BIMETALLIC CATALYTIC BINUCLEAR ELIMINATION REACTION. EXPERIMENTAL, SPECTROSCOPIC AND KINETIC ELUCIDATION

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NATIONAL UNIVERSITY OF SINGAPORE

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BIMETALLIC CATALYTIC BINUCLEAR ELIMINATION REACTION. EXPERIMENTAL, SPECTROSCOPIC AND KINETIC ELUCIDATION

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SUMMARY

The observation of synergism during application of more than one metal in homogeneous catalysis is not entirely uncommon. However, due to the rather widespread lack of detailed in-situ experimental studies, the phenomenological origins of synergism have remained to a considerable extent unproven. Particularly, stoichiometric binuclear elimination between mononuclear complexes leading to the elimination of a new organic product and the formation of a dinuclear complex has been well documented. This rather rare reaction is reviewed as well as the concept of catalytic binuclear elimination reaction (CBER). Catalytic binuclear elimination is exceptionally interesting from both a synthetic as well as kinetic viewpoint and it would constitute a well-defined reaction topological basis for synergism. However, solid experimental (spectroscopic, mechanistic and kinetic) evidence for the existence of CBER has been rather weak until now.

In this dissertation, the bimetallic origins of catalytic synergism were studied using Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of 3,3-dimethylbut-1-ene(33DMB), Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of cyclopentene(CP), and Rh₄(CO)₁₂/HRe(CO)₅ catalyzed hydroformylation of cyclopentene at low temperatures. The in situ FTIR data were analysed using an advanced signal processing technique, i.e., total algebraic system identification, which was shown to be a rapid and effective methodology for spectroscopic system identification of reactive organometallic and homogeneous catalytic systems.

In the Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of 33DMB and Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of cyclopentene, a dramatic increase in both the catalytic rate and turn over frequency(TOF) 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, Rh₄(CO)₁₂, Rh₆(CO)₁₆, HMn(CO)₅ and Mn₂(CO)₁₀. The kinetics of product formation show a distinct linear-bilinear form in observables - k₁[RCORh(CO)₄][CO]⁻¹[H₂] + k₂[RCORh(CO)₄][HMn(CO)₅][CO]ˣ in both Rh/Mn/33DMB(x=-1.5) and Rh/Mn/Cyclopentene(x=-1.6) systems. The first term represents the classic unicyclic rhodium catalysis while the second indicates a hydride attack on an acyl species. In addition, the manganese hydride facilitated fragmentation of Rh₄(CO)₁₂ was found.

In the Rh₄(CO)₁₂/HRe(CO)₅ catalyzed hydroformylation of cyclopentene, a dramatic increase in both the catalytic rate and turn over frequency (TOF) was also observed in the experiments conducted when both metals were used simultaneously. Detailed in-situ FTIR measurements indicated the observable presence of a dinuclear complex RhRe(CO)₉. The kinetics of product formation show a distinct linear-bilinear form in observables-

k₁[RCORh(CO)₄][H₂][CO]⁻¹
+k₂[RCORh(CO)₄][HRe(CO)₅][CO]⁻²
−k₃[RhRe(CO)₉][RCHO][CO]⁻².

The first term represents the classic unicyclic rhodium catalysis while the other two terms indicate a reversible hydride attack on an acyl species. Moreover, it was also observed that the induction period was reduced due to HRe(CO)₅ attack on Rh₄(CO)₁₂.

These spectroscopic and kinetic results strongly suggest that the origin of synergism is the presence of bimetallic catalytic binuclear elimination. This appears to be the first detailed evidence for such a catalytic mechanism. Accordingly, a reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Mn or Rh-Re CBER hydroformylation reactions was proposed.
NOMENCLATURE

Abbreviations

BTEM   Band-Target Entropy Minimization
CBER   Catalytic Binuclear Elimination Reaction
CP     Cyclopentene
DMB    Dimethylbut-1-ene
DMP    Dimethylpentanal
FT     Fourier Transform
FTIR   Fourier Transform Infra Red
GC     Gas Chromatography
IR     Infra Red
LBBL   Lambert-Beer-Bouguer-Law
NMR    Nuclear Magnetic Resonance
SA     Simulated Annealing
S/N    Signal-to-Noise
SSE    Sum of Squares Errors
SVD    Singular Value Decomposition
TOF    Turnover Frequency
UV     Ultraviolet
VIS    Visible

Symbols

A      Arrhenius pre-exponential factor
a_{svv} pure component spectra matrix
\( \mathbf{a}_{xxb} \) integral pure component spectra matrix

\( \hat{\mathbf{a}}_{sxa} \) pure component spectral estimates matrix

\( \hat{\mathbf{a}}_{\text{max}} \) maximum absorbance of resolved pure spectrum

\( \hat{\mathbf{a}}_{\text{target}} \) target band peak absorbance normalized to 1.0 during spectral reconstruction

\( \mathbf{a}_{\text{tar}} \) target pure component spectrum

\( c \) constant used for adjustment of stepsize vectors

\( \text{cond} \) condition number of a matrix

\( \text{dis}_i \) determinant of a dispersion matrix \( (\mathbf{Y}_i^T \cdot \mathbf{Y}_i) \)

\( \mathbf{d}_{sxs} \) a multiplier matrix for the normalized pure component spectra matrix

\( \text{Ea} \) apparent activation energy

\( e \) number of experiments

\( \text{eps} \) convergence criterion

\( h \) Planck’s constant

\( h_{sv} \) discrete probability distribution function

\( j \) stoichiometry

\( k \) number of spectra in one experiment

\( k_s \) reaction rate constants

\( \mathbf{l}_i \) vector representing the intensities changes at each wavenumber in the mixtures

\( \mathbf{l}_{ke,xke} \) path length

\( m \) stoichiometry

\( n \) stoichiometry

\( r \) reaction rate

\( \text{rand} \) random number between \([0,1]\)

\( \mathbf{r}_{ke,rs} \) random matrix with the elements generated on the interval \([-1,1]\)
s number of species

\(v_m\) step size value for optimization

w maximum number of species

x mole fraction

z number of right singular vectors taken more than number of observable species

\(A_{ke}^{\nu}\) absorbance data matrix

\(\hat{A}_{ke}^{\nu}\) estimated absorbance data matrix

\(A^{\text{exp}}_{\nu}\) experimental raw absorbance data

\(A^{\text{pre}}_{\nu}\) preconditioned absorbance data

\(A_{Dml}^{\nu}\) modified absorbance data matrix

\(A_{ke}^{\nu,\text{ref}}\) matrix of spectroscopic data having the largest variance

\(C_{kexs}\) molar concentration matrix

\(\bar{C}_{kexs}\) first concentration estimates

\(\hat{C}_{kexs}\) corresponding expectation for concentrations of observable species

E number of atoms or functional groups

\(F_{\text{obj}}\) objective function value

\(H\) information entropy

\(K_{2q}\) equilibrium reaction constant

\(N_{kexE}\) moles of each element conserved in closed reaction system

\(N_{kexE}^0\) moles of each element initially put inside reactor

\(\overline{N}_{kexE}\) estimated moles of elements

\(N_{kexs}\) time dependent moles of all species

\(N_{kexs}^0\) initial moles of reactants
$\bar{N}_{kexs}$ first estimates of moles of all species

$\overline{N}_{kexs}$ second estimates of moles of all species

$N_{1kexs}$ the optimized moles profiles through kinetic fitting

$N_s$ number of loops before step size adjustment

$N_T$ number of loops before temperature reduction

$O$ correlation matrix

$P$ pressure

$T$ temperature

$T_{\times}$ transformation matrix

$U$ matrix of left singular vectors

$X$ mole fraction

$V^T$ transposed matrix of right singular vectors

$Y_i$ representative set of spectra chosen using a dissimilarity criterion

**Greek Letters**

$\alpha$ maximum absorbance of resolved pure spectrum

$\alpha$ reaction cycle

$\beta$ reaction cycle

$\alpha_1$ offset value in Simplisma and IPCA techniques

$\kappa$ Boltzmann’s constant

$\upsilon$ stoichiometry

$\upsilon_{rxs}$ reaction stoichiometries matrix

$\bar{\upsilon}_{rxs}$ first estimate of reaction stoichiometries

$\upsilon_{a\ rxs}$ observed stoichiometric space
(\(v_{\text{rxn}}\)\text{tar})  target stoichiometries

(\(v_{\text{rxn}}\)\text{proj})  projected stoichiometries

\(\xi_{k\text{exr}}\)  extents of reactions matrix

\(\xi_{\text{a}k\text{exr}}\)  observed extents of reactions space

\(\varepsilon_{k\text{ex}v}\)  experimental error matrix

\(v\)  number of data channels / wavenumber

\(v_{\text{sx}E}\)  dimensional atomic matrix

\(v_{\text{sx}E}^0\)  reactant atomic matrix

\(\overline{v}_{\text{sx}E}\)  first estimate of dimensional atomic matrix

\(\Delta_G\)  Gibb’s energy

\(\Delta_H\)  enthalpy

\(\Delta N_{k\text{exs}}\)  moles changes matrix

\(\Delta N_{\text{con}}\)  subsequent mole differences

\(\Delta S\)  entropy

\(\Delta V\)  volume of reaction

\(\Gamma\)  internal standard

\(\Sigma\)  diagonal matrix of singular values
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CHAPTER 1  INTRODUCTION

The combined application of more than one metal, leading to regio-, chemo- and stereo-selectivities and/or activities which differ significantly from a strictly additive effect, has come to be called "synergism"(Golodov, 1981, 2000; Kosak et al., 1996). 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 phenomenological origins of synergism have remained to a considerable extent unproven. A leading candidate has been "cluster catalysis", a term coined by Muetterties (Muetterties, 1975, 1976,1977; Demitras et al., 1977). In the 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 and every intermediate has one and the same nuclearity. The closed sequence of reactions involving dinuclear or polynuclear organometallic intermediates effects the overall organic transformation of reactants to products. Synergism arising from cluster catalysis has been invoked repeatedly to rationalise observations in bi- or multi-metallic homogeneous catalysis( Golodov, 1981, 2000; Herrmann et al., 1993; Kosak et al., 1996; Adams et al., 1998). It is convenient to regard such synergism via cluster catalysis as a structural explanation for the anomalous observations. The other known sources of synergism in homogeneous catalysis include facile fragmentation of the precursors (Garland, 1993) and promoted abstraction in the I/Ru/Ir system (Sunley et al., 2000;Whyman  et al., 2002).
Simple associative, dissociative and interchange reactions play a significant role in mechanistic organometallic chemistry (Langford et al., 1965), and much of this understanding has developed from the study of reactions between ligands and mononuclear complexes. However, reactions between mononuclear complexes are known. In this regard, the reactions between mononuclear complexes, leading to the fusion of two ligands, the formation of a dinuclear complex and simultaneous elimination of an organic product is particularly interesting. The first example of such a reaction was observed by Breslow and Heck (1960), and the name "binuclear elimination reaction" has consequently been used (Jones et al., 1979).

\[
\text{HCo(CO)}_4 + \text{CH}_3\text{COCo(CO)}_4 \rightarrow \text{CH}_3\text{CHO} + \text{Co}_2(\text{CO})_8
\]  

(1.1)

In this case, the general reaction is expressed as Eq 1.2. Since the starting observable complexes are coordinatively saturated, the general expression for the product formation rate can be expressed as Eq 1.3, where \(x\) is any other solute mole fraction, \(\nu\) is its associated stoichiometry, \(j\) is an index for the solute, and \(\Pi\) represents product.

\[
\begin{align*}
R^1M^1L_n + R^2M^2L_m & \rightarrow R^1R^2 + M^1M^2L_{n+m} \\
\text{Rate} & = k[R^1M^1L_n] [R^2M^2L_m] \cdot \Pi x^\nu_j
\end{align*}
\]

(1.2)  

(1.3)

Circa 28 well-defined binuclear elimination reactions between mononuclear complexes are known, and of these circa 13 occur between complexes possessing different metallic elements. The latter produce organic products ranging from molecular hydrogen, to methane to aldehydes. All the abovementioned reactions between mononuclear complexes are stoichiometric - one equivalent of product is formed.
The concept of catalytic binuclear elimination is exceptionally interesting from both a synthetic as well as kinetic viewpoint. In such a scenario, (I) one metal would undergo one set of transformations, (II) the other metal would undergo another set of transformations, (III) stoichiometric binuclear elimination would occur resulting in product formation and (IV) degradation / fragmentation of the dinuclear complex would allow the sequences I-III to repeat. - making the system catalytic. It is important to note that such a homogeneous catalytic system would consist of a non-trivial reaction topology with 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 (CBER) would constitute a well-defined reaction topological basis for synergism.

The most convincing evidence to date for such a phenomenological basis for synergism comes 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 (Beletskaya et al., 1989). 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 (Beletskaya et al., 1990). However, in-situ spectroscopic and kinetic information was not available. In addition, there exist a few known complicating factors, most notably the tendency for lanthanium hydride Cp to dimerise to form dinuclear lanthanium hydride Cp complexes (Evans et al., 1982), and the omnipresence of cobalt hydride tetracarbonyl under hydroformylation conditions (Marko, 1974; Mirbach, 1984). Finally, it is important to note that the observed kinetics of such a
Co and Ln catalytic system would probably not arise from a CBER alone, but instead, arise from the additive effect of both cobalt catalysis and Co/Ln CBER catalysis.

Rhodium is by far the most active metal for the homogeneous catalyzed hydroformylation of alkenes (van Leeuwen, 2000). Both homoleptic carbonyl clusters as well as phosphine complexes are extensively used. The unmodified system was discovered in the early 1950’s (Schiller, 1956), and the subject has been under considerable study (Csontos et al., 1974). Catalytic hydroformylation is one of the largest volume homogeneous processes (Frohning et al., 1996).

Hydroformylation of alkenes such as 3,3-dimethylbut-1-ene, cyclohexene and styrene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures (Garland and Pino, 1991). Detailed in-situ FTIR spectroscopic studies have shown the presence of only 4 observable organometallics, namely the known species RCORh(CO)₄ (Garland et al., 1989), Rh₂(CO)₈ (Whyman, 1972), Rh₄(CO)₁₂ (Chini et al., 1977), and Rh₆(CO)₁₆ (Chini, 1967), where the latter normally exist at the ppm or sub-ppm level under most catalytic conditions. No evidence for observable quantities of rhodium hydride species could be obtained in the presence of the reactive organic reagent. Analysis of the spectroscopic measurements provide very clean kinetics, where the rate of aldehyde formation is proportional to \([\text{RCORh(CO)}_4][\text{CO}]^{-1}[\text{H}_2][\text{alkene}]^0\). 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 (Dickson, 1985). The reactions and kinetics are very reproducible.
In the abovementioned unmodified rhodium catalyzed hydroformylation reactions, as well as in most homogeneous catalytic systems, the overall organic transformation arises from the action of a set of organometallic species having one and the same nuclearity, e.g. a catalytic cycle composed of only mononuclear species ML_n. Because of this, the reaction network exhibits rates of organic product formation which are first order in the total concentration of organometallic intermediates Σ[I] j where the rate constant is a function of temperature, pressure and the concentrations of organic reactants, k = f (T,P,x).

\[ \text{Rate} = k \Sigma[I]_j \] (1.4)

In the search for bimetallic CBER, proper interpretation of the kinetics will be critical. As mentioned above in the context of Beletskaya’s work, the simultaneous presence of unicyclic catalysis is very probable. Accordingly, any master equation for the kinetic polynomial describing a potential CBER containing system will need to be general enough to accommodate this feature. If such a synthetic system consisting of a unicyclic catalytic reaction network plus a CBER were found, the general form for the rate of organic product synthesis would probably be given as shown in Eq 1.5 where M’ represents a function of M^1L_n and/or M^2L_n. It should be noted that the bilinear term represents a higher order of catalysis.

\[ \text{Rate} = k_1[M'] \cdot \Pi x^v_i + k_2[R^1M^1L_n \cdot R^2M^2L_m \cdot \Pi x^v_j \] (1.5)

Therefore, the confirmation of bimetallic CBER will imply not only a new well grounded phenomenological basis for synergism, but also higher order catalysis.
Accordingly, CBER should impact areas such as alternative synthetic metal mediated strategies, non-linear catalytic kinetics and higher efficiency (TOF) and chemical selectivity.

In particular, although the existence of binuclear elimination reactions associated with the hydroformylation reaction has been clearly demonstrated in the stoichiometric case, solid experimental, mechanistic and kinetic evidence for catalytic binuclear elimination under catalytic conditions has been difficult to obtain.

The aim of the present study is to rationally search for and then identify a bimetallic catalytic binuclear elimination reaction. The starting point will be the use of the well studied unmodified rhodium catalyzed hydroformylation reaction. Since metal carbonyl hydrides have been widely used in stoichiometric binuclear elimination reactions, we would use such metal hydrides as our second metal complex to see if bimetallic CBER could be observed / induced in the unmodified rhodium catalyzed hydroformylation reactions.

Chapter 2 is the literature review.

In Chapter 3, the in situ FTIR experimental work will be introduced first. Given the complexity of the questions being asked in this thesis, new tools have to be developed. In the following, a newly developed methodology called “total algebraic system identification” (Widjaja et al., 2002, 2003) was introduced and it was successfully applied to a single semi-batch homogeneous rhodium-catalyzed alkene hydroformylation and a homogeneous stoichiometric reaction. It was shown that the total algebraic system identification algorithm is feasible for rapid and effective spectroscopic system identification of reactive organometallic and homogeneous catalytic systems.
In the next part, with this tool of total algebraic system identification, we performed the in-situ FTIR studies of the bimetallic catalyzed hydroformylation of alkenes. A total of seven bimetallic systems (\(\text{Rh/Mn/3,3-dimethylbut-1-ene(33DMB)}\), \(\text{Rh/Mn/Cyclopentene, Rh/Mn/styrene, Rh/Mn/methylene cyclohexane, Rh/Re/Cyclopentene, Rh/Re/Styrene, and Rh/Re/Methylenecyclohexane}\)) have been studied to seek for the bimetallic catalytic binuclear elimination reaction (CBER). In the next three chapters (Chapter 4, Chapter 5 and Chapter 6), three bimetallic systems (\(\text{Rh/Mn/33DMB, Rh/Mn/Cyclopentene, and Rh/Re/Cyclopentene}\)) were studied in detail. The other four cases were summarized in Appendix B.

Chapter 4 studied the bimetallic hydroformylation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal (44DMP) using unmodified rhodium and manganese carbonyls as catalyst precursors. A series of well designed experiments were performed at different loadings of precursors HMn(CO)\(_5\)/Mn\(_2\)(CO)\(_{10}\) and Rh\(_4\)(CO)\(_{12}\), substrate 33DMB, different dissolved concentrations of CO and H\(_2\), and at different reaction temperatures. The in-situ FTIR data were analyzed with the total algebraic system identification algorithm to obtain the species present and their mole concentrations. The effects of HMn(CO)\(_5\)/Mn\(_2\)(CO)\(_{10}\) on the transformation of Rh\(_4\)(CO)\(_{12}\) during the initial reaction period, on the production formation rate and the turn over frequencies (TOF) were investigated. Accordingly, the kinetics and catalysis for the Rh/Mn bimetallic catalyzed hydroformylation were examined to search for evidence of bimetallic CBER. Observable kinetics of the form Eq 1.5 was found. This appears to be the first in-situ spectroscopic and kinetic evidence for bimetallic CBER.

In Chapter 5, the Rh\(_4\)(CO)\(_{12}\)/HMn(CO)\(_5\) bimetallic catalyzed hydroformylation was extended to another type of alkenes- cyclopentene. A total of circa 1500 in situ IR
spectra were obtained and analyzed. The recovered spectra, the effects of HMn(CO)\textsubscript{5}/Mn\textsubscript{2}(CO)\textsubscript{10} on the pre catalytic behavior, hydroformylation and the TOF, and the kinetics and catalysis were inspected to find further proof of the existence of CBER.

Again, observable kinetics of the form Eq 1.5 was found. This appears to confirm that the existence of bimetallic CBER, indeed, the same general kinetic polynomial is valid for closely related reactions.

In the above Rh\textsubscript{4}(CO)\textsubscript{12}/HMn(CO)\textsubscript{5} bimetallic catalyzed hydroformylation 33DMB and cyclopentene reactions, the expected dinuclear intermediate was not observed. Chapter 6 is an example of bimetallic CBER where the bimetallic dinuclear complex was identified. The Rh\textsubscript{4}(CO)\textsubscript{12}/HRe(CO)\textsubscript{5} equilibrium under CO/H\textsubscript{2} was studied first and the new dinuclear species RhRe(CO)\textsubscript{9} was identified. Next the Rh\textsubscript{4}(CO)\textsubscript{12}/HRe(CO)\textsubscript{5} bimetallic catalyzed hydroformylation of cyclopentene was systematically studied with in situ FTIR. The influences of HRe(CO)\textsubscript{5} on the fragmentation of Rh\textsubscript{4}(CO)\textsubscript{12}, the product formation and TOF were investigated. The kinetics of product formation was analyzed and the associated catalysis was discussed. The observable kinetics obey a modified form of Eq 1.5. This new result again appears to reconfirm the existence of bimetallic CBER, since a related kinetic polynomial is valid for closely related reactions where the second metal was chosen from the same periodic group. The objective of changing of Mn with Re was to seek another sort of CBER.

In Chapter 7, the conclusions were drawn and the implications of CBER for selectivity and non-linear catalytic activity were accordingly discussed.
CHAPTER 2 LITERATURE REVIEW

2.1 Synergism in homogeneous catalytic systems

The term synergism has become synonymous with the observation of enhanced rates and enhanced selectivities in multi-metallic homogeneous catalytic systems (Golodov, 1981, 2000; Jenner, 1988; Kosak et al., 1996; Adams et al., 1998). In other words, the combined application of more than one metal can lead to chemoselective, regioselective and or kinetic results which differ significantly from the known characteristics of monometallic catalytic systems. 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.

One leading candidate for synergism has been "cluster catalysis", a term coined by Muettterties (Muettterties, 1975, 1976,1977; Demiras et al., 1977). The use of metal clusters in catalysis has been undergoing an impressive renaissance. Many new opportunities are opened by the interdisciplinary studies of large clusters and colloids and of free and oxide-supported nanoparticles. More controlled synthetic methods are being developed for both homo- and heterometallic clusters to yield a much greater variety of clusters which can be used in catalysis. Mechanistic studies and the insights obtained from model cluster complexes are bringing a deeper level of understanding of catalysis to both homo-metallic and heterometallic clusters and its relation to surface catalysis (Puddephatt, 1999). The chemical catalysis by clusters was well reviewed by Lewis (1993). Adams and Cotton recently have a nice review book that surveys the latest
developments at the frontier of catalysis of organic chemical reactions involving multinuclear metal complexes (Adams et al., 1998).

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. In the cluster catalysis, the catalytic system involves a closed sequence of elementary reactions where each and every 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 (Adams et al., 1998). It is convenient to regard such synergism via cluster catalysis as a structural basis for the anomalous observations.

Although synergistic effects are often claimed in cluster catalysis, Garland (1993) recently showed that the rapid fragmentation could be another explanation in polymetallic catalyst systems. In his studies of the hydroformylation of 3,3-dimethylbut-1-ene catalysed by CoRh(CO)\textsubscript{7} and Co\textsubscript{2}Rh\textsubscript{2}(CO)\textsubscript{12}, Garland found that the induction period for formation of the active species rhodium acyl RCORh(CO)\textsubscript{4} is two to three orders of magnitude shorter than that for the monometallic catalyst precursors. The time dependent system activity did not correlate with the time dependent presence of the clusters. Therefore Garland suggested that the observed synergism arise exclusively from the facile fragmentation of CoRh(CO)\textsubscript{7} and Co\textsubscript{2}Rh\textsubscript{2}(CO)\textsubscript{12} under reaction conditions and the rapid and selective formation of rhodium acyl RCORh(CO)\textsubscript{4}.

Another potentially important source of synergism is the catalytic binuclear elimination reaction (CBER), which will be reviewed in detail below. The concept of
catalytic binuclear elimination is exceptionally interesting from both a synthetic as well as kinetic viewpoint. In such a scenario, (I) one metal would undergo one set of transformations, (II) the other metal would undergo another set of transformations, (III) stoichiometric binuclear elimination would occur resulting in product formation and (IV) degradation / fragmentation of the dinuclear complex would allow the sequences I-III to repeat - making the system catalytic. The bimetallic catalytic binuclear elimination reaction would constitute a well-defined reaction topological basis for synergism (Golodov, 1981, 2000).

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 (Sunley et al., 2000; Whyman et al., 2002). 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. 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.

2.2 Binuclear Elimination Reaction (BER)

Most mechanistic work in organometallic chemistry is focused on the associative, dissociative and substitution reactions occurring between organic / inorganic ligands \( L \) and metal complexes (Langford et al., 1965). However, a variety of bimolecular reactions occur between metal complexes, particularly mononuclear complexes. Mononuclear
organometallic complexes undergo a wide variety of elementary reactions, including ligand dissociation and substitution, insertions and eliminations etc. (Collman et al., 1987). Such intra-molecular and bimolecular transformations are essential features of many homogeneous metal-mediated organic syntheses. Indeed, there are many stoichiometric syntheses as well as unicyclic catalytic systems which involve only soluble mononuclear complexes as intermediates. Examples range from simple hydrogenations (James, 1982) to reactions controlling stereo- and regioselectivity (Green and Davies, 1988), and even to total synthesis of complicated natural products (Harriton, 1990).

Stoichiometric bimolecular reactions between mononuclear complexes leading to the elimination of a new organic product and the formation of a dinuclear complex are of particular interest to us in the present context (Norton, 1979). Heck and Breslow were apparently the first to show such a reaction.

During the early studies of the mechanism of the hydroformylation reaction by Heck and Breslow, it was shown that there exists a pathway involving an intermolecular hydride transfer between prepared solutions of HCo(CO)₄ and CH₃COCo(CO)₄ to eliminate aldehyde product and the dinuclear complex Co₂(CO)₈ (Breslow et al., 1960, Heck et al., 1966).

\[
\text{HCo(CO)₄} + \text{CH₃COCo(CO)₄} \rightarrow \text{CH₃CHO} + \text{Co₂(CO)₈} \quad (2.1)
\]

In this landmark investigation, the reactions were performed without dissolved hydrogen and dissolved carbon monoxide, i.e., under conditions far removed from the catalytic case. Accordingly, the name of “binuclear elimination reaction” (BER) has become associated with such mechanism. The general overall stoichiometric expression for this reaction can be written as shown in Eq 2.2.

12
\[ R^1M^1L_m^+ + R^2M^2L_n \rightarrow R^1R^2+M^1M^2L_{m+n} \quad (2.2) \]

Subsequently, numerous studies have shown that stoichiometric binuclear elimination reactions are possible and circa 28 well-defined binuclear elimination between mononuclear complexes are documented in the organometallic and synthetic organic literature. Some of these occur between complexes possessing different metallic elements. The latter reactions produce organic products ranging from molecular hydrogen, to methane and even aldehydes. All the abovementioned reactions between mononuclear complexes are stoichiometric, thus one equivalent of product is formed. Table 2.1 and Table 2.2 list the known homometallic stoichiometric binuclear elimination reactions and bimetallic stoichiometric binuclear elimination reactions respectively.

