36%). Furthermore, and more importantly, less than 1% conversion of either H$_2$ or CO occurred in any experiment.

The experimental design of the experiments involved 300 mL of solvent and the intervals 293–308 K, P_{H2} = 0.5–2.0 MPa, P_{CO} = 1.5–4.0 MPa, initial alkene = 2–10 mL, initial Rh$_4$(CO)$_{12}$ = 25–100 mg, and initial Mn$_2$(CO)$_{10}$ = 50–200 mg. All hydroformylation experiments exhibited product formation rates belonging to infinitely slow reaction compared to gas–liquid mass transfer (category H of the Hatta classifications); hence no experiments were mass transfer controlled.[59] Blank experiments, in the presence of organic reactants but without added complexes, were performed throughout the study. The maximum rates of hydroformylation were less than 10^{-3} of the mean rate for the 21 experiments.

Computational Section

Since featureless baselines were observed in the wavenumber range from 2140 to 2500 cm^{-1}, all experimental spectroscopic data were truncated. The consolidated data gave rise to an absorbance matrix with the following size: rows = 713 vectors (spectra) and columns = 2951 channels (wavenumber range 1550–2140 cm^{-1} and data interval 0.2 cm^{-1}).

Before further spectral analysis, some spectral preprocessing was performed. First, each experimental solution spectrum was precondi-

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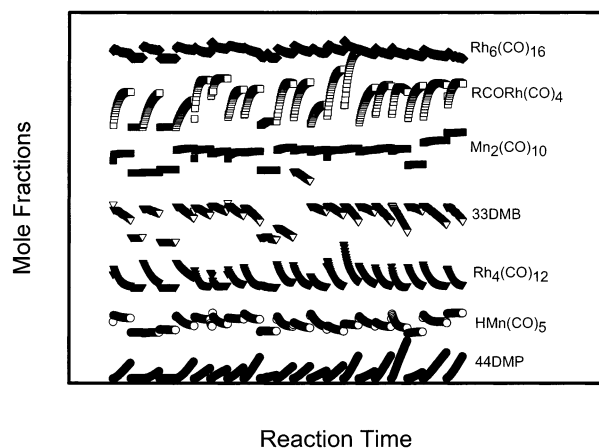
Figure 5. Concentration profiles for the 21 series of experiments.

tioned using entropy techniques[60,61] by subtraction of (i) the background reference, (ii) CaF$_2$ cell with *n*-hexane reference, and (iii) dissolved CO reference, and then automatic baseline correction was carried out by a polynomial fitting technique. The consolidated preconditioned spectra were then subjected to a data decomposition approach using singular value decomposition (SVD). The orthogonal basis vectors that spanned the subspace of observations were transformed into pure component spectral estimates using the band-target entropy minimization (BTEM) algorithm.[31–33] In all, seven pure component spectra were

identified by BTEM; alkene, aldehyde, RCORh(CO)$_4$, Rh$_4$(CO)$_{12}$, Rh$_6$-(CO)$_{16}$, HMn(CO)$_5$, and Mn$_2$(CO)$_{10}$.

Next, a dimensionless approach using an internal standard (hexane) was imposed on the preconditioned absorbance matrix A$_{713 \times 2951}$ to eliminate the data dependency on reaction volume and path length of cell. Based on estimates of pure component spectra obtained through BTEM and knowledge of the amount of reactants put inside the reactor, a reaction invariant model was set up in order to find the real magnitude of the pure component absorptivities. Finally, upon determination of the properly scaled pure absorptivities, the moles of alkene, aldehyde, RCORh(CO)$_4$, Rh$_4$(CO)$_{12}$, Rh$_6$(CO)$_{16}$, HMn(CO)$_5$, and Mn$_2$(CO)$_{10}$ for all experiments in the 21 time series could be obtained using a multiple linear regression/least-squares approach. The concentration profiles for the seven species in the 21 time series experiments are shown in Figure 5. The corresponding numerical values are provided as Supporting Information.

Discussion of the mathematical procedures used can be found in refs 31 and 32.

Supporting Information Available: Mole fractions for Rh−Mn-33DMB CBER. This material is available free of charge via the Internet at http://pubs.acs.org.

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