**Table 2.1** Homometallic stoichiometric binuclear elimination reaction

<table>
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<th>No</th>
<th>Reaction</th>
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<tbody>
<tr>
<td>1</td>
<td>( 2\text{HCo(CO)}_4 \rightarrow \text{Co}_2\text{(CO)}_8+\text{H}_2 )</td>
<td>von Brandes et al., 1966</td>
</tr>
<tr>
<td>2</td>
<td>( 2\text{HMn(CO)}_5 \rightarrow \text{Mn}<em>2\text{(CO)}</em>{10}+\text{H}_2 )</td>
<td>Ungvary et al., 1969</td>
</tr>
<tr>
<td>3</td>
<td>( \text{RCOCo(CO)}_4+\text{HCo(CO)}_4 \rightarrow \text{Co}_2\text{(CO)}_8+\text{RCHO} )</td>
<td>Breslow et al., 1960; Heck, 1974; Ungary et al., 1982; Azran et al., 1984; Kovacs et al., 1986</td>
</tr>
<tr>
<td>4</td>
<td>( \text{RCo(CO)}_4+\text{HCo(CO)}_4 \rightarrow \text{Co}_2\text{(CO)}_8+\text{RH} )</td>
<td>Hoff et al., 1985</td>
</tr>
<tr>
<td>5</td>
<td>( 2\text{Os(CO)}_4\text{H}_2 \rightarrow \text{H}_2\text{Os}_2\text{(CO)}_8+\text{H}_2 )</td>
<td>Norton et al., 1978; Norton, 1979; Edidin et al., 1988</td>
</tr>
<tr>
<td>6</td>
<td>( 2\text{Os(CO)}_4(\text{H})\text{CH}_3 \rightarrow )</td>
<td>Norton et al., 1978; Norton,</td>
</tr>
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</table>
Table 2.2 Bimetallic stoichiometric binuclear elimination reaction

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
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<tbody>
<tr>
<td>1</td>
<td>HMn(CO)₅+CH₃AuPPh₃→Au(PPh₃)Mn(CO)₅+CH₄</td>
<td>Mitchell et al., 1972</td>
</tr>
<tr>
<td>2</td>
<td>HOs(CO)₄Si(CH₃)₃+CH₃AuPPh₃→Au(PPh₃)Os(CO)₄Si(CH₃)₃+CH₄</td>
<td>Mitchell et al., 1972</td>
</tr>
</tbody>
</table>

7  Os(CO)₄H₂+Os(CO)₄(CH₃)₂→HOs(CO)₄Os(CO)₄CH₃+CH₄                           Norton et al., 1978; Norton, 1979; Edidin et al., 1988

8  Os(CO)₄H₂+Os(CO)₄(H)CH₃→H₂Os(CO)₂(CO)₈+CH₄                             Norton et al., 1978; Norton, 1979; Edidin et al., 1988

9  (CO)₅MnR+HMn(CO)₅→Mn₂(CO)₉+RCHO                                      Nappa et al., 1982, 1985

10 2HRh(CO)₂(PPh₃)₂→Rh₂(CO)₂(PPh₃)₂+H₂+2CO                             Brown et al., 1971

11 2HIr(CO)(PPh₃)₃→Ir₂(CO)₂(PPh₃)₄+H₂+2PPh₃                             Schwartz et al., 1974

12 (σ-C₆H₅)Ir(CO)(PPh₃)₂+(n-C₆H₁₃)CD₂CH₂Ir(CO)(PPh₃)₂→C₆H₅D+octane-1-d₁+octane-d₃ | Schwartz et al., 1974

13 EtRe(CO)₅+HRe(CO)₅→EtCHO+Re₂(CO)₉                                    Martin et al., 1986

14 HFe(CO)₄+CH₃CH₂C(=O)FePPh₃(CO)₃→CH₃CH₂CHO+EtFe₂PPh₃(CO)₇           Barborak et al., 1982

15 (η⁵-C₅H₅)Mo(CO)₃H+(η⁵-C₅H₅)Mo(CO)₃R→(η⁵-C₅H₅)Mo₂(CO)₄,₆+RCHO        Jones et al., 1979, 1981
<table>
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<th>Reaction</th>
<th>Authors</th>
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<tbody>
<tr>
<td>3</td>
<td>((\text{CO})_4\text{Si(CH}_3)_3+\text{CH}_4)</td>
<td>Norton, 1979</td>
</tr>
<tr>
<td>4</td>
<td>((\text{CO})_4\text{Os(CH}_3)_2\text{HRe(CH}_3)_2^+\rightarrow(\text{CO})_5\text{H}+(\eta^5-\text{C}_5\text{H}_5)\text{Mo(CH}_3)_3\text{H}\rightarrow(\text{C}_5\text{H}_5)_2\text{CH}_3\text{ZrMo(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Renaut et al., 1978</td>
</tr>
<tr>
<td>5</td>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{Zr(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{Re(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Martin, et al., 1986</td>
</tr>
<tr>
<td>6</td>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{Zr(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{Re(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Martin, et al., 1986</td>
</tr>
<tr>
<td>7</td>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{MoH}_2+\text{CH}_3\text{Mn(CH}_3)_3\text{H}+\text{Re(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Hoxmeier et al., 1979</td>
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<tr>
<td>8</td>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{MoH}_2+\text{CH}_3\text{Mn(CH}_3)_3\text{H}+\text{Re(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Hoxmeier et al., 1979</td>
</tr>
<tr>
<td>9</td>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{ReH}+\text{CH}_3\text{Mn(CH}_3)_3\text{H}+\text{Re(CH}_3)_2\text{HRe(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Hoxmeier et al., 1979</td>
</tr>
<tr>
<td>10</td>
<td>((\text{CO})_5\text{Mn(OH)}+\text{EtOC(O)Co(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Kovacs et al., 1985</td>
</tr>
<tr>
<td>11</td>
<td>((\text{CO})_5\text{Mn(OH)}+\text{EtOC(O)Co(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Kovacs et al., 1985</td>
</tr>
<tr>
<td>12</td>
<td>((\text{CO})_5\text{Mn(OH)}+\text{EtOC(O)Co(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Kovacs et al., 1985</td>
</tr>
<tr>
<td>13</td>
<td>((\text{CO})_5\text{Mn(OH)}+\text{EtOC(O)Co(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{MnCo(CH}_3)_3\text{H}+\text{CH}_4)</td>
<td>Kovacs et al., 1985</td>
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2.3 Catalytic binuclear elimination reaction (CBER)

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 re-occurs. 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 non-trivial 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 (Golodov, 1981, 2000). It is important to note that such homogeneous catalytic systems would consist of both mononuclear and dinuclear intermediates.

Whyman, Alemdaroglu et al., and Mirbach have all undertaken spectroscopic studies of cobalt-catalyzed hydroformylation reactions (Whyman, 1974; Van Hoven et al., 1975; Alemdaroglu et al., 1976; Ungvary et al., 1983; Mirbach et al., 1984). In these experiments, the simultaneous presence of both HCo(CO)₄ and RCo(CO)₄(R=octyl, cyclohexyl) was observed during the catalytic hydroformylation. The interpretation of the reaction has been controversial. Marko indicated that the hydridocobalt complex reacts much faster with acylcobalt complex than does hydrogen. On the other hand, regression of the kinetic data by Mirbach indicated that perhaps 3% of all product formation occurs via
catalytic binuclear elimination reaction (CBER). However, the statistics associated with the regressed coefficients were unfortunately not presented.

Recently, in Garland’s group, Susithra (2002) has undertaken in situ spectroscopic studies of the unmodified homogeneous cobalt catalyzed hydroformylation of cyclooctene. Regression of the kinetic data indicates that there is statistically significant contribution (1-5%) to aldehyde formation from the catalytic binuclear elimination reaction.

During the studies on the elimination mechanism of osmium alkyls and hydrides, Norton (1979) suggested that the dinuclear eliminations are probably much more common than has been realized due to the extraordinary ability of metal hydrides to fill vacant coordination sites on other metals. He argued that the dinuclear elimination is probably involved in the cobalt catalyzed oxo reaction. In his later work (Martin et al., 1986) on the relative nucleophilicity of metal hydrides, Norton further indicated that dinuclear elimination could be the terminal step in catalytic hydroformylation.

In addition, with the studies of a surface-tethered silica-supported rhodium hydroformylation of styrene, Collman and co workers (Collman et al., 1983) found that there was a dependence of the rate of hydroformylation of styrene with the surface concentration of the rhodium catalyst species, accordingly Collman et al. discussed the possibility of dinuclear reductive elimination as the site-site interaction.

Furthermore, Hidai and coworkers (Kayasu et al., 1985; Hidai et al., 1986) indicated that the synergistic effect for cobalt and ruthenium on the hydroformylations of cyclohexene, 1-hexene and styrene might be explained by such a dinuclear elimination between a cobalt acyl and a ruthenium hydride.
The most convincing evidence to date for such a phenomenological 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 tetracarboxyls to give aldehyde (Beletskaya et al., 1989). 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 (Beletskaya et al., 1990). 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 dimerise and form dinuclear lanthanium complexes (Evans et al., 1982), and the omnipresence of cobalt hydride tetracarboxyl under hydroformylation conditions (Marko, 1974; Mirbach, et al., 1984).

Using much higher nominal rhodium concentrations, Garland and his co-workers (Feng and Garland, 1999b) re-examined the kinetics of the homogeneous rhodium-catalyzed hydroformylation of cyclohexene with the explicit purpose of quantifying any possible contribution of a CBER to the product formation. Indeed, the concentrations of the sparingly soluble cluster Rh₆(CO)₁₂ were extended to their solubility limit (circa 2000 mg/liter n-hexane). Regression of the kinetic data indicated that there is no statistically significant contribution from CBER to aldehyde formation under the reaction conditions.

Most recently, using cyclooctene as the substrate, detailed spectroscopic and kinetic studies of the unmodified rhodium hydroformylation of cyclooctene have been made by Liu (2000). Turnover frequency (TOF) analyses showed that there could exist
homometallic catalytic binuclear elimination reaction in the system. Further data analyses are in progress.

In the interest of completeness concerning CBER, a qualifier is required regarding the non-linear kinetic effects in bimetallic CBERs – they are local effects and not global. With respect to this problem, using the hypothetical bimetallic CBER, Garland’s group (Leong, 1999) has found that the complexity of bimetallic CBER is evident from the size of the kinetic polynomials obtained for the steady state expression. The bimetallic CBER was found to be more complicated than a unicyclic catalytic system as well as a monometallic CBER system. At best, the rate of products formation is non-linear with respect to the total concentration of the two metals in the system. Furthermore, Garland’s group (Chan, 1999) has also applied the Feinberg (1989) stability criteria to generalize bimetallic CBER topologies and numerous permutations on the reaction network configuration. It has been shown that both monometallic and bimetallic CBERs should be stable from a systems engineering viewpoint, and should not exhibit oscillatory or other exotic temporal behaviour.

These last results suggest that further search for bimetallic CBER is quite justified, since interesting and useful kinetics will arise, and the systems will be easily controllable due to their stability.

2.4 Hydroformylation

Hydroformylation refers to the addition of hydrogen and carbon monoxide to unsaturated systems. The hydroformylation is also known as the “Oxo synthesis” or the “Roelen reaction” in honor of its inventor (Roelen, 1943, 1948, 1978). It is the largest
homogeneous industrial process for converting alkenes, CO, and H₂ into aldehyde products. By 1994, the world capacity for all hydroformylated products amounted to more than 7 million tons per year. This process has also been developed to produce special olefins and high value added intermediates for fine chemicals and pharmaceuticals (Cornils, 1980; Frohning et al., 2002). Today’s hydroformylation process almost exclusively uses rhodium or cobalt homogeneous catalysts. The active species are believed to be mononuclear complexes. The overall stoichiometry of the hydroformylation reaction is illustrated by Eq 2.3.

\[
\text{CH}_2=\text{CH}_2+\text{CO}+\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} \quad (2.3)
\]

In spite of the high level of sophistication in the implemented commercial processes, hydroformylation still has a large space for development, both for research and for applications. For example, it is surprising to note that although the oxo synthesis has been implemented commercially for nearly 50 years, little information is available about the kinetics of hydroformylation reactions (Frohning et al., 2002), with exception to the Wilkinson/Osborn phosphine modified rhodium system (Osborn et al., 1966; Evans et al., 1968; Yagupsky et al., 1970). Its reaction mechanism has not been clarified in every detail. Some aspects of the proposed reaction pathway are still under investigation. With respect to applications, the hydroformylation of special structures (e.g. asymmetric hydroformylation) is expected to receive increased attention in the near future (Consiglio et al., 1982; Consiglio, 1996). In addition, as a clean and environmentally friendly process, hydroformylation should be given more attention. Furthermore, such topics as biphasic hydroformylation, aqueous-phase catalysis, supercritical fluids, polymer-supported catalysts and bimetallic catalysis will open interesting and promising
perspectives for hydroformylation (Reek et al., 2000; Ojima et al., 2000; Frohning et al., 2002).

2.4.1 Catalysts

The typical hydroformylation catalysts consist of a transition metal atom (M) which enables the formation of metal-carbonyl hydride species. These complexes may be optionally modified by additional ligands (L) and the general composition can be expressed by the formula $H_xM_y(CO)_zL_n$. Commercial hydroformylation plants are run exclusively with catalysts based on Rh or Co, namely $HCo(CO)_4$, $HCo(CO)_3PBu_3$ and $HRh(CO)(PR_3)_3$ (Beller et al., 1995).

2.4.2 Unmodified rhodium hydroformylation

Although the phosphorus modified rhodium catalysts have been used much more extensively than the corresponding unmodified one (Whyman, 2001), unmodified rhodium catalytic precursors, especially Rh$_4$(CO)$_{12}$, are still the subject of detailed investigations. As Cornils indicated, “This is due to their easy availability, their well-known properties and their rather unproblematic handling. Additionally they serve as much simpler models than modified catalysts. But the main reason for their persistent topicality is the fact that the mechanism of hydroformylation is far from being well understood” (Beller et al., 1995).

During the past decade, Garland and coworkers have carried out numerous detailed in situ spectroscopic and kinetic studies of the unmodified rhodium-catalyzed hydroformylation (Garland et al., 1988, 1989, 1990, 1991, 1993; Fyhr et al., 1993; 1993; Feng et al., 1999; Liu et al.; 1999, 2000). In these fundamental investigations, by using
the high pressure in situ IR spectroscopic methods, information on the kinetic aspects of the process and on the reactivity of the acyl-rhodium intermediates has been obtained (Lazzaroni et al., 2000). In addition, Rh₄(CO)₁₂ has also been extensively used by Larzarroni’s group in deuterioformylation experiments at partial substrate conversion with ²H-NMR analyses on the behavior of alkyl-rhodium intermediates (Ucello-Barretta et al., 1991; Lazzaroni et al., 1995, 1996, 1999).

2.4.2.1 Mechanism

In 1961 Heck proposed what is now the generally accepted monometallic mechanism for HCo(CO)₄ catalyzed hydroformylation (Heck et al., 1961). For the rhodium system, since the initial reports concerning the activity of the unmodified complexes as catalyst precursors (Schiller, 1956; Hughes, 1959), numerous studies have focused on elucidating the mechanism of rhodium-catalyzed hydroformylation (Heil et al., 1968; Whyman, 1972; Csontos et al., 1974; Vidal et al., 1981; Oldani et al., 1983). The reaction orders, 1.0 with respect to rhodium, 1.0 with respect to hydrogen, and –1.0 with respect to carbon monoxide have been consistently observed. Moreover, direct spectroscopic evidence for cluster fragmentation and strong indirect experimental evidence for the existence of mononuclear acyl rhodium tetracarbonyls had been obtained. Therefore, a widely accepted mechanism for the unmodified rhodium catalyzed hydroformylation reaction has been developed by analogy to the less reactive but better understood cobalt catalyzed system. This classic mechanism scheme is shown in Figure 2.1 (Dickson, 1986). In this scheme, it is believed that alkene activation occurs via a hydride route, which leads to a coordinatively saturated 18 e- alkyl species RRh(CO)₄. The next step involves CO insertion to generate the coordinatively unsaturated acyl
species RCORh(CO)\textsubscript{3}. Finally, RCORh(CO)\textsubscript{3} undergoes hydrogenolysis to give rise to its respective aldehyde RCHO and regenerate the highly reactive 16e- hydride HRh(CO)\textsubscript{3}. Under the above considerations, the coordinatively saturated 18 e- species HRh(CO)\textsubscript{4} and RCORh(CO)\textsubscript{4} assume roles outside the active cycle, but are in rapid equilibrium exchange with species residing on the catalytic cycle.

**Figure 2.1** The classic mechanism for the unmodified rhodium catalyzed hydroformylation of alkenes
In the extensive in-situ infrared spectroscopic studies performed by Garland and his coworkers (Garland et al., 1989; 1990, 1991, 1993; Fyhr et al., 1993; 1993; Feng et al., 1999; Liu et al., 1999, 2000), the cluster fragmentation of Rh₄(CO)₁₂ was always observed and the observable intermediate acyl rhodium tetracarbonyl during the syntheses was first identified (Garland et al., 1989). Subsequently, during the unmodified rhodium catalyzed hydroformylation of five categories of alkenes (cycloalkenes, terminal alkenes, symmetric internal linear alkenes, methylene cycloalkenes and branched alkenes), a total of 15 acyl rhodium tetracarbonyl intermediates were identified (Liu et al., 1999a). Most recently, using a polymer matrix technique, Poliakoff et al. also observed acyl rhodium intermediates (Zhang et al., 2003).

The other observable organometallic intermediates are the common impurity Rh₆(CO)₁₆ (Chini, 1967), and the indication of fragmentation such as the formation of Rh₂(CO)₈ (Whyman, 1972). Most recently, with new advanced signal processing techniques, the precursor isomer Rh₄(σ-CO)₁₂ (Widjaja et al., 2002) was also successfully identified in the Rh₄(CO)₁₂ / 33DMB system. With the availability of such new advanced signal processing techniques, the long sought for rhodium hydride HRh(CO)₄ was recovered from the Rh₄(CO)₁₂/H₂/CO solution (Li, et al., 2002). However, no evidence for observable quantities of the known rhodium hydride species (Vidal et al., 1981; Whyman, 1992) could be obtained in the presence of very reactive organic alkene substrates.

In addition to the findings of the cluster fragmentation of Rh₄(CO)₁₂ and the observable intermediate acyl rhodium tetracarbonyl during the syntheses, in-situ infrared spectroscopic studies of the unmodified rhodium catalysed hydroformylation have shown that the rate of the aldehyde formation was always proportional to the instantaneous...
concentration of the rhodium acyl species. All this supports the classic unicyclic mechanistic picture.

2.4.2.2 Kinetics

Recently, Garland and his co-workers have formulated a systematic approach to the kinetics for the un-modified rhodium catalyzed hydroformylation reaction. In these studies, the fragmentation of Rh₄(CO)₁₂ in the presence of alkene substrates was firstly investigated and the mechanism of the transformation of rhodium-clusters under oxo conditions became clearer.

As acyl intermediates are the only detectable reaction intermediates under the typical hydroformylation conditions, several clear kinetic and mechanistic aspects of the behaviour of acyl intermediates are resolved. The most interesting aspect of the reactivity is the oxidative addition of H₂ and the following reductive elimination to give the final aldehyde products and regenerate the metal-hydride complex.

The disappearance of the typical bands due to Rh₄(CO)₁₂ and the appearance of those due to acyl-rhodium intermediates were studied under different experimental conditions in order to determine a kinetic expression for the fragmentation process. For 3,3-dimethylbut-1-ene(33DMB), the kinetic expression for the RCORh(CO)₄ formation rate was obtained to be $k₁[Rh₄(CO)₁₂][CO]^{1.8}[H₂]^{0.7}[33DMB]^{0.1}$, with apparent activation enthalpy $ΔH^\ddagger = 74.4 \pm 12.0$ kJ/mol and $ΔS^\ddagger = -19.4 \pm 41.8$ J/(mol⋅K). The whole process for the product formation was found equal to $k₂[RCORh(CO)₄][CO]^{-1.1}[H₂]^{1}[33DMB]^{0.1}$, with $ΔH^\ddagger = 49.3 \pm 4.0$ kJ/mol and $ΔS^\ddagger = 121 \pm 14$ J/(mol⋅K). The above equations are consistent with (a) a preequilibrium between
Rh₄(CO)₁₂, CO and a second unstable cluster and (b) a rate-limiting step involving the activation of the later cluster by H₂ (Garland and Pino, 1991a).

In the case of cyclohexene, the time-dependent concentrations of Rh₄(CO)₁₂, the intermediate C₆H₁₁CORh(CO)₄ and the organic product C₆H₁₁CHO were measured under isobaric and isothermal conditions (Fyhr and Garland, 1993). An apparent pseudo steady state (the concentrations become essentially time-dependent for a long time, circa 300 mins) was reached between the precursor and acyl intermediate after approximately 30 minutes of reaction. The expression for the acyl rhodium concentration is

\[ k₁[Rh₄(CO)₁₂]^{0.3}[CO]^{1.1}[H₂]^{-0.3}[C₆H₁₀]^{0.9}, \]

with the apparent temperature dependence \( ΔH^‡ = -4.7 \pm 0.3 \text{ kJ/mol} \) and \( ΔS^‡ = -27.6 \pm 0.7 \text{ J/(mol⋅K)} \). This affirms (i) an equilibrium between the precursor Rh₄(CO)₁₂, H₂ and the unobserved hydride HRh(CO)₃, and (ii) a pseudo steady state between the unobserved hydride and observed acyl rhodium tetracarbonyl C₆H₁₁CORh(CO)₄. The hydroformylation rate expression is similar to that of 33DMB, with apparent activation parameters \( ΔH^‡ = 84.6 \pm 5.0 \text{ kJ/mol} \) and \( ΔS^‡ = -8.7 \pm 17 \text{ J/(mol⋅K)} \). These reaction orders and activation parameters suggest that (i) an equilibrium between the intermediate rhodium acyl, CO, and a coordinatively unsaturated species \{C₆H₁₁CORh(CO)₃\} and (ii) a rate-limiting step involving the oxidative addition of H₂ to \{C₆H₁₁CORh(CO)₃\} to produce the organic product aldehyde and the highly reactive rhodium carbonyl hydride \{HRh(CO)₃\}.

The detailed homogeneous regioselective catalytic hydroformylation of styrene to (+) 2 phenylpropanal and 3 phenylpropanal was carried out recently (Feng and Garland, 1999a). Both of the isomeric acyl-rhodium intermediates were observed during the 5-h kinetic experiments. The Rh₄(CO)₁₂ disappearance rate was found to follow
k_1[Rh_4(CO)_{12}]^{1}[CO]^{1.3}[H_2]^{0.9}[33DMB]^{0.15}, \text{ with } \Delta H^{\ddagger} = 62.6 \text{ kJ/mol and } \Delta S^{\ddagger} = -37.2 \text{ J/(mol.K). This rate expression also suggests that cluster fragmentation of Rh_4(CO)_{12} proceeds via CO addition and polyhedron opening as the first step (Bor et al, 1978). The kinetic expressions are found to be similar for both of the products, i.e.,}

k[RCORh(CO)_4]^{1.0}[CO]^{-1.0}[H_2]^{1.0}[33DMB]^{0.0} \text{ with } \Delta H^{\ddagger} = 78.8 \text{ or 113(isomer) kJ/mol and } \Delta S^{\ddagger} = 15.2 \text{ or } -102 \text{ J/(mol.K). Of particular interest is the effect of reaction temperature on the reaction rate and the regioselectivity. It was found that the hydrogenolysis rate of the linear acyl-metal intermediate is higher than that for the branched isomer and the regioisomeric ratio between the acyl intermediates at 313K is higher than that between the corresponding aldehydes.}

### 2.4.3 Bimetallic hydroformylation

Bimetallic or polymetallic catalysts for hydroformylation have been studied extensively. For bimetallic homogeneous hydroformylation, Stanley has a thorough review (Stanley, 1998). In Section 2.3, we have mentioned the work by Garland on rapid fragmentation (Garland, 1993), Hidai on Co-Ru (Kayasu et al., 1985; Hidai et al., 1986) and Collman on site-site interaction (Collman et al., 1983) in bimetallic hydroformylation studies. In addition, the most well known bimetallic hydroformylation is the Pt-Sn system for stereoselective synthesis (Haelg et al., 1985). The two leading explanations for the role of Sn are cluster catalysis (a Pt-Sn complex) and Cl abstraction from Pt. In the other studies (Mirbach, 1984; Moser, 1992), the monometallic pathway involving reaction of the acyl intermediate with H_2 has been repeatedly shown to be the dominant catalytic mechanism for 1-alkenes and cyclohexene using cobalt.
With the ligand modified catalysts, in addition to Kalck’s thiolate-bridged rhodium complex (Kalck, 1988), a bimetallic rhodium complex that provides an example of bimetallic cooperativity in hydroformylation catalysis has been reported by Stanley and co-workers (Broussard et al., 1993). They designed a binucleating tetraphosphine ligand that can both bridge and chelate two transition metal centers, producing bimetallic complexes that only have a single, very flexible bridging group. This led Stanley to initially propose a bimetallic cooperativity mechanism involving neutral bimetallic complexes. Since Stanley’s bimetallic system is believed to consist of intermediates having one and the same nuclearity, it belongs to the category of unicyclic mechanisms, and a rate form like Eq 1.5 for CBER should not be observed.

2.5 Total algebraic system identification

In chemical science, in-situ observations of the system are often performed, therefore one or more on-line spectrometers are used to record signal attenuation as a function of frequency. The spectral time series obtained during the reaction contain information about the time dependent concentrations of the reactants, intermediates, and products (Li et al., 2003a). Therefore, a systematic and general methodology for the effective analysis and interpretation of complex-mixture spectroscopic information to gain physically and chemically meaningful insight into reactive systems is of considerable importance (Malinowski, 1991). This methodology can be called total algebraic system identification which includes two primary goals

1. **Goal A**: Determine the number of observable species \( s \), and the pure component spectra of all these observable species \( a_{sv} \) using the spectroscopy measurements.
2. **Goal B**: Given initial conditions on the amount of reagents put into the system, determine the time dependent moles of all observable species $N_{ke}$, the total number of observable reactions, the reaction stoichiometries $v_{rx}$, and their extents of reactions $\xi_{ke}e$.

There have been many studies in this area such as the studies by Furusjo and Danielsson (1998), Bijlsma, et al. (1998, 1999, 2000), de Juan, et al. (2001), and Thurston and Brereton (2002). However, in these studies, kinetic constraints (a priori knowledge of the reaction orders or reaction models) are imposed at the outset on the multivariate analysis, to determine pure component spectra, concentration profiles, and reaction rate constants.

Garland’s group has worked in the total algebraic system identification for more than 10 years (Garland et al., 1997; Zeng and Garland, 1998; Pan and Garland, 2000; Chen and Garland, 2001, 2002, 2003; Chew et al. 2002, 2003; Widjaja et al., 2002, 2003). For Goal A, a novel approach namely Band-Target Entropy Minimization (BTEM) was recently developed (Chew, et al., 2002, Widjaja et al., 2002, 2003, Li et al., 2002). It is an advanced and model-free deconvolution technique based on a Shannon information entropy criterion (Shannon, 1948).

Principally, BTEM’s approach starts with the data decomposition of a set of spectroscopic mixture data using singular value decomposition. It is followed with the transformation of the right singular vectors that span the spectral observations into individual pure component spectrum one at a time. The transformation is processed with the conditions, [a] to retain the selected spectral feature readily observed in the right
singular vectors, which was called as band-target, and \[ b \] to achieve the global minimum of the proposed objective function.

Due to its general characteristics, BTEM has been successfully applied to resolution of various spectroscopic data, such as FTIR, Raman (Ong et al., 2003), NMR (Widjaja et al., 2003), and MS (Zhang et al., 2003) and XRD. The success is not limited to major components having large signal intensities, but more importantly, it is able to retrieve extremely weak pure component spectra, e.g. corresponding to species with less than 0.07% of the integral intensity of the entire spectroscopic data set. Excellent examples of its unique capability include the identification of the long sought after and elusive metal carbonyl hydride HRh(CO)\(_4\) (Li et al., 2002) and its application to complex randomized mixtures of six components (Widjaja et al., 2003). Subsequently, another approach was developed to solve the algebraic inverse problem for Goal B (Widjaja et al., 2003). This novel technique is primarily based on finding the optimum diagonal matrix that will give rise to the real magnitude of absorptivities of all observable species, and in turn, using multiple linear regression, the mole numbers of these species can be obtained. Subsequently, hypothesized reaction stoichiometries can be tested one-at-a-time. The performance of this methodology has been successfully implemented on various real experimental mixtures (Li et al., 2002, 2003; Widjaja, et al., 2002, 2003, Chew, 2002, 2003).

2.6 Summary

The possible existence of catalytic binuclear elimination reactions is particularly exciting from both a synthetic as well as kinetic viewpoint. Bimetallic CBER would constitute a well-defined reaction topological basis for synergism. However, the evidence
for the existence of bimetallic CBER until now seems circumstantial at best (Beletskaya et al., 1989, 1990). Since, the spectroscopic and kinetic aspects of the unmodified rhodium catalyzed hydroformylation of several alkenes have been systematically investigated in detail, these systems provide good starting points for adding a second metal. Most catalytic systems involving one product have been found to support the classic unicyclic hydroformylation mechanism. The philosophy of the present work was to search for bimetallic CBER in the unmodified rhodium catalyzed hydroformylation of alkenes (3,3-dimethylbut-1-ene and cyclopentene, the reactions of both are very regio/chemo-selective, yielding the aldehyde 4,4-dimethylpentanal and cyclopentane carboxaldehyde), promoted with other metal complexes, with the aid of total algebraic system identification, and in situ spectroscopic and kinetic measurements. The reaction conditions were chosen to ensure lack of mass transfer effects (Garland, 2002).
3.1 Introduction

A chemist cannot but wonder at the mechanisms of chemical reactions and how to improve or apply a reaction based on an understanding of mechanism. In-situ spectroscopic experiments would make this natural curiosity much easier and would lead to improved catalysts and processes (Whyman, 1992; James, 2002). Particularly, for homogeneous catalysis, in-situ spectroscopic measurements of such batch reactions could determine the instantaneous concentrations of both the organometallic intermediates and the organic species present. Therefore, the detailed kinetics could be modeled.

A number of chemometric tools can be applied to the in-situ data obtained to identify the number of observable species, reactions and fluxes in such systems, and the reaction stoichiometries involved. This would lead to better understanding of the kinetics of such systems in greater detail and in turn improve its ability to control chemoselectivity, regioselectivity and even stereoselectivity in the synthesis of value-added fine chemicals and pharmaceuticals.

This chapter covers the experimental work and the methodological development, which will be employed in the next three chapters for in-situ FTIR studies of bimetallic catalyzed hydroformylation of alkenes to search for the bimetallic catalytic binuclear elimination reaction (CBER). This chapter includes three major sections. [1] The apparatus and procedures for in-situ FTIR studies of bimetallic catalyzed hydroformylation of alkenes are briefly described; [2] A newly developed chemometric algorithm called total system identification is introduced; [3] The total system
identification is applied to two homogeneous reaction systems (catalytic and stoichiometric) to check the feasibility of this method to analyze the in-situ FTIR data.

3.2 Experimental section

3.2.1 General information

Since all of the metal complexes (Rh₄(CO)₁₂, HMn(CO)₅, Mn₂(CO)₁₀ and HRe(CO)₅) used in the experiments are oxygen, moisture and light sensitive, standard Schlenk techniques (Shriver and Drezdzon, 1986) were employed in the experiments. All solution preparations and transfers were carried out under purified argon (99.9995%, Saxol, Singapore) atmosphere. The argon was further purified before use by passing it through a column containing 100g of reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieves to adsorb trace oxygen and water respectively. Purified carbon monoxide (Research grade, 99.97%, Saxol, Singapore), purified hydrogen (99.9995%, Saxol, Singapore) and purified deuterium (99.7%, Messer) were also further purified through a de-ox and zeolite column before they were used in the hydroformylation experiments.

Weights were measured with a precision of 0.01mg. Volumes were measured with a precision of 0.05 ml. Further microanalytic techniques were not employed (Cheronis, 1954; Ma and Horak, 1976).

3.2.2 Chemicals

Rh₄(CO)₁₂ (98%) was purchased from Strem Chemicals (Newport,MA,USA) and was used as obtained. Mn₂(CO)₁₀(98%) was also purchased from Strem Chemicals and was used without further purification. MnH(CO)₅ was prepared using a modified literature
preparation (Byers and Brown, 1977). The HRe(CO)₅ was custom synthesized by Strem Chemicals. The quoted purity was 99%. The infrared spectrum of this product was measured in hexane. The spectrum was very clean. The product was used as obtained.

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 cyclopentene (Fluka AG) obtained for this study has a purity of 98.5%. To remove the trace possible dienes in it, the cyclopentene was firstly refluxed with 2 equiv of maleic anhydride (99%, Fluka AG) for two hours. 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 in a refrigerator. The resulting purity of the cyclopentene was 99.99%, as determined by GC analysis (HP6890; HP-1 Methyl Siloxane Capillary Column, 100°C; FID, 250°C).

The Puriss quality n-hexane (99.6%, Fluka AG) was distilled from sodium-potassium alloy under purified argon for circa 5 hours to remove the trace water and oxygen.

### 3.2.3 Experiment apparatus and procedure

#### 3.2.3.1 Photo-irradiation

Figure 3.1 is a schematic diagram of the photo-irradiation system. The reaction was performed in a 50 ml Schlenk tube with a magnetic stirrer and a gas distributor inside. H₂ and or CO was further purified before entering the Schlenk tube by passing it through a column containing 100g of reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieves to adsorb trace oxygen and water respectively. The H₂/CO flow rate was monitored by the oil bubblers. The UV source is a 450W Mercury-Vapor Lamp.
(Model 7825-34, ACE Glass, Vineland, NJ). Cooling water was used to cool down the immersion well.

The Schlenk tube and the UV lamp were shielded by a safety reaction cabinet.
HMn(CO)₅ was prepared using a modified literature preparation (Byers and Brown, 1977). The reaction involves the interaction of H₂ with Mn₂(CO)₁₀ according to equation 3.1.

\[
\text{Mn}_2(\text{CO})_{10} + \text{H}_2 + h\nu \rightarrow 2\text{HMn(CO)}_5
\]  

(3.1)

The standard procedure is as follows. Circa 100 mg Mn₂(CO)₁₀ was dissolved in 50 ml n-hexane in a Schlenk tube. The solution was firstly saturated with H₂ and a little CO for circa 15 minutes at room temperature and then irradiated with an immersion lamp. Trace CO is needed during photo-irradiation in order to prevent total decomposition of the manganese carbonyl and hydride. After ten minutes, 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 (circa 25%) of HMn(CO)₅ appeared around 70 minutes and further irradiation would give some yellow precipitate. It was also found that the reproducibility of this photo reaction was not ideal, so the HMn(CO)₅ concentrations for each experiment are somewhat different from run-to-run [note: this has no detrimental effect on the quality of the catalytic data or its analysis since all concentrations can be measured in-situ]. This point will be illustrated in the kinetic analysis. Since the HMn(CO)₅ is very unstable, the HMn(CO)₅ solution was immediately transferred under CO/argon to the autoclave after photo-irradiation.

3.2.3.2 In-situ FTIR

In-situ kinetic studies were performed in a 1.5 L stainless steel (SS316) autoclave (P_max=22.5 MPa, Buchi-Uster, Switzerland) which was connected with a high pressure
infrared cell. Figure 3.2 is a schematic diagram of the batch reactor and the circulation system. The system is the same as that used by Garland and co-workers (Feng et al, 1999a). The autoclave is 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 mixtures were circulated from the autoclave to-and-from the high pressure IR cell with a high membrane pump (Model DMK 30, Orlita AG, Geissen Germany) with a maximum rating of 32.5MPa 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 ($\Delta t \leq 0.5K$) for the range 280-320K. Temperatures are measured at the cryostat and the autoclave with PT-100 thermoresisters. The necessary connections to vacuum and gases were made with 1/4 inch (SS316) high-pressure tubing (Autoclave Engineers) and 1.0, 5.0, 10.0 piezocrystals were used for pressure measurements (Keller AG Winterthur, Switzerland). The entire system is 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 window (Korth Monokristalle, Kiel Germany) has dimensions of 40-mm diameter by 15-mm thickness. Two sets of Viton and silicone gaskets provide the necessary sealing, and Teflon spacers are used between the windows. The construction of the flow through the cell is a variation on the design by Noack (1968) and differs in some respect from other high-pressure infrared cells (Whyman, 1987). This high-pressure infrared cell was situated in a Perkin-Elmer SPECTRUM 2000 FT-IR spectrometer. The spectral resolution was 4cm$^{-1}$ at an interval of
0.2 cm\(^{-1}\) for the range 1000-2500 cm\(^{-1}\) in this study. Purified nitrogen (99.9995\%, Saxol, Singapore) was used to purge the Perkin-Elmer FT-IR spectrometer system.

Figure 3.2 Schematic diagram of apparatus for in-situ FTIR kinetic studies

Here is a typical experimental procedure. Each experiment was carried out in a similar manner. First, single beam background spectra of the IR sample chamber were recorded. Then 150ml 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 a predetermined 2.0 to 5.0 MPa CO and the infrared spectra of the n-hexane at high pressure were recorded. The stirrer and the high pressure membrane pump were started. After equilibrium, infrared spectra of the n-hexane/CO solution in the high pressure cell were recorded. At this point, alkene (33DMB or cyclopentene) was dissolved in 50-ml n-hexane. It was transferred to the reservoir, pressurized and added to the autoclave. After equilibrium, infrared spectra of the alkene/n-hexane/CO solution in the high pressure cell were recorded. Then a solution of Rh₄(CO)₁₂ dissolved in 50ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurized with CO and then added to the autoclave. After equilibrium, infrared spectra of the Rh₄(CO)₁₂/alkene/n-hexane/CO solution in the high pressure cell were recorded. At this time, the solution of HMn(CO)₅/Mn₂(CO)₁₀ or HRe(CO)₅ in 50ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurized with CO and then added to the autoclave. After equilibrium, infrared spectra of the HMn(CO)₅/Mn₂(CO)₁₀ (or HRe(CO)₅)/Rh₄(CO)₁₂/alkene/n-hexane/CO solution in the high pressure cell were recorded. The hydroformylation kinetic runs were initiated by adding hydrogen. At a time t=0, a program was executed to record the spectra every 2-10 minutes. In every 5-7 hour experiment run, circa 30-150 spectra were taken.
3.3 Total algebraic system identification for the liquid-phase reactive systems

3.3.1 Introduction

Significant progress in the chemical sciences is often highly dependent on extracting meaningful chemical knowledge from large amounts of experimental information - in other words, fully utilizing the human and instrumental resources involved. Recently, a novel approach has been developed by Garland and co-workers for the exploratory chemometric studies of liquid-phase reactive systems based on advanced signal processing and statistical techniques (Garland et al, 1997; Zeng and Garland, 1998; Pan et al, 2000; Chew et al, 2002; Widjaja et al, 2002, 2003; Li et al; 2002, 2003; Chen and Garland, 2003).

In summary, there are three important goals to achieve from the in-situ spectroscopic measurements, namely:

1. Determine the number of observable species S.
2. Obtain the pure component spectra for each observable species.
3. Given data on the amounts of reagents put in the reactor (initial conditions), determine all the reaction stoichiometries, the extents of reaction and the time dependence of all moles.

The above approach is also called system identification, a systematic and general methodology for the effective analysis and interpretation of complex-mixture spectroscopic information to gain physically and chemically meaningful insight into reactive systems.

The algorithm for the total algebraic system identification is summarized in the next section. The details can be found elsewhere (Chew et al, 2002; Widjaja, et al., 2002, 2003; Li et al, 2002, 2003).
3.3.2 Algorithm for total algebraic system identification

All the algorithms were implemented in MATLAB® code. Calculations were carried out on a WinNT Pentium III Xeon Work Station which has two 450 MHz processors with 2 GB RAM.

3.3.2.1 Getting the experimental spectral data

The experimental apparatus and the procedures for the in-situ FTIR spectroscopic studies of liquid phase homogeneous catalytic reactions were described in the experimental section (Section 3.2).

Let \( k \) denote the number of spectra taken in each experiment, \( e \) denotes the experiment numbers, and \( \nu \) is the number of data channels associated with the spectroscopic range, then \( A_{ke\nu} \) represents the consolidated spectroscopic data matrix. Each experiment has an initial condition, i.e. the mole numbers of solvent, reactant and metal complexes that were added in the reactor.

3.3.2.2 Lambert-Beer-Bouguer law

In general, infrared spectroscopy more-or-less obeys the Lambert-Beer-Bouguer law, i.e., the set of spectroscopic measurements of absorbance is related to the optical pathlength \( l_{ke\nu} \), the concentrations \( C_{ke\nu} \) of the \( s \) species present, and the pure component absorptivities \( a_{s\nu} \) for the \( s \). The bilinear form in Eq 3.2 is assumed to be locally valid. Therefore in larger composition regions, the error term \( e_{ke\nu} \) includes experimental and
instrumental error as well as nonlinearities in the Lambert-Beer-Bouguer model (Garland et al, 1997).

\[ A_{kexv} = I_{kexle} C_{kexs} a_{sxv} + \epsilon_{kexv} \]  

(3.2)

### 3.3.2.3 Singular value decomposition (SVD)

The absorbance data matrix \( A_{kexv} \) can be subjected to singular value decomposition (SVD) shown in Eq 3.3, to obtain its abstract orthonormal matrices \( U_{kexle} \) and \( V_{svx}^T \) with its diagonal singular matrix \( \Sigma_{kexv} \). For a system where LBBL is locally valid, the significant right singular vectors \( V_{sxv}^T \), obtained form the SVD of \( A_{kexv} \) contain all the necessary information on absorptivities, and \( V_{sxv}^T \) is therefore an abstract representation of pure component spectra. When the LBBL is locally valid, the error is simply random, but in larger composition regions \( \epsilon_{kexv} \) is a combination of experimental error and spectral nonlinearities (Garland et al, 1997).

\[ A_{kexv} = C_{kexs} a_{sxv} + \epsilon_{kexv} = U_{kexle} \Sigma_{kexv} V_{sxv}^T \]  

(3.3)

In a more general setting, \( A_{kexv} \) can be approximated by Eq 3.4, where \( s \) is the number of species recovered and \( z \) is the number of right singular vectors used for spectral reconstruction. Note that \( T_{szx}^{-1} \) is the generalized inverse for a rectangular matrix, \( \hat{a}_{sxv} \) is the matrix of averaged pure component expectations for \( s \) species, \( \hat{C}_{kexs} \) is its corresponding expectation for concentration calculated from Eq 3.5.

\[ A_{kexv} \approx \hat{C}_{kexs} \hat{a}_{sxv} = U_{kexle} \Sigma_{sxz} T_{szx}^{-1} T_{sxz} V_{sxv}^T \quad ke \geq z \geq s \]  

(3.4)
\[
\hat{C}_{kxs} = U_{kxs} \Sigma_{sxs} T_{sxs}^{-1} = A_{kxs} \hat{a}_z^T \left( \hat{a}_{sxs} \hat{a}_s^T \right)^{-1}
\] (3.5)

3.3.2.4 Pure Component Spectra Reconstruction via BTEM

Band Target Entropy Minimization (BTEM) is a newly developed methodology for pure component spectra reconstruction (Chew et al, 2002; Li et al, 2002; Widjaja et al, 2002; 2003). It has been successfully used to obtain the pure component spectra of species at sub-ppm levels, and species whose features contribute less than circa 0.1% of total signal intensity (Li et al, 2002).

BTEM reconstructs each pure component spectrum \( \hat{a}_{jxs} \), in its norm-1 form, by appropriate transformation of the basis vectors \( V_{zxs}^T \) using Eq 3.6. The seminal concept of BTEM is based on the information entropy theory (Shannon, 1948). The transformation shown as Eq 3.6 requires massive numerical computation and optimization to obtain an optimal solution for the elements of \( T_{jxs} \). In summary, BTEM targets a spectral feature to retain, and then combinations of the basis right singular vectors \( V_{zxs}^T \) are searched to achieve the global minimum value of an appropriate objective function involving entropy. The used objective function for the optimization is associated with Shannon’s information entropy criterion and various physically meaningful constraints are imposed to ensure non-negativity of the pure component spectral estimate and its corresponding concentrations. Detailed descriptions of the BTEM algorithm can be found in references (Chew et al, 2002; Widjaja et al, 2002).

\[
\hat{a}_{jxs} = T_{jxs} V_{zxs}^T
\] (3.6)
3.3.2.5 Data re-normalization

As mentioned above, with BTEM, the pure component spectra are obtained in their norm-1 form. Therefore, from BTEM alone, we can not get the real magnitude of each spectrum. Consequently, they can not be used directly to calculate the mole numbers of each species. Of course, the properly scaled spectra are an absolutely needed pre-requisite for regressing the data and analyzing the reaction kinetics. The following steps are used in order to solve the problem.

Before further data calculations can proceed, an important re-normalization of the spectroscopic data must be performed. Since in the measurement of in-situ FTIR, the reaction volume is not constant for each spectrum and the path length of the in-situ high pressure cell is also varying at different pressures, numerical corrections must be performed. The data re-normalization is used in order to eliminate such dependence of the spectroscopic data on the reaction volume and cell-path length variables. This re-normalization is performed using the solvent n-hexane as the internal standard (Chew, 2003).

From the Lambert-Beer-Bouguer Law (LBBL) model, the absorbance data $A_i$ at the $i$-th wavenumber / channel is, to a very good approximation, a linear combination of optical path length $l$, molar absorptivity $a_{ij}$, and molar concentration $c_j$.

$$A_i = \sum_{j=1}^{s} a_{ij} c_j l = \sum_{j=1}^{s} a_{ij} (n_j / V) l = \sum_{j=1}^{s} a_{ij} n_j / V l$$

(3.7)

where $s =$ number of species, $n_j =$ total number of moles of species $s$, $V =$ reaction volume.
The measured absorbance \( A_i \) can be re-normalized by dividing with \( A_{\omega_o}^{\text{std}} \), which is a standard absorbance derived from a reference species (n-hexane) at a certain reference maximum (wavenumber \( \omega \)).

\[
A_{\omega_o}^{\text{std}} = \frac{a_{\omega_o}^{\text{std}} n_{\text{std}}}{V}
\]

\[
\frac{A_i}{A_{\omega_o}^{\text{std}}} = \sum_{j=1}^{s} \left\{ \frac{a_j n_j}{V} \times \left( \frac{V}{a_{\omega_o}^{\text{std}} n_{\text{std}}^l} \right) \right\} = \sum_{j=1}^{s} \left\{ \frac{a_j n_j}{a_{\omega_o}^{\text{std}} n_{\text{std}}^l} \right\}
\]

\[
\frac{a_{\omega_o}^{\text{std}} n_{\text{std}}}{A_{\omega_o}^{\text{std}}} A_i = \sum_{j=1}^{s} (a_j n_j) = A_i^{\text{Dml}}
\]

The internal standard \( \Gamma \) is defined as,

\[
\Gamma = \frac{V}{l} = \frac{a_{\omega_o}^{\text{std}} n_{\text{std}}}{A_{\omega_o}^{\text{std}}}
\]

By multiplying this scalar value \( \Gamma \) with \( A_i \), the modified data \( A_i^{\text{Dml}} \) can be obtained.

\[
A_i^{\text{Dml}} = \Gamma A_i = \sum_{j=1}^{s} a_j n_j
\]

\subsection*{3.3.2.6 Real spectral absorptivities and mole numbers}
As mentioned before, the reconstructed pure component spectra obtained with BTEM are in normalized form, therefore, a diagonal weighting matrix $d_{sx} \times d_{sx}$ is needed to scale the pure component spectra to their real magnitudes, namely, the absorptivities.

\[
A_{k\times \nu}^{Dml} = N_{k\times \nu} a_{s\times \nu} = N_{k\times \nu} d_{s\times \nu} \hat{a}_{s\times \nu}
\]  

(3.13)

If the absorbance matrix $A_{k\times \nu}^{Dml}$ and pure spectra estimates are known, the time dependence of the moles of all species $N_{k\times \nu}$ can be solved as an inverse problem (Ebert et al, 1981; Deuflhard and Hairer, 1983), which is shown in Eq 3.14. $[\hat{a}_{s\times \nu}]^+$ is the pseudo-inverse matrix of $\hat{a}_{s\times \nu}$, and $(d_{s\times \nu})^{-1}$ is the inverse matrix of $d_{s\times \nu}$.

\[
N_{k\times \nu} = A_{k\times \nu}^{Dml} [\hat{a}_{s\times \nu}]^+ (d_{s\times \nu})^{-1}
\]  

(3.14)

In the next procedure, the mass balance principle is applied to get the real absorptivities for each pure component spectrum. Since in a batch reaction, the reaction system is closed, the mole numbers of each element (or appropriate chemical group) will remain constant. Therefore, such a material balance criterion can be employed to optimize the diagonal matrix $d_{s\times \nu}$. The estimated moles of elements (or chemical groups) throughout the reaction period $\overline{N}_{ke\times E}$ can be calculated as a linear combination of moles of species $N_{ke\times \nu}$ and the atomic matrix $\nu_{s\times \nu}$.

\[
\overline{N}_{ke\times E} = N_{ke\times \nu} \nu_{s\times \nu}
\]  

(3.15)
For each experiment, the input of the initial mole numbers of solvent, reagents and precursors are known, therefore the atomic / chemical group matrix $N_{ke\times E}$ is ready to obtain. A least square approach / sum of square error function minimization between $\bar{N}_{ke\times E}$ and $N_{ke\times E}$ is applied to optimize $d_{s\times s}$.

$$\text{Min } G = \sum_{ke} \sum_{E} \left( \bar{N}_{ke\times E} - N_{ke\times E} \right)^2$$

w.r.t $d_{s\times s}$

(3.16)

After obtaining $d_{s\times s}$, the real spectral absorptivities and mole numbers for all species can be calculated accordingly.
3.4 Application of total algebraic system identification algorithm to a semi-batch homogeneous catalytic reaction

3.4.1 Introduction

In this section, we now apply the system identification/BTEM algorithm to a homogeneous catalytic reaction; namely, the well-studied unmodified rhodium catalyzed hydroformylation of alkenes - specifically using 3,3-dimethylbut-1-ene as substrate, to determine the feasibility and/or limitations of the procedure. The above reaction is one of the most studied homogeneous catalysed reactions (Garland and Pino, 1991).

In organometallic chemistry, especially in homogeneous catalysis, multiple experimental runs are usually employed. These multiple experimental runs are very time consuming and resource expensive. The resource may include spectrometer time, the precious complexes, ligands and reagents etc. In our previous studies (Widjaja, et al, 2002), we reported that multiple semibatch data could be used for system identification. Indeed, a single semi-batch experiment is considerably more frugal with resources, but at the same time, the data obtained at multiple reaction conditions will span the vector space of observables. In addition to the application of the system identification/BTEM algorithm, the present work will also check the potential of a single semi-batch analysis with a proper experimental design.

3.4.2 Experimental work

The chemicals and the detailed experiment equipment were introduced in the experimental section (Section 3.2). The single semi-batch experiment was performed in the following procedure. First 150 ml n-hexane was transferred under argon to the autoclave. The total system pressure was raised to 1.0 MPa CO, and the stirrer and high-
pressure membrane pump were started. A solution of 3.3 ml 3,3-dimethylbut-1-ene (33DMB) dissolved in 50ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurised with CO and then added to the autoclave. A solution of 36 mg Rh₄(CO)₁₂ dissolved in 50ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurised with CO and then added to the autoclave. 1.0 MPa hydrogen was then added to initiate the synthesis. In-situ spectra were recorded at 0.2 cm⁻¹ interval in the range 1000-2500 cm⁻¹ with a resolution of 4 cm⁻¹ every 4 minutes.

After 15 spectra were taken in the first step, the partial pressure of carbon monoxide was increased to 2.0MPa to start the second step and then circa 15 spectra were taken. In the following steps, the partial pressures of carbon monoxide and hydrogen, the loadings of precursor (Rh₄(CO)₁₂), reagent (33DMB), solvent(n-hexane) and the reaction temperature were changed according to the experimental design as shown as in Table 3.1. A total of 11 steps were performed and a total of 158 spectra were obtained for the spectral analysis.
### Table 3.1 Experimental design for a Single 11-step Semi-Batch Hydroformylation

<table>
<thead>
<tr>
<th>Step</th>
<th>$P_{\text{H}_2}$</th>
<th>$P_{\text{CO}}$</th>
<th>$\text{Rh}<em>4(\text{CO})</em>{12}$</th>
<th>33DMB</th>
<th>Hexane</th>
<th>T</th>
<th># Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>36.0</td>
<td>3.3</td>
<td>200</td>
<td>293</td>
<td>1 – 15</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>2.0</td>
<td>36.0</td>
<td>3.3</td>
<td>200</td>
<td>293</td>
<td>16 – 28</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>2.0</td>
<td>36.0</td>
<td>3.3</td>
<td>200</td>
<td>293</td>
<td>29 – 45</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>2.0</td>
<td>83.0</td>
<td>3.3</td>
<td>250</td>
<td>293</td>
<td>46 – 59</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>2.0</td>
<td>83.0</td>
<td>3.3</td>
<td>250</td>
<td>293</td>
<td>60 – 75</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>3.0</td>
<td>83.0</td>
<td>3.3</td>
<td>250</td>
<td>293</td>
<td>76 – 91</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>3.0</td>
<td>83.0</td>
<td>6.8</td>
<td>300</td>
<td>293</td>
<td>92 – 106</td>
</tr>
<tr>
<td>8</td>
<td>3.0</td>
<td>3.0</td>
<td>83.0</td>
<td>6.8</td>
<td>300</td>
<td>298</td>
<td>107 – 120</td>
</tr>
<tr>
<td>9</td>
<td>3.0</td>
<td>3.0</td>
<td>83.0</td>
<td>6.8</td>
<td>350</td>
<td>298</td>
<td>121 – 135</td>
</tr>
<tr>
<td>10</td>
<td>4.0</td>
<td>3.0</td>
<td>83.0</td>
<td>6.8</td>
<td>350</td>
<td>298</td>
<td>136 – 149</td>
</tr>
<tr>
<td>11</td>
<td>4.0</td>
<td>4.0</td>
<td>83.0</td>
<td>6.8</td>
<td>350</td>
<td>298</td>
<td>150 - 158</td>
</tr>
</tbody>
</table>

### 3.4.3 Results and discussion

#### 3.4.3.1 Spectral analysis

Figure 3.3 presents a typical in-situ reaction spectrum. Figure 3.3 indicates that the signal contributions in the region of 1000 – 1550 cm$^{-1}$ are almost exclusively from background and solvent. The transmission is very low in this region. Thus the spectral data in this range will be excluded for the spectral analysis. However, the peak of hexane (the internal standard) at 1137 cm$^{-1}$ was used to do data re-normalization to eliminate the dependence of the cell path length and the reaction volume.
Since 158 spectra were obtained in the single semi-batch experiment, the data set can be written as a matrix of $A_{158 \times 4751}$ (4751 represents the wavenumber in the range of 1550 – 2550 cm$^{-1}$ with 0.2 cm$^{-1}$ interval). $A_{158 \times 4751}$ was then subject to singular value decomposition (SVD) to yield the orthonormal matrices $U_{158 \times 158}$ and $V_{4751 \times 4751}^T$, and the diagonal singular value matrix $\Sigma_{158 \times 4751}$. Since there are only 158 experimental spectra, the absorbance matrix could be expressed using truncated vectors as follows.

$$A_{158 \times 4751} = U_{158 \times 158} \Sigma_{158 \times 158} V_{158 \times 4751}^T$$

(3.17)

![Figure 3.3](image)

**Figure 3.3** A typical in-situ reaction spectrum in the hydroformylation of 33DMB

### 3.4.3.2 SVD results-$\mathbf{V^T}$ vectors

Figures 3.4 and 3.5 show eight of the first 14 $\mathbf{V^T}$ vectors and Figure 3.6 presents the 20$^{th}$, 40$^{th}$, 100$^{th}$ and 158$^{th}$ $\mathbf{V^T}$ vectors. As shown in the above figures, the right singular vectors in the $\mathbf{V^T}$ matrix are ranked according to their contribution to the total variance in the observations. Therefore, the first vector in Figure 3.4 is just the average spectrum -
which clearly shows all the components, and therefore appears very similar to the real reaction spectrum as shown in Figure 3.3. The contribution of each additional right singular vector $V^T$ to the total variance of the data set monotonically decreases. Figure 3.6 indicates that the signal-to-noise level is low in the $20^{th}$ and $40^{th}$ vectors, and essentially only randomly distributed white noise can be identified in the last two right singular vectors ($100^{th}$ and $158^{th}$).

![Figure 3.4 First several $V^T$ vectors (1-6)](image)

**Figure 3.4** First several $V^T$ vectors (1-6)
Figure 3.5 Another several $V^T$ vectors (8-14)

Figure 3.6 Last several $V^T$ vectors
3.4.3.3 Pure component spectral reconstruction with BTEM

Ten significant extrema labelled 1-9 (Figures 3.4 and 3.5) were selected from the first fourteen $V^T$ vectors to use BTEM approach to recover the pure components. Table 3.2 lists the selected wavenumber regions, maximum peak absorbance, number of $V^T$ vectors taken for spectral reconstruction and the identity of resolved pure component spectrum.

<table>
<thead>
<tr>
<th>#</th>
<th>Species</th>
<th>$#V^T$ vectors, $z$</th>
<th>Wavenumber region, cm$^{-1}$</th>
<th>Maximum Abs, $\alpha$</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>n-Hexane</td>
<td>25</td>
<td>1550 – 1552</td>
<td>1</td>
<td>Dissolved CO</td>
</tr>
<tr>
<td>2.</td>
<td>Moisture</td>
<td>25</td>
<td>2135 – 2140</td>
<td>1</td>
<td>Moisture</td>
</tr>
<tr>
<td>3.</td>
<td>44DMP</td>
<td>25</td>
<td>1558 – 1560</td>
<td>1</td>
<td>44DMP</td>
</tr>
<tr>
<td>4.</td>
<td>33DMB</td>
<td>50</td>
<td>1733 – 1735</td>
<td>1</td>
<td>33DMB</td>
</tr>
<tr>
<td>5.</td>
<td>444DMP</td>
<td>50</td>
<td>1733 – 1735</td>
<td>1</td>
<td>444DMP</td>
</tr>
<tr>
<td>6.</td>
<td>1640 – 1644</td>
<td>50</td>
<td>1640 – 1644</td>
<td>1</td>
<td>1640 – 1644</td>
</tr>
<tr>
<td>7.</td>
<td>2038 – 2040</td>
<td>50</td>
<td>2038 – 2040</td>
<td>5</td>
<td>2038 – 2040</td>
</tr>
<tr>
<td>8.</td>
<td>Rh$_4$((\sigma)-CO)$_9$((\mu)-CO)$_3$</td>
<td>50</td>
<td>2038 – 2040</td>
<td>5</td>
<td>Rh$_4$((\sigma)-CO)$_9$((\mu)-CO)$_3$</td>
</tr>
<tr>
<td>9.</td>
<td>2M33DMB</td>
<td>50</td>
<td>2038 – 2040</td>
<td>5</td>
<td>2M33DMB</td>
</tr>
</tbody>
</table>

Both major components (hexane, dissolved CO, and H$_2$O), mediate components 4,4-dimethylpentanal (44DMP), 33DMB, Rh$_4$(\(\sigma\)-CO)$_9$(\(\mu\)-CO)$_3$, RCORh(CO)$_4$, and minor ( Rh$_4$(\(\sigma\)-CO)$_{12}$ (Widjaja et al, 2002), and 2-methyl,3,3-dimethylbutanal (2M33DMB)) are resolved. These pure component spectral estimates are shown in Figures 3.7,3.8 and 3.9. Table 3.3 gives the peak position comparison between results obtained from BTEM reconstructions and from previous studies.
Table 3.3 Peak position comparison with the results from previous studies

<table>
<thead>
<tr>
<th>Species</th>
<th>Band maxima, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present results</td>
</tr>
<tr>
<td>33DMB</td>
<td>1590.2 1642.4 1679.4</td>
</tr>
<tr>
<td></td>
<td>1824.6</td>
</tr>
<tr>
<td>44DMP</td>
<td>1734.2</td>
</tr>
<tr>
<td>Rh(_4)((\sigma)-CO)(_9)((\mu)-CO)(_3))</td>
<td>1885.8 2043.8 2070.0</td>
</tr>
<tr>
<td></td>
<td>2074.4</td>
</tr>
<tr>
<td>RCORh(CO)(_4)</td>
<td>1703.2 2021.4 2039.6</td>
</tr>
<tr>
<td></td>
<td>2066.0 2112.2</td>
</tr>
<tr>
<td>Rh(<em>4)((\sigma)-CO)(</em>{12}))</td>
<td>2068.2 2076.4</td>
</tr>
<tr>
<td>2M33DMB</td>
<td>1723</td>
</tr>
</tbody>
</table>

\(^{a}\) ---- obtained from independent experimental work

\(^{b}\) ---- using different type of FTIR(PE 983)
Figure 3.7 Three major components reconstructed with BTEM

n-hexane

CO

moisture
Figure 3.8 Four mediate components reconstructed with BTEM

Figure 3.9 Two minor components reconstructed with BTEM
From Figures 3.7-3.9 and Table 3.3, it can be observed that all reconstructed pure component spectra are consistent with the spectra obtained in previous studies from both batch experimentals and multi-experiments/three semi-batch experiments (Garland, 1989, Widjaja, 2002, Li, 2003). The spectral similarities of the estimates with the references are very high. It can also be seen that most of the resolved pure spectra are smooth except for Rh₄(σ-CO)₁₂ and 2M33DMB which are in very low concentrations in the reaction mixture.

Some spectral artefacts, particularly in the last two components mentioned, are clearly seen in the noisy baseline features. In addition, the estimate of Rh₄(σ-CO)₁₂ shows some localized absorbance at ca. 1642, 1734, 1885 and 2041 cm⁻¹, which are associated with 33DMB, 44DMP, and Rh₄(σ-CO)₆(µ-CO)₃. The estimate of 2M33DMB also shows a localized signal at 2070 cm⁻¹, which corresponds to Rh₄(σ-CO)₆(µ-CO)₃. Artefacts are frequently observed in spectroscopic studies, particularly when spectral subtractions are performed on non-stationary bands and when spectral reconstruction attempts are made on minor components with very low signal intensity (just above noise level). However, these spectral artefacts often do not seriously prevent identification since the primary bands are usually well resolved. It should be noted that this problem of artefacts is essentially eliminated if more experimental spectra are measured. Indeed, in a previous study with 475 experimental spectra, even trace components representing only 0.15% of the integrated signal were recovered with no noticeable artifacts (Li, et al, 2003). The total integrated intensities for the major and minor species are shown in Table 3.4. The effort to recover Rh₆(CO)₁₆ was unsuccessful.
Table 3.4  Percentage of integrated absorbance of each component compared to the total original experimental data

<table>
<thead>
<tr>
<th>Component</th>
<th>Integrated Intensity of each component, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>65.8</td>
</tr>
<tr>
<td>Dissolved CO</td>
<td>28.0</td>
</tr>
<tr>
<td>Moisture</td>
<td>1.9</td>
</tr>
<tr>
<td>44DMP</td>
<td>2.8</td>
</tr>
<tr>
<td>33DMB</td>
<td>1.3</td>
</tr>
<tr>
<td>Rh₄(σ-CO)₆(µ-CO)₃</td>
<td>0.8</td>
</tr>
<tr>
<td>RCORh(CO)₄</td>
<td>1.9</td>
</tr>
<tr>
<td>Rh₄(σ-CO)₁₂</td>
<td>0.05</td>
</tr>
<tr>
<td>2M33DMB</td>
<td>0.23</td>
</tr>
<tr>
<td>Total</td>
<td>102.7</td>
</tr>
</tbody>
</table>

The data above indicates that only circa 8% of the overall spectroscopic signals are due to the medium and minor components. Furthermore, Rh₄(σ-CO)₁₂ and 2M33DMB, contribute to less than 0.3% of the overall signals. This is an independent confirmation that these two components are very minor components in this reaction system. The total intensity ca. 103% is due to the fact that the reconstructed pure component spectra are mean representations over all observations (bands are usually just a little bit broader). Thus, pure component spectral estimates have slightly larger integrated intensities than any particular true component spectrum.
3.4.3.4 Data re-normalization

As discussed in the Section 3.3, the raw experimental absorbance data matrix must be re-normalized to eliminate variable reaction volume and variable path length dependency.

The standard $A_{\omega}^{std}$ used for each reaction spectrum is obtained from the solvent n-hexane’s absorbance data at a reference wavenumber $\omega = 1137$ cm$^{-1}$. In addition, the moles of solvent n-hexane used $n_{std}$ can be calculated from its initial prepared volume and the experimental molar absorptivity of n-hexane (2.18 L/(mole$\cdot$cm)) at $\omega = 1137$ cm$^{-1}$.

3.4.3.5 Real IR absorptivities and time dependent moles

The initial moles of reagents put into the reactor are known and the normalized pure spectral estimates are obtained via BTEM as above. Therefore, a reaction invariant model was set up to calculate the real magnitude of absorptivities according to Eq 3.16.

Since the concentrations of Rh$_4$(\(\sigma\)-CO)$_{12}$ and 2M33DMB are very low, these two components are not included in the regression (their contribution to the mass balances is negligible). Therefore, in the present rhodium catalyzed hydroformylation of 33DMB, only the two organometallics species Rh$_4$(\(\sigma\)-CO)$_9$(\(\mu\)-CO)$_3$ and RCORh(CO)$_4$ contain Rh-, and only 33DMB, 44DMP and RCORh(CO)$_4$ contain the organic fragment (Org-) (CH$_3$)$_3$CCHCH$_2$. Accordingly, the chemical group matrix was used to do the mass balance. In other words, the rhodium (Rh-) is conserved in the liquid phase and as is the organic fragment (Org-) (CH$_3$)$_3$CCHCH$_2$. 


Since there are seven primary observable species in the spectroscopic data - n-hexane, dissolved CO, H$_2$O, 44DMP, 33DMB, Rh$_4$(σ-CO)$_9$(μ-CO)$_3$, and RCORh(CO)$_4$, - a chemical group matrix $v_{sxE}$ can be constructed as follows.

$$v_{sxE} = \begin{bmatrix}
0 & 0 \\
0 & 0 \\
0 & 0 \\
0 & 1 \\
0 & 1 \\
4 & 0 \\
1 & 1
\end{bmatrix}$$

(3.18)

Because there are no Rh- and Org- groups in n-hexane, dissolved CO, or H$_2$O (note also that this last component is not in the liquid phase system), the corresponding matrix elements are zero. Thus, in the present context, it is not possible to calculate the real magnitudes of the absorptivities for these latter three components. However, their inclusion in the $d_{sx}$ optimization is important, since a full spectral range fitting is performed using multiple linear regression to estimate the moles of all species. All primary and significant pure component spectra are required in the calculation.

The number of decision variables in the diagonal matrix $d_{sx}$ is only 4, and these correspond to 44DMP, 33DMB, Rh$_4$(σ-CO)$_9$(μ-CO)$_3$, and RCORh(CO)$_4$. The weightings for the first three components \{d(1,1), d(2,2), and d(3,3)\} (corresponding to n-hexane, dissolved CO, and H$_2$O) were assigned arbitrary non-zero numbers of a proper magnitude to prevent matrix ill-conditioning. The downscaling factor $10^{-2}$ was also applied to the 2$^{nd}$ column of the $N_{kevE}$ matrix which is associated with the group Org-. The purpose was to adjust the magnitude of both columns since Org- is roughly 100 times larger than Rh-. 
With this adjustment, it was expected that the numerical sensitivity would be minimized and that good optimal values of $d_{y,x}$ could be obtained.

The minimization of the sum of square error function was performed using Corana’s SA (Corana et al, 1987). Upon attaining the optimum values of $d_{y,x}$, the properly scaled absorptivities of these pure component spectra can be calculated. Furthermore, the moles of these primary species can also be obtained by a pseudo-inverse calculation. The maximum absorbance of the properly scaled pure component spectra are shown in Table 3.5, and the moles of all species are presented in Figure 3.10. As shown in Table 3.5, the calculated absorptivities are quite close to the results obtained from other studies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Max Peak, cm(^{-1})</th>
<th>Absorptivities, L/(mole⋅cm) (present results)</th>
<th>Absorptivities L/(mole⋅cm) (other studies)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44DMP</td>
<td>1734.2</td>
<td>264.7</td>
<td>303.5(^a) 360(Garland 1991)(^b)</td>
</tr>
<tr>
<td>33DMB</td>
<td>1642.6</td>
<td>37.9</td>
<td>41.6(^a) 41.6(^a) 50(Garland, 1991)(^b)</td>
</tr>
<tr>
<td>Rh(_4)(σ-CO)(_3)(μ-CO)(_3)</td>
<td>2070</td>
<td>15680</td>
<td>15713(Liu, 2002) 15517 (^a) ()</td>
</tr>
<tr>
<td>RCORh(CO)(_4)</td>
<td>2021.4</td>
<td>4657.6</td>
<td>4569.2 (^a) ()</td>
</tr>
</tbody>
</table>

\(^a\)----obtained from independent experimental work

\(^b\)----using different type of FTIR(PE983)
3.4.4 Discussion

The total algebraic system identification was successfully applied to a well known reactive system, namely, the unmodified rhodium catalysed hydroformylation of 33DMB. All pure component spectra, both major and minor components, could be effectively recovered with good quality using the BTEM algorithm. Based on an invariant model of the reaction system, the absorptivities of the primary observable components such as 44DMP, 33DMB, \( \text{Rh}_4(\sigma\text{-CO})_9(\mu\text{-CO})_3 \), and \( \text{RCORh(CO)}_4 \) were regressed and accordingly the mole numbers of each species could be obtained. It should be pointed out that the
The present methodology may be limited to species with ppm concentrations or above for spectral reconstruction from in-situ FTIR.

The present results also demonstrate that only a few well-planned perturbations of a reaction system (in this case it is an 11-step single semi-batch) are needed for spectral reconstruction. The reasoning is that a proper experimental design of a reactive system ensures that the vector spaces of observations are properly spanned by the orthonormal right singular vectors.

In this section, the chemometric analyses were performed in the collaboration with Dr Widjaja Effendi.

3.5 Application of total algebraic system identification to a homogeneous stoichiometric reaction

Another really good example of total system identification is provided by the identification of the long sought species HRh(CO)_4. In the interest of conserving thesis space, a reprint of the Angewandte Chemie IE paper is placed in Appendix A.

3.6 Summary

In this chapter, the chemicals, experimental apparatus and procedures for the in-situ FTIR studies on homogeneous catalysis were briefly described first.

Secondly, a newly developed algorithm which is called total algebraic system identification algorithm was introduced. With good experimental design, this methodology was successfully applied to the homogeneous rhodium-catalyzed 3,3-dimethylbut-1-ene hydroformylation reaction and a stoichiometric reaction system of
Rh₄(CO)₁₂ / H₂/D₂ / CO in the solvent n-hexane using in-situ FTIR spectroscopy. The algebraic chemical information retrieved included the number of observable species, the pure component spectra of observable species and the time dependent moles. The results demonstrate that total algebraic system identification algorithm is feasible for rapid and effective spectroscopic system identification of reactive organometallic and homogeneous catalytic systems.

In the next, with this tool of total algebraic system identification and the experimental design approach, we will perform the in-situ FTIR studies of the bimetallic catalyzed hydroformylation of alkenes. A total of seven bimetallic systems (Rh/Mn/DMB, Rh/Mn/Cyclopentene, Rh/Mn/Styrene, Rh/Mn/methylene cyclohexane, Rh/Re/Cyclopentene, Rh/Re/Styrene, and Rh/Re/Methylene cyclohexane) have been studied to search for the bimetallic catalytic binuclear elimination reaction (CBER). In the following three chapters (Chapter 4-Chapter 6), three bimetallic systems (Rh/Mn/DMB, Rh/Mn/Cyclopentene, and Rh/Re/Cyclopentene) will be studied in detail.
CHAPTER 4  \( \text{Rh}_4(\text{CO})_{12}/\text{HMn}(\text{CO})_5 \) BIMETALLIC CATALYZED HYDROFORMYLATION OF 3,3-DIMETHYLBUT-1-ENE

4.1 Introduction

From Chapter 4, we will begin to study the bimetallic catalyzed hydroformylation to search for the evidence of bimetallic catalytic binuclear elimination reaction (CBER). The detailed in situ FTIR experiments will be carried out using the equipment and methods described in Chapter 3. The obtained in situ infrared spectra will be analyzed using the total algebraic system identification method which has been introduced in Chapter 3.

As mentioned in Chapter 2, the unmodified rhodium catalyzed hydroformylation of 3,3-Dimethylbut-1-ene (33DMB) has been well studied and the clean kinetics has been produced. Therefore, this system shall be the good starting point for bimetallic catalyzed hydroformylation studies. Since HMn(CO)_5 has been widely used in stoichiometric binuclear eliminations and it is inert at the present reaction conditions, it will be used as the second metal complex in the bimetallic catalyzed hydroformylation.

The pre-hydroformylation experiments using only \( \text{Rh}_4(\text{CO})_{12}/\text{Mn}_2(\text{CO})_{10}/\text{MnH}(\text{CO})_5 \) under CO/H\(_2\)/Argon in the absence of 33DMB in n-hexane will be studied first. The semi batch experimental design will be used to carry out the experiments and BTEM will be employed to analyze the in situ IR spectra.

Next, a series of well designed experiments will be performed to study the homogeneous hydroformylation of 33DMB with precursors \( \text{Rh}_4(\text{CO})_{12} \) and \( \text{HMn}(\text{CO})_5 \). The obtained in situ infrared spectra will be analyzed with the total algebraic system.
identification method. Subsequently, the spectral analyses, the time-dependent concentration profiles of each species, turnover frequency (TOF) interpretations, the kinetics and catalysis will be studied to search for the evidence of bimetallic CBER.

4.2 Experimental Section

4.2.1 Pre-hydroformylation

7 experiments were performed using only Rh₄(CO)₁₂/Mn₂(CO)₁₀ under CO/H₂/Argon in n-hexane. All the experiments were carried out using the semi-batch algorithm. The experimental design is shown in Table 4.1. All the experiments were performed in a similar manner. First, single beam background spectra of the IR sample chamber were recorded. Then 200 ml n-hexane was transferred under argon to the autoclave. Under 0.2 MPa CO/Argon pressure, infrared spectra of the n-hexane in the high-pressure cell were recorded. The total system pressure was raised to the set pressure, 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 100 mg Mn₂(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 Mn₂(CO)₁₀/HMn(CO)₅/CO/n-hexane solution in the high-pressure cell were recorded. A solution of 50 mg Rh₄(CO)₁₂ dissolved in 50ml n-hexane 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 Rh₄(CO)₁₂/Mn/CO/ n-hexane / solution in the high-pressure cell were recorded. In the next steps, the pressures of CO/H₂ were changed according to Table 4.1. The in-situ spectra were taken every 5-10 minutes in the range of 1000-2500 cm⁻¹.
Table 4.1 Experimental design

<table>
<thead>
<tr>
<th># Expt</th>
<th>Step</th>
<th>$P_{H_2}$, bar</th>
<th>$P_{\text{argon}}$, bar</th>
<th>$P_{\text{CO}}$, bar</th>
<th>Rh$<em>4$(CO)$</em>{12}$, mg</th>
<th>Mn$<em>2$(CO)$</em>{10}$, mg</th>
<th>Hexane, mL</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Semi-Batch Exp.</td>
<td>1</td>
<td>0</td>
<td>4.5</td>
<td>0.5</td>
<td>51.0</td>
<td>103.0</td>
<td>300</td>
<td>25.0</td>
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<tr>
<td></td>
<td>2</td>
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<td>0.5</td>
<td>51.0</td>
<td>103.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11</td>
<td>4.5</td>
<td>0.5</td>
<td>51.0</td>
<td>103.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td>2nd Semi-Batch</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>53.8</td>
<td>105.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>53.8</td>
<td>105.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td>3rd Semi-Batch</td>
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<td>0</td>
<td>5.0</td>
<td>0.5</td>
<td>50.0</td>
<td>104.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>5.0</td>
<td>0.5</td>
<td>50.0</td>
<td>104.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20</td>
<td>5.0</td>
<td>0.5</td>
<td>50.0</td>
<td>104.0</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td>4th Semi-Batch</td>
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<td>0</td>
<td>0</td>
<td>10</td>
<td>51.0</td>
<td>101.0</td>
<td>300</td>
<td>25.0</td>
</tr>
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<td>10</td>
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<td>25.0</td>
</tr>
<tr>
<td>5th Semi-Batch</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>103.0</td>
<td>250</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>48.0</td>
<td>101.0</td>
<td>300</td>
<td>25.0</td>
</tr>
<tr>
<td>6th Semi-Batch</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>50.65</td>
<td>250</td>
<td>50.0</td>
</tr>
<tr>
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<td>2</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>55.87</td>
<td>50.65</td>
<td>300</td>
<td>50.0</td>
</tr>
<tr>
<td>7th Semi-Batch</td>
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<td>0</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>52.80</td>
<td>250</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>49.70</td>
<td>101.0</td>
<td>300</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>49.70</td>
<td>101.0</td>
<td>300</td>
<td>25.0</td>
</tr>
</tbody>
</table>

4.2.2 Hydroformylation

All the experiments were performed in a similar manner. The typical procedure is as following. First, single beam background spectra of the IR sample chamber were recorded. Then 150 ml 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 3,3-
dimethylbut-1-ene (33DMB) dissolved in 50ml 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 Rh₄(CO)₁₂ dissolved in 50ml n-hexane
and a solution of 100 mg Mn₂(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 Rh₄(CO)₁₂/Mn/33DMB /CO/ n-hexane / solution in
the high-pressure cell were recorded. 1.0 MPa hydrogen was then added to initiate the
syntheses. The detailed experimental design for this study is shown in Table 4.2.

Table 4.2 Experimental design

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mn₂(CO)₁₀,mg</th>
<th>CO,MPa</th>
<th>H₂,MPa</th>
<th>33DMB,ml</th>
<th>Rh₄(CO)₁₂,mg</th>
<th>Temperature,K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>103.0</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
<td>51.0</td>
<td>298</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
<td>0</td>
<td>298</td>
</tr>
<tr>
<td>Pure Rh</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
<td>51.6</td>
<td>298</td>
</tr>
<tr>
<td>Pure Mn</td>
<td>105.0</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
<td>0</td>
<td>298</td>
</tr>
<tr>
<td>CO Variation</td>
<td>108.0</td>
<td>1.0</td>
<td>1.0</td>
<td>5</td>
<td>54.0</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>107.0</td>
<td>3.0</td>
<td>1.0</td>
<td>5</td>
<td>53.5</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>109.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5</td>
<td>51.0</td>
<td>298</td>
</tr>
<tr>
<td>H₂ Variation</td>
<td>105.6</td>
<td>2.0</td>
<td>0.5</td>
<td>5</td>
<td>50.7</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>106.0</td>
<td>2.0</td>
<td>1.5</td>
<td>5</td>
<td>51.0</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>104.4</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
<td>55.0</td>
<td>298</td>
</tr>
<tr>
<td>33DMB Variation</td>
<td>108.0</td>
<td>2.0</td>
<td>1.0</td>
<td>2</td>
<td>52.0</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>105.0</td>
<td>2.0</td>
<td>1.0</td>
<td>10</td>
<td>52.0</td>
<td>298</td>
</tr>
<tr>
<td>Rh₄(CO)₁₂ variation</td>
<td>105.0</td>
<td>2.0</td>
<td>1.0</td>
<td>5</td>
<td>26.0</td>
<td>298</td>
</tr>
</tbody>
</table>
The experimental design of the experiments involved 300 ml solvent and the intervals 293-308K, $P_{H_2} = 0.5$-$2.0$ MPa, $P_{CO} = 1.5$-$4.0$ MPa, initial alkene = 2-10ml, initial $\text{Rh}_4(\text{CO})_{12} = 25$-$100$mg and initial $\text{Mn}_2(\text{CO})_{10} = 50$-$200$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) (Garland, 2002). The experimentally measured overall mass transfer coefficients $K_{l_a}$ for hydrogen and carbon monoxide into n-hexane was approximately 0.1 and 0.6 s$^{-1}$ respectively, as determined using the method of Deimling (Deimling et al, 1984), when the stirring speed was at 200 rpm. Since the maximum rate of the hydroformylation in this study was $10^{-5}$ mol/s, the gas-liquid mass transfer control can be ignored in all the experiments. Indeed, the liquid phase of each experiment became essentially saturated with dissolved CO and H$_2$ in the first 60s. Mass transfer effects are well known to severely complicate the kinetics interpretation in the hydroformylation reactions (Bhattacharya and Chaudary, 1987).

Blank experiments, in the presence of organic reactants but without added complexes, were performed throughout the study.
4.3 Spectral analysis for pre-hydroformylation

The pre-hydroformylation spectra were analyzed using BTEM algorithm. Figure 4.1 presents the reconstructed spectra of pure components. As shown in the figure, only four species could be recovered, namely, Mn$_2$(CO)$_{10}$, HMn(CO)$_5$, Rh$_4$(CO)$_{12}$, and Rh$_6$(CO)$_{16}$.

![Figure 4.1](image)

Figure 4.1 The reconstructed pure components in pre-hydroformylation

4.4 Spectral analysis for hydroformylation

The total algebraic system identification algorithm is used to analyse the in-situ FTIR spectra.
4.4.1 Data Pre-Processing

The number of spectra recorded in each experiment was in the range of 28 – 35, thus the 21 experiments gave rise to 713 spectra. A typical raw experimental spectrum before any spectral pre-processing is shown in Figure 4.2.

Figure 4.2 Raw experimental spectrum before any spectral pre-processing

Figure 4.2 shows that the data in the range of 1300 – 1550 cm\(^{-1}\) has a very high, even semi-infinite absorbance. Since there is no particular important information for the organometallic species in this region, this region was excluded for the further processing. Accordingly, two spectral windows with the region of 1000 – 1300 cm\(^{-1}\) and 1550 – 2500 cm\(^{-1}\) are obtained. The first region only contains information for the solvent n-hexane, and the second region contains the spectroscopic information for both the organic and organometallic species.

4.4.2 Preconditioning

The experimental absorbance matrix can be preconditioned to subtract background and solvent. Chen (Chen, 2001; Chen and Garland, 2003) developed the preconditioning
algorithm, which was based on an entropy minimization approach to determine the optimum value of subtraction factor. According to Eq 4.1, each experimental spectrum $A_{\text{exp}}^{\nu \times 1}$ was preconditioned by subtracting (i) the background reference for moisture, $A_{\text{ref, water}}^{\nu \times 1}$, and carbon dioxide, $A_{\text{ref, CO}_2}^{\nu \times 1}$, (ii) the CaF$_2$ cell with n-hexane reference, $A_{\text{cell+hex}}^{\nu \times 1}$, and (iii) dissolved CO reference, $A_{\text{CO}}^{\nu \times 1}$. The coefficients $x_i$ are scalar subtraction factors.

$$A_{\text{exp}}^{\nu \times 1} = A_{\text{exp}}^{\nu \times 1} - \sum_i x_i A_i^{\text{ref}}$$ (4.1)

After subtracting $A_{\text{ref, water}}^{\nu \times 1}$, $A_{\text{ref, CO}_2}^{\nu \times 1}$, $A_{\text{ref, cell+hex}}^{\nu \times 1}$, and $A_{\text{CO}}^{\nu \times 1}$ from the raw spectrum, the preconditioned spectrum $A_{\text{pre, bxv}}^{\nu \times 1}$ was obtained. Figure 4.3 presents the reference spectra used for subtraction, a typical raw reaction spectrum and the preconditioned spectrum. Close inspection indicates that there is no special feature observed in the wavenumber range of 2140 – 2500 cm$^{-1}$ and this region can be omitted; therefore the preconditioned matrix can be reduced to $A_{713 \times 2951}$. 
4.4.3 Baseline Correction

Chen (Chen, 2001; Chen and Garland, 2002, 2003) proposed a simple but automatic baseline correction based on polynomial fitting technique. Using this simple approach, a smooth and straight baseline can be obtained. Figure 4.4 shows the first 15 reaction spectra after preconditioning/base line correction from a typical experiment.
4.4.4 Total algebraic system identification

The preconditioned baseline-corrected absorbance data matrix $A_{713 \times 2951}$ was firstly subjected to singular value decomposition (SVD) to give the orthonormal matrices $U_{713 \times 713}$ and $V^T_{2951 \times 2951}$, and the diagonal singular value matrix $\Sigma_{713 \times 2951}$. Since only 713 reaction spectra were in the original data array, only the first 713 $V^T$ vectors were physically meaningful. Thus the absorbance data array could be expressed using truncated matrices as follows.

$$A_{713 \times 2951} = U_{713 \times 713} \Sigma_{713 \times 713} V^T_{713 \times 2951} \quad (4.2)$$
As shown in Figure 4.5, the first few right singular vectors were inspected to identify the significant spectral extrema which were targeted with the BTEM algorithm. The selected wavenumber regions, the maximum peak absorbance, the number of $V^T$ vectors taken for spectral reconstruction and the identity of resolved pure component spectrum are listed in Table 4.3.

![Graph showing absorbance vs. wavenumber for several $V^T$ vectors](image)

**Figure 4.5** The first several $V^T$ vectors showing eight spectral extrema
### Table 4.3 Spectral reconstruction parameters and species identities

<table>
<thead>
<tr>
<th># Species</th>
<th># $V^T$ vectors, $z$</th>
<th>Wavenumber region</th>
<th>Maximum Abs, α</th>
<th>Species identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>20</td>
<td>2014.5 – 2015.5</td>
<td>1</td>
<td>Mn$<em>2$(CO)$</em>{10}$</td>
</tr>
<tr>
<td>2.</td>
<td>15</td>
<td>2015.5 – 2017</td>
<td>1</td>
<td>HMn(CO)$_5$</td>
</tr>
<tr>
<td>3.</td>
<td>20</td>
<td>1732 – 1736</td>
<td>1</td>
<td>44DMP</td>
</tr>
<tr>
<td>4.</td>
<td>30</td>
<td>1640 – 1644</td>
<td>1</td>
<td>33DMB</td>
</tr>
<tr>
<td>5.</td>
<td>30</td>
<td>1885 – 1887</td>
<td>5</td>
<td>Rh$<em>4$(CO)$</em>{12}$</td>
</tr>
<tr>
<td>6.</td>
<td>30</td>
<td>2039 – 2041</td>
<td>5</td>
<td>RCORh(CO)$_4$</td>
</tr>
<tr>
<td>7.</td>
<td>100</td>
<td>1818 – 1820</td>
<td>5</td>
<td>Rh$<em>6$(CO)$</em>{16}$</td>
</tr>
<tr>
<td>8.</td>
<td>50</td>
<td>2067 – 2069</td>
<td>1</td>
<td>Rh$<em>4$(σ-CO)$</em>{12}$</td>
</tr>
</tbody>
</table>

A total of 8 components were recovered with BTEM. Figure 4.6 presents the reconstructed pure component spectra. As shown in the figure, the quality of the BTEM reconstructions is very good and the signal-to-noise level is very high except for Rh$_4$(σ-CO)$_{12}$. The Rh$_4$(σ-CO)$_{12}$ estimate shows some localized signals belonging to other species at 1640 (33DMB), 1819 (Rh$_6$(CO)$_{16}$), 2015 (Mn$_2$(CO)$_{10}$), and 2041 (Rh$_4$(CO)$_{12}$) cm$^{-1}$, and one sigmoid feature at 1886 (Rh$_4$(CO)$_{12}$) cm$^{-1}$. However, the two primary bands of Rh$_4$(σ-CO)$_{12}$ are still well-resolved at 2067.8 and 2076.6 cm$^{-1}$. 
Table 4.4 gives the individual integrated signals compared to the total integrated signals for all preconditioned experiments. As shown in Table 4.4, the 8 recovered pure
component spectra with BTEM could account for more than 98.6% of the total integrated signals arising from the 21 experiments performed for this system.

Table 4.4 Percentage of integrated absorbance for each component

<table>
<thead>
<tr>
<th>Component</th>
<th>Integrated Intensities, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>44DMP</td>
<td>21.1</td>
</tr>
<tr>
<td>HMn(CO)₂*</td>
<td>7.4</td>
</tr>
<tr>
<td>Rh₄(σ-CO)₆(μ-CO)₃</td>
<td>5.1</td>
</tr>
<tr>
<td>33DMB</td>
<td>12.6</td>
</tr>
<tr>
<td>Mn₂(CO)₁₀*</td>
<td>36.3</td>
</tr>
<tr>
<td>RCORh(CO)₄</td>
<td>15.3</td>
</tr>
<tr>
<td>Rh₆(CO)₁₆</td>
<td>0.6</td>
</tr>
<tr>
<td>Rh₄(σ-CO)₁₂</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>98.6</strong></td>
</tr>
</tbody>
</table>

* These reference spectra used for these two components were obtained from additional experiment and spectral work.

Table 4.4 indicates that the Rh₆(CO)₁₆ and Rh₄(σ-CO)₁₂ together contribute less than 1%. This could explain why the BTEM results are somewhat noisy for these two species. The real signal intensities are just above the noise levels.

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.
As introduced in Chapter 3, before calculating the real magnitude of each species’ pure component spectrum, the re-normalization of the spectroscopic data is required to eliminate the dependence of variable reaction volume and variable path length of cell. The detailed procedure was described in Chapter 3.

In the present case, the solvent n-hexane was used as the standard reference $A_{\omega}^{\text{std}}$ at $\omega = 1137$ cm$^{-1}$. As the input of n-hexane in each experiment is known, the mole numbers can be accordingly calculated. The molar absorptivity of n-hexane at $\omega = 1137$ cm$^{-1}$ was obtained from experimental data as 2.18 L/(mole·cm).

As Rh-, Org-, and Mn- are conserved in the closed reaction system, they are used to establish the reaction invariant model. As discussed before, the contribution of Rh$_4$(\sigma-CO)$_{12}$ is very small, therefore, it is not included in the mass balance. Accordingly, the proposed chemical group matrix is as follows.

$$
\mathbf{v}_{s \times E} = \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
4 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 2 \\
1 & 1 & 0 \\
6 & 0 & 0
\end{bmatrix}
$$

(4.3)

The rows of this matrix are associated with 44DMP, HMn(CO)$_5$, Rh$_4$(CO)$_{12}$, 33DMB, Mn$_2$(CO)$_{10}$, RCORh(CO)$_4$, and Rh$_6$(CO)$_{16}$ species sequentially.
The matrix \( D_{xk} \) was used according to the procedure outlined in Chapter 3 to determine the diagonal scaling matrix \( d \) and hence the absolute magnitudes of the pure component spectra. Table 4.5 lists the maxima of these seven reconstructed pure component spectra.

**Table 4.5** The maximum absorptivities for each pure component spectral estimate

<table>
<thead>
<tr>
<th>Species</th>
<th>Max Peak, cm(^{-1})</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>44DMP</td>
<td>1734.2</td>
<td>343.7</td>
</tr>
<tr>
<td>HMn(CO)(_5)</td>
<td>2015.8</td>
<td>32256</td>
</tr>
<tr>
<td>Rh(<em>4)(CO)(</em>{12})</td>
<td>2070</td>
<td>25101</td>
</tr>
<tr>
<td>33DMB</td>
<td>1642.6</td>
<td>43.8</td>
</tr>
<tr>
<td>Mn(<em>2)(CO)(</em>{10})</td>
<td>2014.8</td>
<td>23240</td>
</tr>
<tr>
<td>RCORh(CO)(_4)</td>
<td>2021.4</td>
<td>5413</td>
</tr>
<tr>
<td>Rh(<em>6)(CO)(</em>{16})</td>
<td>2075.4</td>
<td>12205</td>
</tr>
</tbody>
</table>

Upon obtaining the real magnitudes of the absorptivities, the time dependent mole numbers for the seven observable components in all 21 experiments can be directly calculated. These are presented in Figure 4.7 (X axis represents the time-dependent spectra number in each experiment and Y axis represents the mole numbers).
Figure 4.7 The time dependent moles for the seven observable components

From all the above time-dependent concentration profiles of both organic and organometallic species, it should be noted that even under reaction conditions of circa 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.
4.5 Experiment results

4.5.1 Spectral aspects

4.5.1.1 Pre-hydroformylation

From the seven semi-batch experiments with Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ Mn$_2$(CO)$_{10}$ under CO/H$_2$/Argon in n-hexane, spectra for only Rh$_4$(CO)$_{12}$, HMn(CO)$_5$, Mn$_2$(CO)$_{10}$, and Rh$_6$(CO)$_{16}$ were recovered. Although BTEM has been able to identify species at ppm level, no other complex was found in the present system. It was reported that HMn(CO)$_5$ undergoes rapid exchange with other metal carbonyl dimers under mild conditions, as in the case of Co$_2$(CO)$_8$ and HMn(CO)$_5$ reacting to form HCo(CO)$_4$ and MnCo(CO)$_9$ (Kovacs et al, 1985). However, the similar Rh-Mn complex was not observed in Rh$_4$(CO)$_{12}$/HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ system.

4.5.1.2 Hydroformylation

Hydroformylation of 3,3-dimethylbut-1-ene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures. Detailed in-situ FTIR spectroscopic studies have shown the presence of only 5 observable organometallics, namely the known species RCORh(CO)$_4$(Garland et al, 1989), Rh$_2$(CO)$_8$ (Whyman, 1972), Rh$_4$(CO)$_{12}$ (Chini and Heaton, 1977), Rh$_6$(CO)$_{16}$ (Chini, 1967), and Rh$_4$(σ-CO)$_{12}$ (Widjaja et al, 2002a), 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 (Vidal and Walker, 1981; Whyman, 1992; Li et al, 2002) could be obtained in the presence of the very reactive organic reagent 3,3-dimethylbut-1-ene.
In the present Rh₄(CO)₁₂ /HMn(CO)₅ bimetallic catalyzed hydroformylation of 3,3-dimethylbut-1-ene, in addition to the solvent hexane and the dissolved carbon monoxide, chemometric analyses (section 4.4) of the in situ infrared spectra of the reaction recovered the precursor Rh₄(CO)₁₂, the precursor HMn(CO)₅, Mn₂(CO)₁₀ and the reagent 33DMB(Figure 4.6). The common impurity of the cluster Rh₆(CO)₁₆ and the isomer Rh₄(σ-CO)₁₂ (Figure 4.6) were apparently very weak in the spectra. There was no indication of fragmentation such as the formation of Rh₂(CO)₈ (ν_CO=2086,2061,1860,1845 cm⁻¹)(Whyman, 1972).

During the hydroformylation, two new species appeared. One is due to the rhodium intermediate RCORh(CO)₄ (R=CH₂CH₂C(CH₃)₃ ) and the other is the organic product RCHO (Figure 4.6). No Rh-Mn complex was observed.

4.5.2 Calculations

Solubility data for hydrogen and carbon monoxide in n-hexane were calculated with the same method used by Garland (Garland and Pino,1991). The Henry’s law was employed to calculate the mole fraction of species because of the low gas concentrations in the bulk solvent. The Henry constants were calculated using the following equations respectively.

\[ H_{H₂}(P,T) = P_{sat} \exp(-4.96+4050/T) \times \exp[V_{H₂}(P-P₀)/RT] \]  \hspace{1cm} (4.4)

\[ H_{CO}(P,T) = P_{sat} \exp(-5.05+3880/T) \times \exp[V_{CO}(P-P₀)/RT] \]  \hspace{1cm} (4.5)

In the above two equations, the temperature-dependent form is called Jonah expression (Jonah, 1983) and the pressure-dependent form is called the Krichevsky-
Kasarnovsky correction (Krichevsky and Kasarnovsky, 1935), where the temperature $T$ is in Kelvin, $P_0$ is the standard reference pressure 0.1MPa and $P_{sat}$ is the saturation vapor pressure of the solvent n-hexane (Grigorien and Meilikhov, 1997). The partial molar volumes $V_{H_2}$ and $V_{CO}$ in aliphatic hydrocarbons including n-hexane are 43ml/mol and 52ml/mol respectively. These equations are strictly valid only for pure hexane and the dissolved hydrogen and carbon monoxide are considered to be ideal solutes. No further mixing rules are invoked to compensate for the non-ideality in the two-phase system.

Based on the calculated Henry constants $H_{H_2}$ and $H_{CO}$, the mole fractions and moles of dissolved hydrogen and carbon monoxide can be calculated from the partial pressure of $H_2$ and CO by the following equations:

$$X_{H_2} = \frac{P_{H_2}}{H_{H_2}}$$

(4.6)

$$X_{CO} = \frac{P_{CO}}{H_{CO}}$$

(4.7)

$$n_{H_2} = X_{H_2} \times (n_{hex} + n_{33DMB})_0$$

(4.8)

$$n_{CO} = X_{CO} \times (n_{hex} + n_{33DMB})_0$$

(4.9)

The partial pressures of hydrogen and carbon monoxide in the closed batch autoclave changed less than 2% during the 6 hour hydroformylation experiments. Therefore this small 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.
The time-dependent in situ concentrations of 33DMB, Rh₄(CO)₁₂, RCORh(CO)₄, HMn(CO)₅, Mn₂(CO)₁₀ and the product 4,4-dimethylpentanal (44DMP) were calculated by using the time-dependent moles obtained from the chemometric analyses (Section 4.4).

The rates of the formation of 44DMP were calculated in terms of turnover frequency (TOF) by using a finite difference equation.

\[
TOF_t = \frac{d[44DMP]_t}{dt} / [RCORh(CO)₄]_t
\]  \hspace{1cm} (4.10)

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 10 min. This expression was chosen since it provides an accurate approximation of derivatives from smooth monotonically increasing or decreasing experimental data (Daviers, 1984).

4.5.3 Results

As introduced in the experimental work (section 4.2), a total of 21 experiments in six series (the variations of Mn₂(CO)₁₀/HMn(CO)₅ loading, Rh₄(CO)₁₂ loading, 33DMB loading, CO pressure, H₂ pressure and reaction temperature) were performed. In the following, the results of studies on the Rh₄(CO)₁₂ /HMn(CO)₅ bimetallic catalyzed hydroformylation of 3,3-dimethylbut-1-ene will be presented in detail.

4.5.3.1 With only Mn₂(CO)₁₀/HMn(CO)₅
Manganese complexes have played a critical role in the development of organometallic chemistry. They are key intermediates in numerous stoichiometric and catalytic reactions. Manganese carbonyl has been described as being Oxo active under high temperature and high pressure (King, 1978). There is one patent to describe use of HMn(CO)₅ as hydroformylation catalyst at high temperature (Klopf, 1962). It has previously been observed that manganese hydrides can be used to reduce conjugated alkenes and polynuclear arenes (Sweany et al., 1981). These reactions are believed to proceed via hydrogen-atom transfer to form solvent-caged radical pairs which may combine or diffuse apart. In this case, internal return of cage radical pair is believed to lead to aldehyde and separation of radicals by diffusion leads to reduction to alkane. HMn(CO)₅ is also reported to reduce conjugated dienes via the same mechanism (Wassink et al., 1995).

To determine the activities of Mn₂(CO)₁₀/HMn(CO)₅ in the present 33DMB system, a blank experiment with only Mn₂(CO)₁₀/HMn(CO)₅ as the precursor was carried out. The 6 hour experiment showed there is no observable reaction under our reaction conditions (2.0MPa CO, 1.0MPa H₂, 298K).

4.5.3.2 With Rh₄(CO)₁₂ and HMn(CO)₅: Changing HMn(CO)₅ initial loadings

In this section, the hydroformylation of 33DMB with simultaneous addition of Rh₄(CO)₁₂ and HMn(CO)₅ was studied. The initial concentration of the precursor HMn(CO)₅ was systematically varied in five hydroformylations while other reaction conditions were kept constant. The five kinetic experiments were performed at 298K, 2.0MPa CO and 1.0MPa H₂ to investigate the effect of HMn(CO)₅ on the unmodified rhodium catalyzed hydroformylation. The corresponding concentrations of H₂ and CO
were 0.0102 and 0.0503 respectively. The initial input of 33DMB was 5 ml and the concentration was 0.016 mole fraction. The initial loadings of Mn$_2$(CO)$_{10}$ were 0, 50.8, 103.0, 153.5 and 210.0 mg while the initial loading of Rh$_4$(CO)$_{12}$ were between 51.0-54.1 mg. Accordingly, the initial concentrations of HMn(CO)$_5$ in mole fraction were $X_{\text{HMn(CO)5}}=0$, $3\times10^{-7}$, $2.5\times10^{-5}$, $3.0\times10^{-5}$ and $3.3\times10^{-5}$ respectively. The corresponding initial concentrations of Rh$_4$(CO)$_{12}$ were circa $3\times10^{-5}$ mole fraction.

4.5.3.2.1 Initial reaction times

The 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)$_4$ are shown in Figures 4.8, 4.9 and 4.10 respectively. Some errors could be observed in the first data points. This is due to the fact that the first spectrum was taken immediately when all the reagents were added to the autoclave, which means that there was not enough time for the mixing for the reaction mixture from the autoclave to the in-situ IR.
Figure 4.8 The time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$

Figure 4.9 The time dependent mole fractions of $\text{HMn(OC)}_5$
Figure 4.10 The time dependent mole fractions of $\text{Mn}_2(\text{CO})_{10}$

Figure 4.11 The time dependent mole fractions of $\text{RCORh(CO)}_4$
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 declined in all the four experiments (Figure 4.8) and the concentration of RCORh(CO)_4 (Figure 4.11) monotonically increased in all experiments - until reaching its upper mass balance limit within circa 5 hours.

As observed previously in the other study with 33DMB as substrate pure Rh_4(CO)_12 catalyzed hydroformylation, the disappearance of the precursor Rh_4(CO)_12 during the initial phase of the hydroformylation with 33DMB is a well-behaved pseudo-first-order process over at least circa 2 half-lives at 293 K (Garland and Pino, 1991). However, when Rh_4(CO)_12, Mn_2(CO)_10, HMn(CO)_5 were added simultaneously, the data presented in Figure 4.8 and Figure 4.11 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 occurs. The concentration of HMn(CO)_5 has a big effect on the transformation of Rh_4(CO)_12. Generally speaking, the higher concentration of HMn(CO)_5, the faster the transformation of Rh_4(CO)_12 to RCORh(CO)_4.

The half-life for Rh_4(CO)_12 in the mixed Rh/Mn system is circa 10 minutes when 210.0 mg Mn_2(CO)_10 was used, whereas a half-life under similar reaction conditions for pure Rh systems is circa 1 hour. This atypical initial time behavior means that there could be 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 $\text{Rh}_4(\text{CO})_{12}$. Mononuclear hydride attack and subsequent opening of metal clusters are well documented in the literature (Churchill et al., 1986).

The concentrations of $\text{HMn(\text{CO})}_5$ (Figure 4.9) and $\text{Mn}_2(\text{CO})_{10}$ (Figure 4.10) also monotonically changed, but the direction depended on the experimental conditions used. The concentrations of $\text{HMn(\text{CO})}_5$ never approached zero in any 5 hour experiment. The concentrations of $\text{Rh}_6(\text{CO})_{16}$ monotonically decreased as shown in (Figure 4.12).

![Figure 4.12 The time dependent mole fractions of $\text{Rh}_6(\text{CO})_{16}$](image)

4.5.3.2 Product formation

The concentration profiles of the reagent alkene and the product aldehyde are shown in Figure 4.13 and Figure 4.14 respectively. The concentrations of 33DMB
monotonically declined and the concentrations of the product 44DMP monotonically increased in all the five experiments. The production of aldehyde could be identified within the first few minutes when H\text{Mn(CO)}_5/\text{Mn}_2(\text{CO})_{10} were added simultaneously.

![Graph showing time dependent mole fractions of 33DMB](image)

**Figure 4.13** The time dependent mole fractions of 33DMB
As shown in Figure 4.14, 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. With the exception of the first 50 minutes, the rates of product formation are constants. The rates are circa $5.28 \times 10^{-6}$, $7.18 \times 10^{-6}$, $1.15 \times 10^{-5}$, $1.78 \times 10^{-5}$, and $2.39 \times 10^{-5}$ (mol fraction)/min and the final conversions of 33DMB after 280 minutes were 9.6%, 12.1%, 19.4%, 26.4% and 31.6% in the five experiments starting with $X_{\text{HMn(CO)}_5}$ of 0, $3 \times 10^{-7}$, $2.5 \times 10^{-5}$, $3.0 \times 10^{-5}$ and $3.3 \times 10^{-5}$ respectively. When 210.0 mg Mn$_2$(CO)$_{10}$ was used with Rh$_4$(CO)$_{12}$, the rate of hydroformylation is as great as 450% of the rate that was anticipated from the rhodium loading alone. Since HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ is nearly inert towards transformations of alkenes at the present reaction conditions, the
present result implies that $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$ may get involved in the rhodium catalytic pathway to produce aldehyde.

### 4.5.3.2. 3 TOF analyses

The effect of loading of $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$ on the TOF is shown in Figure 4.15. The turn over frequencies (TOF) based on rhodium acyl as defined in Eq 4.10 were $0.09\pm0.005 \text{ min}^{-1}$, $0.09\pm0.005 \text{ min}^{-1}$, $0.15\pm0.02 \text{ min}^{-1}$, $0.21\pm0.007 \text{ min}^{-1}$ and $0.25\pm0.02 \text{ min}^{-1}$ starting with $X_{\text{HMn(CO)}_5}$ of $0$, $3\times10^{-7}$, $2.5\times10^{-5}$, $3.0\times10^{-5}$ and $3.3\times10^{-5}$ respectively. The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The monometallic rhodium TOF value obtained in this study is consistent with the previous studies (Garland and Pino, 1991).

![Figure 4.15](image-url)  
**Figure 4.15** The effect of $\text{HMn(CO)}_5$ on TOF
The TOF values demonstrate that HMn(CO)\textsubscript{5} is very active with Rh\textsubscript{4}(CO)\textsubscript{12} for the hydroformylation of 33DMB. In the hydroformylation of 33DMB with pure unmodified rhodium carbonyl, it has been repeatedly shown that turn-over frequencies are only dependent on the temperature, hydrogen pressure and carbon monoxide pressure (Garland, et al, 1990, 1993). The present results clearly show that TOFs increase with the increased loading of HMn(CO)\textsubscript{5}. When the initial concentration of HMn(CO)\textsubscript{5} was 3.3\times10^{-5}, the TOF is as great as 260\% of that was anticipated from the rhodium loading alone. This is a clear-cut quantitative confirmation of the contribution of HMn(CO)\textsubscript{5} to the final product and that HMn(CO)\textsubscript{5} must be involved in at least one step of the catalytic cycle of the hydroformylation. It is possible that HMn(CO)\textsubscript{5} could interact with the most active rhodium intermediate RCORh(CO)\textsubscript{4}.

4.5.3.3. Changing Rh\textsubscript{4}(CO)\textsubscript{12} initial loadings

The initial concentration of Rh\textsubscript{4}(CO)\textsubscript{12} was systematically varied in four hydroformylation experiments performed at 298K, 5 ml 33DMB, 2.0MPa carbon monoxide, 1.0MPa hydrogen and circa 100mg Mn\textsubscript{2}(CO)\textsubscript{10} in 300 ml n-hexane. The corresponding concentrations of H\textsubscript{2} and CO were 0.0102 and 0.0503 respectively. The initial input of 33DMB was 5 ml and the concentration was 0.016 mole fraction. The initial loading of Rh\textsubscript{4}(CO)\textsubscript{12} was 26.0, 51.0 76.8 and 103.0 mg. Accordingly, the calculated initial concentrations of Rh\textsubscript{4}(CO)\textsubscript{12} in mole fractions were X_{Rh4(CO)12}=1.5\times10^{-5}, 3.0\times10^{-5}, 4.5\times10^{-5}, 6.0\times10^{-5} respectively. The initial loading of Mn\textsubscript{2}(CO)\textsubscript{10} was circa 100 mg and the corresponding initial concentrations of HMn(CO)\textsubscript{5} were circa 1.5\times10^{-5} to
3.3×10^{-5} mole fraction. The variation of HMn(CO)₅ concentration is due to the irreproducibility of the photo-irradiation of Mn₂(CO)₁₀ with H₂. For easy comparison, the concentration profiles of pure rhodium catalyzed hydroformylation of 33DMB was also included in the following figures.

4.5.3.3.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HMn(CO)₅ and Mn₂(CO)₁₀, and the only observable intermediate RCORh(CO)₄ are shown in Figures 4.16-4.19. Similarly, some errors could be observed in the first data points due to the mixing problems. For the pure rhodium system, it can be seen that the concentrations of HMn(CO)₅ and Mn₂(CO)₁₀ are not zero. Although the autoclave was washed between two experiments, it is still possible some Mn complexes deposit on the wall of reactor and may be regenerated back in the following experiments.
Figure 4.16 Time dependent mole fractions of Rh$_4$(CO)$_{12}$

Figure 4.17 Time dependent mole fractions of HMn(CO)$_5$
Figure 4.18 Time dependent mole fractions of Mn$_2$(CO)$_{10}$

Figure 4.19 Time dependent mole fractions of acyl
As shown in Figures 4.16 and 4.19, the concentrations of Rh₄(CO)₁₂ monotonically declined in all the four experiments and the concentration of RCORh(CO)₄ monotonically increased in all experiments. Unlike the pure Rh₄(CO)₁₂ catalyzed hydroformylation, when Rh₄(CO)₁₂, Mn₂(CO)₁₀, HMn(CO)₅ were added simultaneously, the decrease of Rh₄(CO)₁₂ and increase of RCORh(CO)₄ are not simple monotonic functions at initial reaction times. Instead, a very rapid decline in the catalyst precursor concentration and a rapid increase in acyl complex concentration were observed.

Figure 4.19 indicates that increased initial Rh₄(CO)₁₂ concentrations lead to increased pseudo-state concentrations of RCORh(CO)₄, but these two quantities are not proportional. Indeed, the final concentrations of RCORh(CO)₄ were 0.5×10⁻⁴, 0.95×10⁻⁴, 1.27×10⁻⁴, 1.67×10⁻⁴, when X_Rh₄(CO)₁₂=1.5×10⁻⁵, 3.0×10⁻⁵, 4.5×10⁻⁵, 6.0×10⁻⁵ respectively. The half-life at present conditions for Rh₄(CO)₁₂ in the mixed Rh/Mn system is circa 30 minutes when circa 100.0 mg Mn₂(CO)₁₀ was used.

The concentrations of HMn(CO)₅ (Figure 4.17) and Mn₂(CO)₁₀ (Figure 4.18) also monotonically changed. The concentrations of HMn(CO)₅ never approached zero in any 5 hour experiment. The concentrations of Rh₆(CO)₁₆ monotonically decreased as shown in Figure 4.20.
4.5.3.3.2 Product formation

The time-dependent concentrations of the reagent 33DMB and the hydroformylation product 44DMP are shown in Figures 4.21 and 4.22. The sensitivity of the 33DMB concentrations could be attributed to its low absorptivities.

With the exception of the first 50 minutes, the rates of product formation are constants. The rates are circa $0.8 \times 10^{-5}$, $1.2 \times 10^{-5}$, $1.8 \times 10^{-5}$, and $2.7 \times 10^{-5}$ (mol fraction)/min. The final conversions of 33DMB after 280 minutes were 15%, 25%, 31%, and 44% in the four experiments starting with $X_{\text{Rh}4(\text{CO})12}=1.5 \times 10^{-5}$, $3.0 \times 10^{-5}$, $4.5 \times 10^{-5}$, $6.0 \times 10^{-5}$ respectively. The variation in the initial concentration of $\text{Rh}4(\text{CO})12$ has a big effect on the formation of 44DMP. One obvious reason is that the higher concentration of
Rh$_4$(CO)$_{12}$ gives rise to higher concentration of RCorh(CO)$_4$, which produces the final product.

**Figure 4.21** Time dependent mole fractions of 33DMB

**Figure 4.22** Time dependent mole fractions of 44DMP
However, Figure 4.22 also shows that the bimetallic system activity is much higher than pure rhodium system. At the same loading of Rh$_4$(CO)$_{12}$ loading (circa 50 mg), the hydroformylation rate of Rh/Mn bimetallic system was circa two times faster than that of pure rhodium system. Furthermore, it is worth noting, when 26.0 mg Rh$_4$(CO)$_{12}$ was used with HMn(CO)$_5$/Mn$_2$(CO)$_{10}$, the hydroformylation reaction is much faster than the use of 51.6 mg Rh$_4$(CO)$_{12}$ alone.

4.5.3.3 TOF analyses

The effect of loading of Rh$_4$(CO)$_{12}$ on TOF is shown in Figure 4.23. The average turnover frequencies were 0.21±0.06 min$^{-1}$, 0.15±0.02 min$^{-1}$, 0.18±0.02 min$^{-1}$ and 0.19±0.005 min$^{-1}$ in the four experiments starting with $X_{Rh_4(CO)_{12}}=1.5 \times 10^{-5}$, $3.0 \times 10^{-5}$, $4.5 \times 10^{-5}$, and $6.0 \times 10^{-5}$ respectively.

![Figure 4.23 The effect of Rh$_4$(CO)$_{12}$ on TOF](image-url)
Some errors could be seen in the experiment with low loading of Rh₄(CO)₁₂ (26.0mg). This is because with low initial concentration of Rh₄(CO)₁₂, both the acyl mole fractions and reaction rate are very low during the initial reaction period and this could result in calculating sensitivity.

It seems that the influence of initial concentration of Rh₄(CO)₁₂ on the turn over frequencies is very small. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland and Pino, 1991). The small TOF differences could be traced to the effect of HMn(CO)₅ concentration differences in the four experiments. Indeed, as shown in Figure 4.17, the concentration of HMn(CO)₅ is highest when the rhodium loading is 26.0 mg. This highest HMn(CO)₅ concentration could contribute to the highest TOF $0.21 \pm 0.06 \text{min}^{-1}$, which again means that HMn(CO)₅ was involved in the formation of the organic product 44DMP.

4.5.3.4 Changing 33DMB initial loadings

The initial concentration of substrate 33DMB was systematically varied in three hydroformylation experiments performed at 298K, 2.0MPa carbon monoxide, 1.0MPa hydrogen, circa 50 mg Rh₄(CO)₁₂ and circa 100mg Mn₂(CO)₁₀ in 300 ml n-hexane. The corresponding concentrations of H₂ and CO were 0.0102 and 0.0503 respectively. The calculated initial concentrations of Rh₄(CO)₁₂ in mole fractions were circa $3.0 \times 10^{-5}$. The initial loading of 33DMB was 2, 5 and 10 ml. Accordingly, the calculated initial concentrations of 33DMB in mole fractions were $X_{\text{DMB}} = 0.0062, 0.0155, 0.0310$ respectively. The initial loading of Mn₂(CO)₁₀ was circa 100 mg and the corresponding
initial concentrations of HMn(CO)$_5$ were circa $1.75 \times 10^{-5}$ to $2.8 \times 10^{-5}$ mole fraction. This is due to the irreproducibility of the photo-irradiation of Mn$_2$(CO)$_{10}$ with H$_2$.

4.5.3.4.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HMn(CO)$_5$ and Mn$_2$(CO)$_{10}$, and the only observable intermediate RCORh(CO)$_4$ are shown in Figures 4.24-4.27. Similarly, some errors could be observed in the first data points due to the mixing problems.

![Figure 4.24](image-url) Time dependent mole fractions of Rh$_4$(CO)$_{12}$
Figure 4.25 Time dependent mole fractions of HMn(CO)$_5$

Figure 4.26 Time dependent mole fractions of Mn$_2$(CO)$_{10}$
According to Figure 4.24, unlike the pure Rh$_4$(CO)$_{12}$ catalyzed hydroformylation, when Rh$_4$(CO)$_{12}$, Mn$_2$(CO)$_{10}$, HMn(CO)$_5$ were added simultaneously, a very rapid decline in the catalyst precursor concentration and a rapid increase in acyl complex concentration occurs.

Figure 4.27 indicates that 33DMB concentration appears to have a minimal effect on the transformation of Rh$_4$(CO)$_{12}$ to RCORh(CO)$_4$. Previous kinetic studies show for unmodified catalyzed hydroformylation of 33DMB, that the rate of Rh$_4$(CO)$_{12}$ disappearance is nearly zero order in the alkene (Garland and Pino, 1991).

The half-life at present conditions for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system is circa 30 minutes when circa 100.0 mg Mn$_2$(CO)$_{10}$ was used.
The concentrations of HMn(CO)_5 (Figure 4.25) decreased and Mn_2(CO)_10 (Figure 4.26) also monotonically increased. HMn(CO)_5 is very unstable and readily converted to Mn_2(CO)_10. However, the concentrations of HMn(CO)_5 never approached zero in any 5 hour experiment. The concentrations of Rh_6(CO)_16 monotonically decreased as shown in Figure 4.28.

Figure 4.28 Time dependent mole fractions of Rh_6(CO)_16

4.5.3.4. 2 Product formation

The time-dependent concentrations of the reagent 33DMB and the hydroformylation product 44DMP are shown in Figures 4.29 and 4.30. It appears that the variation in the initial concentration of 33DMB has a small effect on the formation of
44DMP. This is again consistent with pure rhodium catalyzed hydroformylation (Garland and Pino, 1991).

**Figure 4.29** Time dependent mole fractions of 33DMB

**Figure 4.30** Time dependent mole fractions of 44DMP
With the exception of the first 50 minutes, the rates of product formation are constants. The rates are circa $1.3 \times 10^{-5}$, $1.2 \times 10^{-5}$, and $1.2 \times 10^{-5}$ (mol fraction)/min with $X_{\text{DMB}}=0.0062, 0.016, 0.031$ respectively.

### 4.5.3.4. 3 TOF analyses

The effect of loading of 33DMB on TOF is shown in Figure 4.31. The average turn over frequencies were $0.15 \pm 0.02 \text{min}^{-1}$, $0.15 \pm 0.02 \text{min}^{-1}$ and $0.15 \pm 0.01 \text{min}^{-1}$ in the three experiments starting with $X_{\text{DMB}}=0.0062, 0.016, 0.031$ respectively.

It seems that the influence of initial concentration of 33DMB on the turn over frequencies is very small. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland and Pino, 1991).

![Figure 4.31 The effect of DMB on the TOF](image)

Figure 4.31 The effect of DMB on the TOF
4.5.3.5 Changing CO pressure

The initial concentration of CO was systematically varied in four hydroformylation experiments performed at 298K, 1.0MPa hydrogen in 300 ml n-hexane. The pressures of carbon monoxide were 1.0, 2.0, 3.0 and 4.0 MPa. Accordingly, the concentrations of CO in mole fractions were $X_{\text{CO}} = 0.0262, 0.0513, 0.0754$ and 0.09840.

The corresponding concentration of H$_2$ was 0.0102. Circa 50 mg Rh$_4$(CO)$_{12}$ was used and the calculated initial concentrations of Rh$_4$(CO)$_{12}$ in mole fractions were circa $3.0 \times 10^{-5}$. The initial loading of 33DMB was 5ml and the mole fraction was $X_{\text{DMB}} = 0.016$. The initial loading of Mn$_2$(CO)$_{10}$ was circa 100 mg and the corresponding initial concentrations of HMn(CO)$_5$ were circa $2.5 \times 10^{-5}$ to $3.3 \times 10^{-5}$ mole fraction. This is because of the irreproducibility of the photo-irradiation of Mn$_2$(CO)$_{10}$ with H$_2$.

4.5.3.5.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HMn(CO)$_5$ and Mn$_2$(CO)$_{10}$, and the only observable intermediate RCORh(CO)$_4$ are shown in Figures 4.32-4.35. Similarly, some errors could be observed in the first data points due to the mixing problems.
Figure 4.32 Time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$

Figure 4.33 Time dependent mole fractions of $\text{HMn(\text{CO})}_5$
**Figure 4.34** Time dependent mole fractions of $\text{Mn}_2(\text{CO})_{10}$

**Figure 4.35** Time dependent mole fractions of acyl
According to Figure 4.32, it can be observed again, in the Rh$_4$(CO)$_{12}$ catalyzed hydroformylation promoted with Mn$_2$(CO)$_{10}$/HMn(CO)$_5$, that the decrease of Rh$_4$(CO)$_{12}$ and increase of RCORh(CO)$_4$ are not simple monotonic functions at initial reaction times, instead, a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occurs.

The half-lives at the present conditions for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system were circa 140, 25, 10 and less than 10 minutes respectively with $X_{CO}= 0.0262$, 0.0513, 0.0754 and 0.09840. Accordingly, the final concentrations of RCORh(CO)$_4$ were 5.9$\times 10^{-5}$, 9.5$\times 10^{-5}$, 1.01$\times 10^{-4}$, and 1.03$\times 10^{-4}$. This indicates that increased initial CO concentrations lead to faster transformation of Rh$_4$(CO)$_{12}$ to RCORh(CO)$_4$.

As shown in Figure 4.33 and Figure 4.35, the activity of HMn(CO)$_5$ on the transformation of Rh$_4$(CO)$_{12}$ to RCORh(CO)$_4$ is obvious. For example, for the two experiments at 3.0 and 4.0 MPa CO, the concentration profiles of Rh$_4$(CO)$_{12}$ and RCORh(CO)$_4$ are almost the same. Except for the different CO pressures for the two experiments, the only other difference could be the slightly different HMn(CO)$_5$ concentrations in the two experiments as shown in Figure 4.33. This suggests that HMn(CO)$_5$ is very active on the attack to Rh$_4$(CO)$_{12}$.

Figure 4.33 and Figure 4.34 show that the concentrations of HMn(CO)$_5$ slightly decreased and the concentrations of Mn$_2$(CO)$_{10}$ slightly increased in the four hydroformylation reactions. The concentrations of Rh$_6$(CO)$_{16}$ monotonically decreased as shown in Figure 4.36.
4.5.3.5.2 Product formation

The time-dependent concentrations of the reagent 33DMB and the hydroformylation product 44DMP are shown in Figures 4.37 and 4.38. It appears that the variation in the initial concentration of CO has a big effect on the formation of 44DMP. Generally, the rate of hydroformylation tended to decrease with increasing liquid carbon monoxide concentrations. This is consistent with Garland’s work (Garland et al, 1991, 1993, 1999). It is known that in the pure rhodium catalyzed hydroformylation system there exists an one-to-one relationship between \([\text{RCORh(CO)}_4]\_t\) and the rate of aldehyde formation \((\text{d}[44\text{DMP}]/\text{dt})_t=k[\text{RCORh(CO)}_4]_t[\text{CO}]^{-1}[\text{H}_2]\). The present results support a negative effect of CO on the product formation to some extent.
Figure 4.37 Time dependent mole fractions of 33DMB

Figure 4.38 Time dependent mole fractions of 44DMP
However, the present bimetallic system with Rh$_4$(CO)$_{12}$ and HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ is more complicated. It is interesting to note that during the first circa 130 minutes, the product aldehyde concentration profiles are almost the same. This is in part due to the big differences of the RCORh(CO)$_4$ concentrations for the four experiments (Figure 4.35) during this period. In other words, the aldehyde production rate is a combined result of low CO concentrations but high RCORh(CO)$_4$ concentrations.

During the last phase (from 160-280 minutes) of the hydroformylation, the contribution of the HMn(CO)$_5$ to the product formation is very clear. Indeed, in this period, the rates of 44DMP formation are constants. The rates are circa $1.9 \times 10^{-5}$, $1.2 \times 10^{-5}$, $1.2 \times 10^{-5}$, and $7.9 \times 10^{-6}$ (mol fraction)/min. It is worth noting that the two reaction rates (CO= 2.0 MPa , 3.0MPa) are almost the same. Except for the slightly different acyl RCORh(CO)$_4$ concentrations in these two experiments (Figure 4.35), the other big variation is the different HMn(CO)$_5$ mole fractions, which could be involved in the final product formation.

**4.5.3.5.3 TOF analyses**

The effect of loading of CO on TOF is shown in Figure 4.39. The average turnover frequencies were $0.39 \pm 0.04\text{min}^{-1}$, $0.15 \pm 0.02\text{min}^{-1}$, $0.11 \pm 0.005\text{min}^{-1}$ and $0.096 \pm 0.05 \text{min}^{-1}$ in the four experiments starting with $X_{CO} = 0.0262$, 0.0513, 0.0754 and 0.09840 respectively.
The TOF results suggest that the influence of CO concentration on the turn over frequencies is very big when all the other conditions are the same (CO=1.0 and 4.0 MPa). This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland et al, 1991, 1993).

However, looking into three experiments with CO=2.0, 3.0 and 4.0 MPa, although the general trend is consistent with the pure unmodified rhodium catalyzed hydroformylation system, the big TOF differences were not observed. This could be again traced to the effect of HMn(CO)$_5$ concentration differences in the there experiments (Figure 4.33).

4.5.3.6. Changing H$_2$ pressure
Three experiments were performed to study the influence of hydrogen. The experiments were conducted at 298K, 2.0MPa CO, and 5ml 33DMB in 300 ml n-hexane. The corresponding concentrations of CO were 0.0513. The initial input of 33DMB was 5 ml and the concentration was 0.016 mole fraction. The initial loading of Rh₄(CO)₁₂ was circa 50 mg and X_{Rh₄(CO)₁₂} was circa 3.0×10⁻⁵. The initial loading of Mn₂(CO)₁₀ was circa 100 mg and the corresponding initial concentrations of HMn(CO)₅ were circa 2.5×10⁻⁵ to 3.3×10⁻⁵ mole fraction. This is due to the irreproducibility of the photo-irradiation of Mn₂(CO)₁₀ with H₂. The pressures of hydrogen were 0.5, 1.0 and 1.5 MPa. The corresponding concentrations of H₂ in mole fractions were X_{H₂}= 0.0052, 0.0102, and 0.0152 respectively.

4.5.3.6.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HMn(CO)₅ and Mn₂(CO)₁₀ , and the only observable intermediate RCORh(CO)₄ are shown in Figures 4.40-4.43. Similar errors could be observed in the first data points due to the mixing problems.
Figure 4.40 Time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$

Figure 4.41 Time dependent mole fractions of $\text{HMn}$(CO)$_5$
Figure 4.42 Time dependent mole fractions of Mn₂(CO)₁₀

Figure 4.43 Time dependent mole fractions of acyl
It can be observed again, upon addition of Mn$_2$(CO)$_{10}$, HMn(CO)$_5$ and H$_2$, that a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occurs.

The half-lives at the present conditions for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system were circa 25 minutes for all the three experiments. Accordingly, the final concentrations of RCORh(CO)$_4$ were $8.4 \times 10^{-5}$, $9.5 \times 10^{-5}$, and $8.5 \times 10^{-5}$.

According to the classic fragmentation mechanism, \( \frac{d[Rh_4(CO)_{12}]}{dt} = k[Rh_4(CO)_{12}][CO]^2[H_2] \), the disappearance rate of Rh$_4$(CO)$_{12}$ should be proportional to the molecular hydrogen concentration in the solution. However, from Figure 4.43, this kind of relationship is not clear. Actually, Figure 4.43 indicates that when H$_2$=0.5 MPa the disappearance rate of Rh$_4$(CO)$_{12}$ is even slightly faster than that of H$_2$=1.0 MPa at the first 150 minutes. Further inspection of Figure 4.41 shows that the difference of HMn(CO)$_5$ concentrations in these two experiments might be responsible for this result. This suggests that HMn(CO)$_5$ is very active on the attack to Rh$_4$(CO)$_{12}$.

Figure 4.41 and Figure 4.42 show that the concentrations of HMn(CO)$_5$ monotonically decreased and the concentrations of Mn$_2$(CO)$_{10}$ slightly increased in the three hydroformylation reactions. The concentrations of Rh$_6$(CO)$_{16}$ monotonically decreased as shown in Figure 4.44.
Figure 4.44 Time dependent mole fractions of Rh₆(CO)₁₆

4.5.3.6. 2 Product formation

The time-dependent concentrations of the reagent 33DMB and the hydroformylation product 44DMP are shown in Figures 4.45 and 4.46. It appears that the variation in the initial concentration of H₂ (H₂=0.5 and 1.5 MPa) has a big effect on the formation of 44DMP when all the other conditions are the same. Except for the first 70 minutes, the product formation rates in these two experiments are constants, namely $1.2 \times 10^{-5}$ and $2.33 \times 10^{-5}$. The reaction rate is faster with higher H₂ concentration. This is consistent with the classic product formation kinetics to some extent, i.e., $(d[44DMP]/dt)=k[RCORh(CO)₄][CO]^{-1}[H₂]$ for hydroformylation of alkene catalyzed by unmodified Rh₄(CO)₁₂ alone (Garland et al, 1991, 1993).
However, the complexities of the present bimetallic system with Rh₄(CO)₁₂ and HMn(CO)₅/Mn₂(CO)₁₀ are also observed. It is worth noting that the product concentration profiles are very similar in the two experiments (H₂ = 0.5 MPa, 1.0MPa). Close inspection
of the time-dependent mole fractions of all the species (both organic and organic) shows that only a big difference can be seen in HMn(CO)$_5$ concentrations between these two experiments (Figure 4.41). This again supports that HMn(CO)$_5$ has a significant activity in the catalytic pathways to promote the 44DMP formation.

4.5.3.6. 3 TOF analyses

The effect of loading of H$_2$ on TOF is shown in Figure 4.47. The average turn over frequencies were $0.16 \pm 0.01 \text{min}^{-1}$, $0.15 \pm 0.02 \text{min}^{-1}$, and $0.30 \pm 0.01 \text{min}^{-1}$ in the three experiments starting with $X_{H2}=0.0052, 0.0102, \text{and } 0.0152$ respectively.

![Figure 4.47 The effect of H$_2$ on TOF](image)

The TOF results suggest that the influence of H$_2$ concentration on the turn over frequencies ($H_2=0.5$ and 1.5 MPa) is strong when all the other conditions are the same.
The higher H\textsubscript{2} concentration results in a higher TOF. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland et al, 1991, 1993).

However, by comparing the two experiments (H\textsubscript{2}=0.5 and 1.0 MPa), we can see that the TOF at H\textsubscript{2}=0.5 MPa is even higher than the TOF at H\textsubscript{2}=1.0 MPa. This could be again traced to the effect of HMn(CO)\textsubscript{5} concentration differences in the two experiments. As shown in (Figure 4.41), the average concentration of HMn(CO)\textsubscript{5} at H\textsubscript{2}=0.5 MPa is much higher the average concentration of HMn(CO)\textsubscript{5} at H\textsubscript{2}=1.0 MPa. This again indicates HMn(CO)\textsubscript{5} may have a significant contribution to the production of the organic product aldehyde in the catalytic cycles.

4.5.3.7. Changing temperature

Four experiments were performed at 293K, 298K, 303K and 308K respectively. Each experiment was taken in a similar manner to the standard experiment. These were at 1.0MPa hydrogen, 2.0MPa carbon monoxide, 5ml 33DMB, circa 50mg Rh\textsubscript{4}(CO)\textsubscript{12} and circa 100mg Mn\textsubscript{2}(CO)\textsubscript{10}. Accordingly, the initial concentration of 33DMB was 0.016 mole fraction, the initial of X\textsubscript{Rh\textsubscript{4}(CO)\textsubscript{12}} was circa 3.0\times10^{-5} and the initial concentrations of HMn(CO)\textsubscript{5} were circa 2.1\times10^{-5} to 3.3\times10^{-5} mole fraction. This small variation in the HMn(CO)\textsubscript{5} concentrations was due to the irreproducibility of the photo-irradiation of Mn\textsubscript{2}(CO)\textsubscript{10} with H\textsubscript{2}.

4.5.3.7. 1 Initial reaction times
The instantaneous concentrations of the precursors $\text{Rh}_4(\text{CO})_{12}$, $\text{HMn(\text{CO})}_5$ and $\text{Mn}_2(\text{CO})_{10}$, and the only observable intermediate $\text{RCORh(\text{CO})}_4$ are shown in Figures 4.48-4.51. Again, some errors could be observed in the first data points due to the mixing problems.

**Figure 4.48** Time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$

**Figure 4.49** Time dependent mole fractions of $\text{HMn(\text{CO})}_5$
Figure 4.50 Time dependent mole fractions of $\text{Mn}_2(\text{CO})_{10}$

Figure 4.51 Time dependent mole fractions of acyl
The concentrations of Rh₄(CO)₁₂ monotonically declined in all the four experiments and the concentration of RCORh(CO)₄ monotonically increased in three of the experiments (T=293, 298K and 303K). However, in the other experiment with higher temperature (T=308K), it can be noted that RCORh(CO)₄ reached a maximum at circa 150 minutes and then began to decrease.

Figure 4.48 shows that higher temperature leads to a faster disappearance of Rh₄(CO)₁₂. The half-lives are circa 40, 35, 15 and <5 minutes in the four experiments when T=293, 298, 303 and 308 K respectively. The corresponding final concentrations of RCORh(CO)₄ were 8.2×10⁻⁵, 9.5×10⁻⁵, 9.0×10⁻⁵, and 8.1×10⁻⁵.

Figure 4.49 and Figure 4.50 show that the concentrations of HMn(CO)₅ monotonically decreased and the concentrations of Mn₂(CO)₁₀ correspondingly increased in the three hydroformylation reactions. The concentrations of Rh₆(CO)₁₆ monotonically decreased as shown in Figure 4.52.

Figure 4.52 Time dependent mole fractions of Rh₆(CO)₁₆
4.5.3.7.2 Product formation

The time-dependent concentrations of the reagent 33DMB and the hydroformylation product 44DMP are shown in Figures 4.53 and 4.54.

**Figure 4.53** Time dependent mole fractions of 33DMB

**Figure 4.54** Time dependent mole fractions of 44DMP
The temperature has a strong effect on the formation of 44DMP. Generally, the rate of hydroformylation tended to be faster with higher reaction temperature. This is consistent with Garland’s work (Garland et al, 1991, 1993, 1999). Except for the first 50 minutes, the reaction rates are constant in the four experiments. The production rates are circa \(7.7 \times 10^{-6}\), \(1.2 \times 10^{-5}\), \(2.5 \times 10^{-5}\), and \(3.7 \times 10^{-5}\) (mol fraction)/min when the temperature is 293, 298, 303 and 308 K respectively. The corresponding final conversions of 33DMB in 280 minutes are circa 17%, 24%, 43% and 66%.

Further inspection demonstrates that the product concentration profiles at \(T= 293\) and \(298\) K are quite close. The possible reason could be that the average \(\text{HMn(CO)}_5\) concentration at \(293\) K is higher than the average \(\text{HMn(CO)}_5\) concentration at \(298\) K (Figure 4.49). This again implies \(\text{HMn(CO)}_5\) is very active to facilitate the product formation in the Rh/Mn bimetallic system.

4.5.3.7. 3 TOF analyses

The effect of temperature on TOF is shown in Figure 4.55. The average turnover frequencies were \(0.12 \pm 0.02\) min\(^{-1}\), \(0.15 \pm 0.02\) min\(^{-1}\), \(0.29 \pm 0.01\) min\(^{-1}\) and \(0.50 \pm 0.06\) min\(^{-1}\) in the three experiments starting with \(T= 293\), 298, 303 and 308K respectively. This suggests that the influence of temperature on the turnover frequencies is strong. The TOF is higher with higher temperature. This result is consistent with previous kinetic studies of unmodified rhodium catalyzed hydroformylation of alkenes. As shown in Figure 4.49, the average concentration of \(\text{HMn(CO)}_5\) at \(T=293\)K is higher than the average concentration of \(\text{HMn(CO)}_5\) at \(T=298\)K. Except for the temperature variation, this is the only observable
difference between these two experiments, which means that HMn(CO)$_5$ could be playing a big role in the organic product formation.

![Figure 4.55](image-url)  The effect of temperature on TOF

### 4.6 Catalysis and Kinetics

#### 4.6.1 Pre-catalytic

From the above six sub-series of experiments performed at different loadings of precursors HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ and Rh$_4$(CO)$_{12}$, substrate 33DMB, different dissolved concentrations of CO and H$_2$, and at different reaction temperatures, the effect of the HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ on the disappearance of Rh$_4$(CO)$_{12}$ is clear. The data 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
H₂, a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occurs. The half-life for Rh₄(CO)₁₂ in the mixed Rh/Mn system is circa 10 minutes when 210 mg Mn₂(CO)₁₀ was used, whereas a half-life under similar reaction conditions for pure Rh systems is circa 1 hour. This atypical initial time behavior suggests that there could exist a second parallel precatalytic pathway for the transformation of Rh₄(CO)₁₂ to RCORh(CO)₄ in the presence of manganese carbonyls. In other words, the hydride facilitated the degradation of the cluster Rh₄(CO)₁₂. Mononuclear hydride attack and subsequent opening of metal clusters are well documented in the literature (Churchill et al, 1986). In the present case, and in the presence of numerous organic reactants, a sequence of steps leading to the rapid formation of RCORh(CO)₄ occurs.

In the classic unmodified rhodium catalyzed reaction, the catalyst precursor Rh₄(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 as shown in Eq 4.11.

\[
\frac{d[RCORh(CO)4]}{dt}=k_1'[Rh_4(CO)_{12}][CO]^2[H_2] \tag{4.11}
\]

In the rhodium/manganese bimetallic system, under the present experimental condition, the following two term equation (Eq 4.12) provided a good fit for the observable kinetics of the acyl formation in the 18 experiments at 298K. The first term represents the fragmentation mechanism in the pure rhodium system, while the second term represents the second parallel precatalytic pathway for the transformation of Rh₄(CO)₁₂ to RCORh(CO)₄ by the HMn(CO)₅ attack. Different integer values of the
exponent for CO in the second term were tested, but an exponent equal to two gave the best results.

\[
d[\text{RCORh(CO)}_4]/dt = k_1' [\text{Rh}_4(\text{CO})_{12}] [\text{CO}]^2 [\text{H}_2] + k_2' [\text{Rh}_4(\text{CO})_{12}] [\text{CO}]^2 [\text{HMn(CO)}_5]
\]  

(4.12)

The regressed numerical values of the rate constants were

\[
k_1' = (7.02 \pm 0.7) \times 10^2 \text{ min}^{-1}
\]

\[
k_2' = (1.53 \pm 0.4) \times 10^5 \text{ min}^{-1}.
\]

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The rate constant $k_1'$ is consistent with our previous studies (Garland and Pino, 1991).

Temperature was systematically varied in four unmodified rhodium catalyzed hydroformylations of 33DMB promoted with HMn(CO)$_5$ at 2.0MPa CO and 1.0MPa H$_2$ to regress the reaction activation parameters. The four temperatures are 293, 298, 303 and 308K. The activation parameters are regressed using the following definitions.

\[
d[\text{RCORh(CO)}_4]/dt = k_1' [\text{Rh}_4(\text{CO})_{12}] [\text{CO}]^2 [\text{H}_2] + k_2' [\text{Rh}_4(\text{CO})_{12}] [\text{CO}]^2 [\text{HMn(CO)}_5]
\]  

(4.13)

where

\[
k_1' = \kappa T/h \times \exp(-\Delta H^\neq/RT + \Delta S^\neq/R)
\]

\[
k_1' = A \times \exp(-\Delta E_a/RT)
\]

\[
k_2' = \kappa T/h \times \exp(-\Delta H^\neq/RT + \Delta S^\neq/R)
\]

\[
k_2' = A \times \exp(-\Delta E_a/RT)
\]
κ is Boltzmann’s constant, h is Planck’s constant, A is Arrhenius pre-exponential factor, Ea is the apparent activation energy, \( \Delta H^\neq \) is the standard enthalpy of activation, and \( \Delta S^\neq \) is the standard entropy of activation.

With respect to the rhodium acyl RCORh(CO)₄ formation, the above two term linear-bilinear form was used to regress the kinetic data at four temperatures. Table 4.6 lists the regressed constants \( k'_1 \) and \( k'_2 \) at different reaction temperatures, where the regression failed at T=303K.

**Table 4.6** The regressed k values at different temperatures

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Temperature (K)</th>
<th>( k'_1 ) (1/min)</th>
<th>( k'_2 ) (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1</td>
<td>293</td>
<td>660</td>
<td>( 1.3 \times 10^5 )</td>
</tr>
<tr>
<td>T-2</td>
<td>298</td>
<td>702</td>
<td>( 1.6 \times 10^5 )</td>
</tr>
<tr>
<td>T-3</td>
<td>303</td>
<td>Fail</td>
<td>Fail</td>
</tr>
<tr>
<td>T-4</td>
<td>308</td>
<td>1.15</td>
<td>( 4.6 \times 10^5 )</td>
</tr>
</tbody>
</table>

The reaction constants \( k'_1 \) and \( k'_2 \) as shown in Table 4.6 for the 3 temperature variation series were analyzed by using Eq 4.13 to get \( \Delta E_a \), \( \Delta H^\neq \) and \( \Delta S^\neq \).

For \( k'_1 \),
\[
\Delta E_a = 32 \pm 103 \text{ KJ/mol}
\]
\[
\Delta H^\neq = 29 \pm 103 \text{ KJ/mol}
\]
\[
\Delta S^\neq = -126 \pm 340 \text{ J/(mol·K)}
\]

For \( k'_2 \),
\[
\Delta E_a = 66 \pm 145 \text{ KJ/mol}
\]
\[
\Delta H^\neq = 64 \pm 145 \text{ KJ/mol}
\]
$\Delta S^\circ = 36 \pm 550 \text{ J/(mol·K)}$

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit.
The regressed results show that some errors are incurred, especially for the entropies. This is because the reactions were carried out in a small temperature range (15K). With respect to the $k'_1$, the first term in the Eq 4.13, which represents the classic unicycle hydroformylation mechanism, the present activation parameters are consistent with previous work (Garland and Pino, 1991).

4.6.1 Hydroformylation

Twenty-one kinetic experiments in six sub-series 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.

The kinetic results clearly show that with simultaneous addition of Rh$_4$(CO)$_{12}$ and Mn$_2$(CO)$_{10}$/HMn(CO)$_5$, the hydroformylation rate of 33DMB increased significantly. The turnover frequencies and hydroformylation rate of 33DMB are strongly dependent on HMn(CO)$_5$. The activity of HMn(CO)$_5$ was as well shown in other sub-series experiments. Since pure HMn(CO)$_5$ showed no observable activity for the hydroformylation of 33DMB, it could be concluded that HMn(CO)$_5$ is strongly involved in the catalytic cycles of rhodium-catalyzed hydroformylation of 33DMB.

Hydroformylation of 3,3-dimethylbut-1-ene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures (Garland and
Analysis of the spectroscopic measurements provide very clean kinetics, where the rate of aldehyde formation is

$$r = k [\text{RCORh(CO)}_4][\text{CO}]^{-1}[\text{H}_2][\text{alkene}]^0. \quad (4.14)$$

The rate expression is consistent with the equilibrium generation of a coordinatively unsaturated intermediate $\text{RCORh(CO)}_3$ followed by the subsequent activation of molecular hydrogen. The kinetics supports the widely accepted unicyclic catalytic reaction mechanism where all intermediates are mononuclear. 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. (Garland, 1993) Detailed kinetic studies using cyclohexene and styrene as substrate have also shown a functional form of $[\text{RCORh(CO)}_4][\text{CO}]^{-1}[\text{H}_2][\text{alkene}]^0$ during the rhodium catalyzed hydroformylation (Fyhr and Garland, 1993; Feng and Garland, 1999).

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

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

$$\text{HMn(CO)}_4 + \text{RCORh(CO)}_3 \rightarrow \text{RCHO} + \text{RhMn(CO)}_7 \quad (4.15)$$
\[ \text{HMn(CO)}_5 + \text{RCORh(CO)}_3 \rightarrow \text{RCHO} + \text{RhMn(CO)}_8 \] (4.16)

Substituting for the pseudo-equilibrium concentration of \( \text{HMn(CO)}_X \) in term of \( \text{HMn(CO)}_5 \) and \( \text{RCORh(CO)}_Y \) in term of \( \text{RCORh(CO)}_4 \), the corresponding formation rates of aldehyde by CBER are expressed as follows.

\[
\begin{align*}
\text{r} &= k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^{-1} \\
\text{r} &= k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^{-2}
\end{align*}
\] (4.17) (4.18)

The reaction rate for unicyclic hydroformylation mechanism is well determined, in with the order for \( \text{RCORh(CO)}_4 \) being 1, the order for \( \text{CO} \) being –1 and the order for \( \text{H}_2 \) being 1. 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 4.19.

\[
\text{r}_{\text{Total}} = k_1[\text{RCORh(CO)}_4][\text{H}_2][\text{CO}]^{-1} + k_2[\text{RCORh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^X
\] (4.19)

With respect to the catalysis of product formation, the above two term linear-bilinear form in organometallic species provided an excellent fit for the observable kinetics of the aldehyde formation. Circa 700 sets of mole fraction data were used in the regression (See Method). The activity of the system (rate of product formation) did not correlate with the presence of any other observables.

Using the non-linear regression program(Matlab), the regressed numerical values of the rate constants at 298 K were

\[
\begin{align*}
k_1 &= 0.446 \pm 0.018 \text{ min}^{-1} \\
k_2 &= 44.5 \pm 14 \text{ min}^{-1}
\end{align*}
\]
\[ x = -1.5 \pm 0.1 \]

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 (Garland and Pino, 1991). The first term corresponds to a turnover frequency of circa 0.1 min\(^{-1}\) at the mean conditions - again consistent with the previous studies.

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 circa 1:1. In particular, according to the above kinetics, at 298K, 2.0MPa CO, 1.0MPa H\(_2\), 5 ml 33DMB, 50mg \( \text{Rh}_4(\text{CO})_{12} \) and 210mg \( \text{Mn}_2(\text{CO})_{10} \) (\( X_{\text{MnH(CO)5}}=3.3 \times 10^{-5} \)), the contribution of CBER to the final product formation is 57%.

Rearrangement of the two terms leads to the conclusion that \( \text{HMn(CO)}_5 \) is circa 170 times more efficient than \( \text{H}_2 \), 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.

Temperature was systematically varied in four unmodified rhodium catalyzed hydroformylations of 33DMB promoted with \( \text{HMn(CO)}_5 \) at 2.0MPa CO and 1.0MPa H\(_2\) to regress the reaction activation parameters. The four temperatures are 293, 298, 303 and 308K. The activation parameters are regressed using the following definitions.

\[
\frac{r_{\text{Total}}}{k_1[R\text{C}O\text{Rh(CO)}_4][\text{H}_2][\text{CO}]}+k_2[R\text{C}O\text{Rh(CO)}_4][\text{HMn(CO)}_5][\text{CO}]^{-1.5} \quad (4.20)
\]

where

\[ k_1 = \kappa T/h \times \exp(-\Delta H^*/RT+\Delta S^*/R) \]
\[ k_1 = A \times \exp(-\Delta E_a/RT) \]
\[ k_2 = \kappa T/h \times \exp(-\Delta H^\neq/RT + \Delta S^\neq/R) \]
\[ k_2 = A \times \exp(-\Delta E_a/RT) \]

The definitions are the same as in Section 4.6.1.

With respect to the product aldehyde formation, the above two term linear-bilinear form was used to regress the kinetic data at four temperatures. Table 4.7 lists the regressed constants \( k_1 \) and \( k_2 \) at different reaction temperatures.

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Temperature (K)</th>
<th>( k_1 ) (1/min)</th>
<th>( k_2 ) (1/min)</th>
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<td>44.1</td>
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<td>0.446</td>
<td>44.5</td>
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</tbody>
</table>

The reaction constants \( k_1 \) and \( k_2 \) as shown in Table 4.7 for the 4 temperature variation series were analyzed by using Eq 4.20 to get \( \Delta E_a \), \( \Delta H^\neq \) and \( \Delta S^\neq \).

For \( k_1 \),
\[ \Delta E_a = 89 \pm 45 \text{ KJ/mol} \]
\[ \Delta H^\neq = 87 \pm 45 \text{ KJ/mol} \]
\[ \Delta S^\neq = 4 \pm 160 \text{ J/mol-K} \]

For \( k_2 \),
\[ \Delta E_a = 63 \pm 56 \text{ KJ/mol} \]
\[ \Delta H^\circ = 61 \pm 56 \text{ KJ/mol} \]
\[ \Delta S^\circ = -42 \pm 180 \text{ J/mol} \cdot \text{K} \]

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The regressed results show that some errors are incurred. This could be in part due to that the reactions were carried out in a small temperature range (15K) and the temperature dependencies of the solubilities. With respect to \( k_1 \), the first term in Eq 4.20, which represents the classic unicycle hydroformylation mechanism, the present activation parameters are consistent with previous work (Garland and Pino, 1991).

4.7 Discussion

4.7.1 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 coordinatively 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)\(_3\) on RCORh(CO)\(_3\) and/or [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 analog) was un-observable 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 (James, 1982; Oro et al., 2001), is known to occur exceptionally rapidly, even at low temperatures, on heterometallic dinuclear carbonyl complexes - where CoRh(CO)7 is perhaps the best example(Garland and Pino, 1990).

The proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Mn CBER hydroformylation reactions is shown in Figure 4.56. All intermolecular transformations in the unicyclic topology are 1st order in the mononuclear metal complexes. Two elementary steps in Scheme 1 are highlighted by the labels $\alpha$ and $\beta$. These labels are used to identify the key mechanisms which give rise to the existence of the bimetallic CBER. The $\alpha$ step denotes the simultaneous generation of the crucial mononuclear hydrides HRh(CO)3 and HMn(CO)5 from the dinuclear complex H2RhMn(CO)8. The $\beta$ step is the binuclear elimination step. The steps $-\alpha$ and $\beta$ are bimolecular in metal complexes. The binuclear elimination step has been drawn as if the process proceeds through a concerted 4-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 4-center transition state, but instead through 2 or more simple transition states, additional intermediates exist on the reaction pathway.
Concerning other details in Figure 4.56, 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 5-coordinate rhodium structures, namely, axially substituted trigonal bipyramidal geometries.

The interconnected topology of a unicyclic mechanism and a CBER mechanism as shown in Figure 4.56 gives rise to the complex linear-bilinear form of the observed kinetics of product formation.
4.7.2 Initial Reaction Times and Precatalytic Steps

In the present bimetallic system, a good two term equation was obtained to fit the kinetic data of the 21 experiments.

\[
\frac{d[R\text{CORh(CO)}_4]}{dt}=k_1' [\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2[H_2]+k_2' [\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2[\text{HMn(CO)}_5]
\]  
(4.21)

The functional form used for the first term is that which was previously shown to arise in simple monometallic rhodium hydroformylations. The common factor $[\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2$ suggests a rate limiting step involving a pre-equilibrated open polyhedron intermediate $\{\text{Rh}_4(\text{CO})_{14}\}$. Kinetic evidence for open polyhedral clusters as intermediates in cluster fragmentation reactions is readily available (Bor et al, 1978). 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 $\{\text{Rh}_4(\text{CO})_{14}\}$.

In addition, redistribution of manganese carbonyl complexes also occurs at initial reaction times. In the particular experiment shown in Figures 4.9 and 4.10, the Mn$_2$(CO)$_{10}$ concentration declines somewhat from its initial value at $t=0$ and the HMn(CO)$_5$ concentration increases from its non-zero initial value. The manganese carbonyl concentrations then remain essentially constant for the remainder of the experiment. In some other experiments, the HMn(CO)$_5$ concentration monotonically decreased and the Mn$_2$(CO)$_{10}$ concentration monotonically increased. But the HMn(CO)$_5$ concentration never reached zero in any of the 5 hour hydroformylations.
Redistribution of Mn$_2$(CO)$_{10}$ and HMn(CO)$_5$ in the bimetallic system may occur for many reasons, including hydrogen activation on Mn$_2$(CO)$_{10}$ and reaction of HMn(CO)$_5$ with the trace impurities in the 300 ml reaction autoclave solution. It is well known that the manganese hydride is extremely sensitive to traces of 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.

### 4.7.3 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)$_{16}$ (Slivinski, et al 1990). 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 the Garland group, its decline as a function of time during Rh$_4$(CO)$_{12}$ initiated syntheses is unusual. The present mixed Rh-Mn hydroformylation exhibits a steady decline in the Rh$_6$(CO)$_{16}$ in spite of 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.

### 4.8 Conclusions

In situ spectroscopic and kinetic measurements have been performed for the homogeneous rhodium and manganese catalyzed hydroformylation of 3,3-dimethylbut-1-
ene. A series of well-defined experiments were conducted to search for the bimetallic catalytic binuclear elimination. The in-situ FTIR spectroscopic data were analyzed using the total system identification algorithm.

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. Regression of the kinetic data strongly suggests that there is statistically significant contribution to aldehyde formation from the bimetallic catalytic binuclear elimination of manganese hydride complexes with acyl rhodium tetracarbonyl. As secondary effects, manganese carbonyl hydride leads to a reduction in the induction period by promoting the pre-catalytic transformation of the rhodium precursor to rhodium intermediates and retards, or even reverses, deactivation due to cluster formation. This is the first solid evidence on the existence of bimetallic CBER. The result could be an important complement to the classic unicyclic hydroformylation mechanism.

*Part of the results of this chapter has been reported in Journal of the American Chemical Society (2003), 125(18), 5540-5548.*
CHAPTER 5  \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) BIMETALLIC CATALYZED HYDROFORMYLATION OF CYCLOPENTENE

5.1 Introduction

In Chapter 4, the \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) bimetallic catalyzed hydroformylation of 33DMB was studied systematically. The spectroscopic and kinetic analyses proved the existence of bimetallic CBER. This chapter will extend the \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) bimetallic system to the homogeneous catalyzed hydroformylation of another type of alkene, namely cyclopentene. The objective is to see if the synergistic effects arising from bimetallic CBER that were observed with \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) under hydroformylation conditions are restricted to the use of 33DMB. If not, the \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) bimetallic catalyzed hydroformylation of cyclopentene will provide another example of bimetallic CBER.

5.2. Experimental Section

All the experiments were performed in a similar manner. A typical procedure is as follows.

First, single beam background spectra of the IR sample chamber were recorded. Then 150 ml 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 2.0MPa 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 cyclopentene(CP)
dissolved in 50ml 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 CP/CO/n-hexane solution in the high-pressure cell were recorded. A solution of circa 50 mg Rh₄(CO)₁₂ dissolved in 50ml n-hexane and a solution of circa 100 mg Mn₂(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 Rh₄(CO)₁₂/Mn/CP/CO/n-hexane/solution in the high-pressure cell were recorded. 2.0 MPa hydrogen was then added to initiate the syntheses. The detailed experimental design for this study is shown in Table 5.1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mn₂(CO)₁₀,mg</th>
<th>CO ,MPa</th>
<th>H₂ ,MPa</th>
<th>CP,ml</th>
<th>Rh₄(CO)₁₂,mg</th>
<th>Temperature,K</th>
</tr>
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<td>Standard</td>
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<td>5</td>
<td>51.60</td>
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<td>2.0</td>
<td>5</td>
<td>0</td>
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</tr>
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<td>5</td>
<td>51.89</td>
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<td>2.0</td>
<td>5</td>
<td>0</td>
<td>289.7</td>
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<td>CO Variation</td>
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<td>103.07</td>
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<td>2.0</td>
<td>5</td>
<td>53.73</td>
<td>289.7</td>
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<td>108.45</td>
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<td>54.32</td>
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<td>108.97</td>
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<td>2.0</td>
<td>5</td>
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<td>289.7</td>
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<td>5</td>
<td>49.46</td>
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<td>52.48</td>
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<td>104.57</td>
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<td>47.74</td>
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<td>Cyclopentene Variation</td>
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<tr>
<td>100.37</td>
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<td>289.7</td>
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<tr>
<td>109.36</td>
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<td>2.0</td>
<td>10</td>
<td>5</td>
<td>50.63</td>
<td>289.7</td>
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<tr>
<td>Mn₂(CO)₁₀ variation</td>
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<tr>
<td>25.00</td>
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<td>2.0</td>
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<td>51.04</td>
<td>289.7</td>
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<td>2.0</td>
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<td>49.80</td>
<td>289.7</td>
</tr>
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<td>2.0</td>
<td>2.0</td>
<td>5</td>
<td>51.84</td>
<td>289.7</td>
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<td>229.00</td>
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<td>2.0</td>
<td>5</td>
<td>50.63</td>
<td>289.7</td>
</tr>
<tr>
<td>Temperature Variation</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>104.79</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
<td>48.12</td>
<td>281.5</td>
</tr>
<tr>
<td>108.28</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
<td>5</td>
<td>49.00</td>
<td>293.7</td>
</tr>
<tr>
<td>104.50</td>
<td>2.0</td>
<td>2.0</td>
<td>5</td>
<td>5</td>
<td>52.05</td>
<td>299.4</td>
</tr>
</tbody>
</table>
The experimental design of the experiments involved 300 ml solvent and the intervals 281.5-308.9K, $P_{H_2} = 1.0-4.0$ MPa, $P_{CO} = 1.0-4.0$ MPa, initial alkene = 2-10ml, initial $Rh_4(CO)_{12} = 24.05-106.47$mg and initial $Mn_2(CO)_{10} = 25.0-229$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)(Garland, 2002). As discussed in Chapter 4, 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.

The in-situ spectra were taken every 10 minutes during each six hour 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.

5.3 Spectral analyses

The total system identification algorithm is used to analyse the in-situ FTIR spectra.

One of the raw experimental spectra before any spectral pre-processing is shown in Figure 5.1.
As discussed before (in Chapter 4, Section 4.4.1), two spectral windows with the region of 1000 – 1300 cm\(^{-1}\) (containing information for the solvent n-hexane) and 1550 – 2500 cm\(^{-1}\) (containing the spectroscopic information for both the organic and organometallic species) will be used for further spectral analyses.

As discussed in Chapter 3, the experimental spectra can be subjected to singular value decomposition (SVD) directly without preconditioning (Widjaja et al., 2002). Therefore, SVD was firstly employed to decompose the experimental absorbance data matrix \(A_{1461 \times 2951}\) to give the orthonormal matrices \(U_{1461 \times 1461}\) and \(V_{2951 \times 2951}^T\), and the diagonal singular value matrix \(\Sigma_{1461 \times 2951}\). Although 2951 vectors were obtained from the \(V^T\) matrix after data decomposition only 1461 vectors are physically meaningful. The significant spectral extrema in the first few right singular vectors were inspected and were used as targets in the BTEM algorithm. Six significant bands (indicated by numbers in Figure 5.2) were selected for the reconstructions. Table 5.2 lists the selected wavenumber
regions, the maximum peak absorbance, number of $V^T$ vectors taken for spectral reconstruction and the identity of resolved pure component spectra.

Figure 5.2 Six significant spectral extrema used to recover pure spectra

Reconstructed pure component spectra via BTEM are presented in Figure 5.3.
Figure 5.3 The recovered pure component spectra using BTEM.

The quality of the BTEM reconstructions is very high. Flat and smooth baselines are observed.

From a spectroscopic / observable viewpoint, the present 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.
Table 5.2  Spectral Reconstruction Parameters and Species Identities

<table>
<thead>
<tr>
<th># Species</th>
<th># VT vectors, z</th>
<th>Wavenumber region</th>
<th>Maximum Abs, α</th>
<th>Species identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>20</td>
<td>1732 – 1736</td>
<td>1</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>2.</td>
<td>30</td>
<td>1614-1616</td>
<td>1</td>
<td>Cyclopentene</td>
</tr>
<tr>
<td>3.</td>
<td>20</td>
<td>2014.5 – 2015.5</td>
<td>1</td>
<td>Mn₂(CO)₁₀</td>
</tr>
<tr>
<td>4.</td>
<td>15</td>
<td>2015.5 – 2017</td>
<td>1</td>
<td>HMn(CO)₅</td>
</tr>
<tr>
<td>5.</td>
<td>30</td>
<td>1885 – 1887</td>
<td>5</td>
<td>Rh₄(CO)₁₂</td>
</tr>
<tr>
<td>6.</td>
<td>30</td>
<td>2039 – 2041</td>
<td>5</td>
<td>RCORh(CO)₄</td>
</tr>
</tbody>
</table>

As introduced in Chapter 3, before calculating the mole numbers of each observable, an important re-normalization of the spectroscopic data must be performed in order to eliminate the dependence on variable reaction volume and variable path length of cell.

In the present study, the standard $A_{\omega}^{std}$ of each reaction spectrum is derived from solvent n-hexane’s absorbance data at a reference wavenumber $\omega = 1137 \text{ cm}^{-1}$. In addition, the moles of solvent n-hexane $n_{std}$ can be calculated from its initial volume and the molar absorptivity of n-hexane at $\omega = 1137 \text{ cm}^{-1}$ can be obtained from experimental data as 2.18 L/(mole⋅cm).

Upon obtaining the above-mentioned results, further numerical analysis is carried out to solve the material balance problem in order to obtain the real quantification of the observable species.
Since Rh-, Org-, and Mn- are conserved before and after reaction, they are used to establish the reaction invariant model. Accordingly, the proposed chemical group matrix is as follows.

\[
\begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
4 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 2 \\
1 & 1 & 0
\end{bmatrix}
\]

(5.1)

Sequentially the rows of this matrix are associated with aldehyde, HMn(CO)₅, Rh₄(CO)₁₂, cyclopentene, Mn₂(CO)₁₀, and RCORh(CO)₄ species.

As described in Chapter 3, a diagonal weighting matrix \(d_{sys} \times s \times s\) is required to calculate the absolute magnitude of the time series of moles for the observable species. This diagonal matrix can be obtained using a reaction invariant / material balance model, in which the sum of squares error minimization between the estimated \(N_{ke} \times E\) and the initial reaction condition \(N_{ke} \times E\) I was utilized. The minimization of this error objective function was carried out using Corana’s SA.

The obtained optimum matrix \(d_{sys} \times s \times s\) is employed to calculate the real magnitudes of the constructed pure component spectra. The maxima of these six pure component spectra are shown in the Table 5.3.
Table 5.3  The maximum absorptivities for each pure component spectral estimate

<table>
<thead>
<tr>
<th>Species</th>
<th>Max Peak, cm$^{-1}$</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehyde</td>
<td>1732.6</td>
<td>286</td>
</tr>
<tr>
<td>HMn(CO)$_5$</td>
<td>2015.8</td>
<td>25135</td>
</tr>
<tr>
<td>Rh$<em>4$(CO)$</em>{12}$</td>
<td>2070.0</td>
<td>18370</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>1615.0</td>
<td>5.85</td>
</tr>
<tr>
<td>Mn$<em>2$(CO)$</em>{10}$</td>
<td>2014.8</td>
<td>22528</td>
</tr>
<tr>
<td>RCORh(CO)$_4$</td>
<td>2021.2</td>
<td>4233</td>
</tr>
</tbody>
</table>

The absorptivities of aldehyde, HMn(CO)$_5$, Rh$_4$(CO)$_{12}$, Mn$_2$(CO)$_{10}$ and RCORh(CO)$_4$ are quite close to the values obtained in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ catalysed hydroformylation of 33DMB (Chapter 4).

After obtaining the real magnitudes of the absorptivities, the time series of moles for the seven observable components in all the 23 experiments can be directly generated. These are presented in Figure 5.4.

From all the time-dependent concentration profiles of both organic and organometallic species, it can be noted that even under reaction conditions of circa 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.
In this section 5.3, the chemometric analyses were performed in collaboration with Dr Widjaja Effendi.
5.4 Results

5.4.1 Spectral aspects

Hydroformylation of alkene in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low temperatures. As mentioned before, the previous detailed in-situ FTIR spectroscopic studies have shown the presence of only 5 observable organometallics (RCORh(CO)₄, Rh₂(CO)₈, Rh₄(CO)₁₂, Rh₆(CO)₁₆, and Rh₄(σ-CO)₁₂), and the last two normally exist at the ppm or sub-ppm level under most catalytic conditions. No evidence for observable quantities of the known rhodium hydride species, could be obtained.

In the present Rh₄(CO)₁₂/HMn(CO)₅ bimetallic catalyzed hydroformylation of cyclopentene, the chemometric analyses of the in situ infrared spectra of the reaction recovered, the precursors Rh₄(CO)₁₂, HMn(CO)₅, and Mn₂(CO)₁₀, the organic reagent cyclopentene, the rhodium intermediate RCORh(CO)₄ and the organic product RCHO.

Unlike the Rh/Mn/33DMB system, the cluster Rh₆(CO)₁₆ and the isomer Rh₄(σ-CO)₁₂ were not successfully recovered. There was no indication of fragmentation such as the formation of Rh₂(CO)₈ (ν_CO=2086,2061,1860,1845 cm⁻¹). As with the Rh₄(CO)₁₂/HMn(CO)₅/Mn₂(CO)₁₀ catalyzed hydroformylation of 33DMB system, no Rh-Mn complex analogous to MnCo(CO)₉ (Kovacs et al, 1985) was observed in the Rh₄(CO)₁₂/HMn(CO)₅/Mn₂(CO)₁₀ catalysed hydroformylation of cyclopentene.

5.4.2 Calculations

The methods to calculate the solubilities of H₂ and CO and the reactant and product concentrations are the same as those used in the Rh₄(CO)₁₂/HMn(CO)₅
/\text{Mn}_2(\text{CO})_{10}\) catalyzed hydroformylation of 33DMB system (Chapter 4). The rates of the formation of aldehyde were calculated in terms of turnover frequency (TOF) by using the similar finite difference equation as used in Chapter 4.

5.4.3 Results

As introduced in the experimental work (Section 5.2), a total of 23 experiments in six series (the variations of \(\text{Mn}_2(\text{CO})_{10}/\text{HMn}(\text{CO})_5\) loading, \(\text{Rh}_4(\text{CO})_{12}\) loading, cyclopentene loading, CO pressure, \(\text{H}_2\) pressure and reaction temperature) were performed. In the following, the results of studies on the \(\text{Rh}_4(\text{CO})_{12} /\text{HMn}(\text{CO})_5\) bimetallic catalyzed hydroformylation of cyclopentene will be presented in detail.

5.4.3.1. With only \(\text{Mn}_2(\text{CO})_{10}/\text{HMn}(\text{CO})_5\)

Similar to Chapter 4, in order to determine the activities of \(\text{Mn}_2(\text{CO})_{10}/\text{HMn}(\text{CO})_5\) in the cyclopentene system, two experiments with only \(\text{Mn}_2(\text{CO})_{10}/\text{HMn}(\text{CO})_5\) as the precursor were carried out at both reference temperature (289.7K) and high temperature (301.5K). The two 6 hour experiments showed there was no observable reaction under our reaction conditions (2.0MPa CO, 2.0MPa \(\text{H}_2\), 5ml cyclopentene, 289.7K and 301.5K).

5.4.3.2 With \(\text{Rh}_4(\text{CO})_{12}\) and \(\text{HMn}(\text{CO})_5\): Changing \(\text{HMn}(\text{CO})_5\) initial loadings

In this section, the hydroformylation of cyclopentene with simultaneous addition of \(\text{Rh}_4(\text{CO})_{12}\) and \(\text{HMn}(\text{CO})_5\) were studied. The initial concentration of the precursor \(\text{HMn}(\text{CO})_5\) was systematically varied in six hydroformylations. The five kinetic
experiments were performed at 289.7K, 2.0MPa CO and 2.0MPa H₂ to investigate the effect of HMn(CO)₅ on the unmodified rhodium catalyzed hydroformylation of cyclopentene. The corresponding concentrations of H₂ and CO were 0.0198 and 0.0504 respectively. The initial input of cyclopentene was 5 ml and the concentration was 0.025 mole fraction. The initial loadings of Mn₂(CO)₁₀ were 0, 25.0, 50.0, 117.36, 150.5 and 229.0 mg while the initial loadings of Rh₄(CO)₁₂ were between 49.8-52.2 mg. Accordingly, the initial concentrations of HMn(CO)₅ in mole fraction were \( X_{\text{HMn(CO)₅}=0}, 1.4\times10^{-5}, 2.2\times10^{-5}, 3.9\times10^{-5}, 3.5\times10^{-5} \) and \( 4.1\times10^{-5} \) respectively. The corresponding initial concentrations of Rh₄(CO)₁₂ were circa \( 3\times10^{-5} \) mole fraction.

5.4.3.2.1 Initial reaction times

The time-dependent concentrations of the precursors Rh₄(CO)₁₂, HMn(CO)₅ and Mn₂(CO)₁₀, and the only observable intermediate RCORh(CO)₄ are shown in Figures 5.5-5.8. Some errors could be observed in the first data points. This is due to the fact that the first spectrum was taken immediately when all the reagents were added to the autoclave, which means there was not enough time for the mixing of the reaction mixture and its transport from the autoclave to the in-situ IR.
Figure 5.5 Time dependent mole fractions of Rh$_4$(CO)$_{12}$

Figure 5.6 Time dependent mole fractions of HMn(CO)$_5$
Figure 5.7 Time dependent mole fractions of Mn$_2$(CO)$_{10}$

Figure 5.8 Time dependent mole fractions of acyl
It can be noted that after the simultaneous addition of the manganese carbonyls HMn(CO)₅ and Mn₂(CO)₁₀ and hydrogen to the systems initially containing Rh₄(CO)₁₂, alkene, hexane and CO, the concentrations of Rh₄(CO)₁₂ monotonically declined in all the six experiments and the concentration of RCORh(CO)₄ correspondingly increased in all experiments for the first 6 hours.

As discussed in Chapter 4, in the previous study with 33DMB as substrate catalyzed with pure Rh₄(CO)₁₂, the disappearance of the precursor Rh₄(CO)₁₂ during the initial phase of the hydroformylation with 33DMB is a well-behaved pseudo-first-order process over at least circa 2 half-lives. However, when Rh₄(CO)₁₂, Mn₂(CO)₁₀, and HMn(CO)₅ were added simultaneously, the data presented in Figure 5.5 indicate that the decrease of Rh₄(CO)₁₂ and increase of RCORh(CO)₄ are not simple monotonic functions at initial reaction times. Indeed, like Rh/Mn/33DMB system, upon addition of Mn₂(CO)₁₀, HMn(CO)₅ and H₂, a rapid decline in the catalyst precursor concentration and the corresponding increase in acyl complex concentration occur. The concentration of HMn(CO)₅ has a big effect on the transformation of Rh₄(CO)₁₂. Generally speaking, the higher the concentration of HMn(CO)₅, the faster the transformation of Rh₄(CO)₁₂ to RCORh(CO)₄.

The half-life for Rh₄(CO)₁₂ in the mixed Rh/Mn system was circa 60 minutes when 229.0 mg Mn₂(CO)₁₀ was used, whereas a half-life under similar reaction conditions for pure Rh systems is circa 2 hours. This atypical initial time behavior is again indicative of the existence of a second parallel precatalytic pathway for the transformation of Rh₄(CO)₁₂ to RCORh(CO)₄ in the presence of manganese carbonyls, namely, the hydride facilitated degradation of the cluster Rh₄(CO)₁₂.
In both cases with and without $\text{Mn}_2(\text{CO})_{10}/\text{HMn( CO)}_5$, the equilibrium controlled precursor conversion, as observed with cyclohexene as substrate, did not occur (Fyhr and Garland, 1993). This is explained by the significantly higher reactivity of cyclopentene.

The concentrations of $\text{HMn( CO)}_5$ monotonically declined and $\text{Mn}_2(\text{CO})_{10}$ correspondingly changed. The concentrations of $\text{HMn( CO)}_5$ never approached zero in any 6 hour experiment.

The present results concerning initial reaction times are in good agreement with those obtained in the $\text{Rh}_4(\text{CO})_{12}/\text{HMn( CO)}_5$ bimetallic catalyzed hydroformylation of 33DMB.

5.4.3.2.2 Product formation

The concentration profiles of the product aldehyde are shown in Figure 5.9. The concentrations of the product aldehyde monotonically increase in all the six experiments. The production of aldehyde could be identified within the first few minutes when $\text{HMn( CO)}_5/\text{Mn}_2(\text{CO})_{10}$ were added simultaneously.
Similar to Rh₄(CO)₁₂/HMn(CO)₅ bimetallic catalyzed hydroformylation of 33DMB system, 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 minutes, the rates of product formation are more-or-less constant. The rates are circa \(8.2 \times 10^{-6}\), \(1.1 \times 10^{-5}\), \(1.3 \times 10^{-5}\), \(1.6 \times 10^{-5}\), \(1.8 \times 10^{-5}\), and \(2.3 \times 10^{-5}\) (mol fraction)/min when \(X_{\text{HMn(CO)5}}=0\), \(1.4 \times 10^{-5}\), \(2.2 \times 10^{-5}\), \(3.9 \times 10^{-5}\), \(3.5 \times 10^{-5}\) and \(4.1 \times 10^{-5}\) respectively. When 229.0 mg Mn₂(CO)₁₀ was used with Rh₄(CO)₁₂, the rate of hydroformylation is as great as 300% of the rate that was anticipated from the rhodium loading alone. Since HMn(CO)₅/Mn₂(CO)₁₀ is nearly inert towards transformations of alkenes at the present
reaction conditions, it implies that \( \text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10} \) is involved in the rhodium catalytic pathway to produce aldehyde.

5.4.3.2.3 TOF analyses

The effect of loading of \( \text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10} \) on the TOF is shown in Figure 5.10. The turnover frequencies (TOF) based on rhodium and defined in the experimental section were 0.12±0.01 min\(^{-1}\), 0.15±0.01min\(^{-1}\), 0.20±0.02min\(^{-1}\), 0.23±0.002min\(^{-1}\), 0.21±0.02min\(^{-1}\) and 0.28±0.02 min\(^{-1}\) when \( X_{\text{HMn(CO)}_5} = 0, 1.4\times10^{-5}, 2.2\times10^{-5}, 3.9\times10^{-5}, 3.5\times10^{-5} \) and \( 4.1\times10^{-5} \) respectively. The errors are listed as twice the standard deviation, i.e., the 95% confidence limit.

![Figure 5.10 Effect of HMn(CO)_5 on TOF](image)

The TOF values demonstrate that \( \text{HMn(CO)}_5 \) is very active with \( \text{Rh}_4(\text{CO})_{12} \) for the hydroformylation of cyclopentene. As discussed in Chapter 4, in the hydroformylation of
33DMB with pure unmodified rhodium carbonyl, it has been repeatedly shown that turnover frequencies are only dependent on the temperature, hydrogen pressure and carbon monoxide pressure (Garland, et al, 1990, 1993). Our present results clearly show that TOFs increase with the increased loading of HMn(CO)₅. When the initial concentration of HMn(CO)₅ was $4.1 \times 10^{-5}$, the TOF is as great as 230% of that was anticipated from the rhodium loading alone.

Furthermore, it should be noted that the TOF with Mn₂(CO)₁₀=150.25 mg is quite close to that of Mn₂(CO)₁₀=50.0 mg and even smaller than the TOF with Mn₂(CO)₁₀=117.36 mg. This can be traced to the HMn(CO)₅ concentration profiles shown in Figure 5.6. Indeed, the average HMn(CO)₅ concentrations of Mn₂(CO)₁₀=50.0 mg and Mn₂(CO)₁₀=150.25 mg are quite similar, while the average HMn(CO)₅ concentrations of Mn₂(CO)₁₀=117.36 mg are higher. This means that only HMn(CO)₅ is associated with the high activities in the Rh/Mn bimetallic system. The higher the HMn(CO)₅ concentration, the higher the TOF.

The present results are consistent with those of the Rh₄(CO)₁₂ /HMn(CO)₅ bimetallic catalyzed hydroformylation of 33DMB. This is again a clear-cut quantitative confirmation of the contribution of HMn(CO)₅ to the final product and proves that HMn(CO)₅ must be involved in at least one step of the catalytic cycle of the hydroformylation. As discussed in Chapter 4, it is possible that HMn(CO)₅ would interact with the most active rhodium intermediate RCORh(CO)₄.

5.4.3.3. Changing Rh₄(CO)₁₂ initial loadings
The initial concentration of Rh₄(CO)₁₂ was systematically varied in four hydroformylation experiments performed at 289.7K, 5 ml cyclopentene, 2.0MPa carbon monoxide, 2.0MPa hydrogen and circa 100 mg Mn₂(CO)₁₀ in 300 ml n-hexane. The corresponding concentrations of H₂ and CO were 0.0198 and 0.0504 respectively. The initial input of cyclopentene was 5 ml and the concentration was 0.025 mole fraction. The initial loading of Rh₄(CO)₁₂ was 24.05, 51.60 82.11 and 106.47 mg. Accordingly, the calculated initial concentrations of Rh₄(CO)₁₂ in mole fractions were \( X_{\text{Rh}_4(\text{CO})_{12}} = 1.4 \times 10^{-5}, 3.0 \times 10^{-5}, 4.8 \times 10^{-5}, 6.2 \times 10^{-5} \) respectively. The initial loading of Mn₂(CO)₁₀ was circa 100 mg and the corresponding initial concentrations of HMn(CO)₅ were circa 2.5\( \times 10^{-5} \) to 4.0\( \times 10^{-5} \) mole fraction. This is because of the irreproducibility of the photo-irradiation of Mn₂(CO)₁₀ with H₂.

For easy comparison, the concentration profiles for pure rhodium catalyzed hydroformylation are also included in the following figures.

### 5.4.3.3.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HMn(CO)₅ and Mn₂(CO)₁₀, and the only observable intermediate RCORh(CO)₄ are shown in Figures 5.11-5.14. Similar errors could be observed in the first data points due to the mixing problems.
Figure 5.11 Time dependent mole fractions of Rh₄(CO)₁₂

Figure 5.12 Time dependent mole fractions of HMn(CO)₅
Figure 5.13 Time dependent mole fractions of Mn$_2$(CO)$_{10}$

Figure 5.14 Time dependent mole fractions of acyl
Figure 5.11 indicates, that unlike the pure Rh₄(CO)₁₂ catalyzed hydroformylation, when Rh₄(CO)₁₂, Mn₂(CO)₁₀, and HMn(CO)₅ were added simultaneously, a faster decrease of Rh₄(CO)₁₂ and a faster increase of RCORh(CO)₄ occurred at initial reaction times.

Figure 5.14 indicates that concentrations of RCORh(CO)₄ increase with increasing initial Rh₄(CO)₁₂ concentrations, but these two quantities are not proportional. Indeed, the final concentrations of RCORh(CO)₄ were 0.5×10⁻⁴, 0.91×10⁻⁴, 1.5×10⁻⁴, 1.8×10⁻⁴, when X_{Rh₄(CO)₁₂}=1.4×10⁻⁵, 3.0×10⁻⁵, 4.8×10⁻⁵, 6.2×10⁻⁵ respectively. The half-life under the present conditions for Rh₄(CO)₁₂ in the mixed Rh/Mn system was circa 90 minutes when circa 100 mg Mn₂(CO)₁₀ was used, while the half-life with pure rhodium system is circa 120 minutes. The results again demonstrate that in the present Rh/Mn bimetallic system, another pre-catalytic mechanism to transfer Rh₄(CO)₁₂ to RCORh(CO)₄ by hydride attack is available.

In particular, one test experiment (when Rh₄(CO)₁₂ =82.11mg) was performed to check the HMn(CO)₅ attack on the Rh₄(CO)₁₂. In this experiment, after HMn(CO)₅ was added a short period (5 minutes) was allowed to transpire before molecular hydrogen was added to the system and the spectral acquisition started. In the other standard experiments, the H₂ was added to the autoclave immediately after HMn(CO)₅ with immediate spectral acquisition. As shown in Figure 5.14 (when Rh₄(CO)₁₂ =82.11mg) the rhodium acyl complex appeared immediately in the first spectrum. This means the HMn(CO)₅ can attack Rh₄(CO)₁₂ in the presence of substrate to produce RCORh(CO)₄. This is an independent confirmation of the manganese hydride facilitated Rh₄(CO)₁₂ fragmentation.
The concentrations of HMn(CO)$_5$ (Figure 5.12) slightly decreased and Mn$_2$(CO)$_{10}$ (Figure 5.13) correspondingly increased at increasing reaction times. In one of the four experiments (Rh$_4$(CO)$_{12}$=106.47 mg), a fast decline of HMn(CO)$_5$ was observed.

5.4.3.3.2 Product formation

The time-dependent concentrations of the hydroformylation product are shown in Figure 5.15. With the exception of the first 80 minutes, the rates of product formation are more-or-less constant. The rates are circa $0.8 \times 10^{-5}$, $1.6 \times 10^{-5}$, $2.5 \times 10^{-5}$, and $2.2 \times 10^{-5}$ (mol fraction)/min in the four experiments starting with $X_{\text{Rh}_4(\text{CO})_{12}}=1.4 \times 10^{-5}$, $3.0 \times 10^{-5}$, $4.8 \times 10^{-5}$, $6.2 \times 10^{-5}$ respectively. The variation in the initial concentration of Rh$_4$(CO)$_{12}$ appears to have a big effect on the formation of aldehyde. As discussed in Chapter 4, one reason is that the higher initial concentrations of Rh$_4$(CO)$_{12}$ give rise to higher concentrations of RCORh(CO)$_4$, which produces the final product.
However, close inspection shows that the bimetallic system activity is much higher than the pure rhodium system. As shown in figure 5.15, at the same loading of Rh₄(CO)₁₂ (circa 50 mg), the hydroformylation rate of the Rh/Mn system was more than two times faster than that of the pure rhodium system. Furthermore, it is worthy to note, when 24.05 mg Rh₄(CO)₁₂ was used with HMn(CO)₅/Mn₂(CO)₁₀, the hydroformylation reaction rate is almost the same as that when 51.6 mg Rh₄(CO)₁₂ was used alone.

When we compare the other two experiments (Rh₄(CO)₁₂=82.1, 106.47 mg), Figure 5.15 shows that the two aldehyde concentration profiles are quite close and the product formation rate(Rh₄(CO)₁₂=106.47 mg) is even slower than that of Rh₄(CO)₁₂=82.1mg. Again, this can be attributed to the big difference in HMn(CO)₅ concentration profiles as shown in Figure 5.12, which implies that the system activity is
higher with higher HMn(CO)$_5$ mole fractions. The present results are again consistent with that of the Rh/Mn/33DMB bimetallic catalysed hydroformylation reaction.

### 5.4.3.3 TOF analyses

The effect of loading of Rh$_4$(CO)$_{12}$ on TOF is shown in Figure 5.16. The average turnover frequencies were $0.17 \pm 0.03 \text{min}^{-1}$, $0.23 \pm 0.02 \text{min}^{-1}$, $0.20 \pm 0.02 \text{min}^{-1}$ and $0.16 \pm 0.04 \text{min}^{-1}$ in the four experiments starting with $X_{\text{Rh}_4\text{(CO)}_{12}} = 1.4 \times 10^{-5}$, $3.0 \times 10^{-5}$, $4.8 \times 10^{-5}$, and $6.2 \times 10^{-5}$ respectively. For pure Rh$_4$(CO)$_{12}$, the measured TOF at present reaction conditions is $0.12 \pm 0.01 \text{min}^{-1}$.

![Figure 5.16 The effect of Rh$_4$(CO)$_{12}$ initial loading on TOF](image)

It appears that the influence of initial concentrations of Rh$_4$(CO)$_{12}$ on the turnover frequencies is very small. This is consistent with the previous kinetic study with
unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland and Pino, 1991). The small TOF differences could be traced to the effect of HMn(CO)₅ concentration differences in the four experiments. Indeed, as shown in Figure 5.12, the concentration of HMn(CO)₅ is highest when the rhodium loading is 51.6mg. This highest HMn(CO)₅ concentration contributes to the highest TOF 0.23±0.02min⁻¹, while the lowest HMn(CO)₅ concentration is responsible for the lowest TOF 0.16±0.04min⁻¹ when the rhodium loading is 106.5 mg. This again means that HMn(CO)₅ was involved in the formation of the organic product aldehyde.

The present results also support the findings of the Rh₄(CO)₁₂ /HMn(CO)₅ bimetallic catalyzed hydroformylation of 33DMB system.

5.4.3.4 Changing CP initial loadings

The initial concentration of substrate cyclopentene was systematically varied in three hydroformylation experiments performed at 289.7K, 2.0MPa carbon monoxide, 2.0MPa hydrogen, circa 50 mg Rh₄(CO)₁₂ and circa 100 mg Mn₂(CO)₁₀ in 300 ml n-hexane. The corresponding concentrations of H₂ and CO were 0.0198 and 0.0504 respectively. The calculated initial concentrations of Rh₄(CO)₁₂ in mole fractions were circa 3.0×10⁻⁵. The initial loadings of cyclopentene were 2, 5 and 10 ml. Accordingly, the calculated initial concentrations of cyclopentene in mole fractions were Xₜₐₚ=0.01,0.025, and 0.05 respectively. The initial loading of Mn₂(CO)₁₀ was circa 100 mg and the corresponding initial concentrations of HMn(CO)₅ were circa 3.3×10⁻⁵ to 4×10⁻⁵ mole fraction. This is because of the irreproducibility of the photo-irradiation of Mn₂(CO)₁₀ with H₂.
5.4.3.4.1 Initial reaction times

The instantaneous concentrations of the precursors $\text{Rh}_4(\text{CO})_{12}$, $\text{HMn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$, and the only observable intermediate $\text{RCORh}(\text{CO})_4$ are shown in Figures 5.17-5.20. Again, some errors could be observed in the first data points due to the mixing problems.

**Figure 5.17** Time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$
**Figure 5.18** Time dependent mole fractions of HMn(CO)$_5$

**Figure 5.19** Time dependent mole fractions of Mn$_2$(CO)$_{10}$
As shown in Figure 5.17, when Rh₄(CO)₁₂, Mn₂(CO)₁₀, and HMn(CO)₅ were added simultaneously, a very rapid decline in the catalyst precursor concentration and increase in rhodium acyl complex concentration were observed again.

Figure 5.20 indicates that cyclopentene concentration appears to have a minimal effect in the transformation of Rh₄(CO)₁₂ to RCORh(CO)₄. Previous kinetic studies show that for unmodified catalyzed hydroformylation of 33DMB, the rate of Rh₄(CO)₁₂ disappearance is nearly zero order in the alkene.

The half-life at the present conditions for Rh₄(CO)₁₂ in the mixed Rh/Mn system was circa 70 minutes when circa 100.0 mg Mn₂(CO)₁₀ was used.
The concentrations of \( \text{HMn(CO)}_5 \) monotonically decreased and \( \text{Mn}_2(\text{CO})_{10} \) correspondingly increased. In one of the three experiments (CP=2 ml), a fast decline of HMn(CO)_5 was observed.

5.4.3.4.2 Product formation

The time-dependent concentrations of the reagent cyclopentene and the hydroformylation product aldehyde are shown in Figures 5.21 and 5.22.

![Figure 5.21](image)

**Figure 5.21** Time dependent mole fractions of CP
Figure 5.22 Time dependent mole fractions of aldehyde

It appears that the effect of the initial concentration of cyclopentene is not straightforward. With the exception of the first 50 minutes, the rates of product formation are more-or-less constant. The rates are circa $1.2 \times 10^{-5}$, $1.8 \times 10^{-5}$, and $1.5 \times 10^{-5}$ (mol fraction/min) with $X_{\text{CP}}=0.01, 0.025, 0.05$ respectively. Actually, previous kinetic studies have shown that the aldehyde formation rate is nearly zero order in alkene.

However, the product formation rate is apparently associated with the $\text{HMn(CO)}_5$ concentration profiles in the three experiments. As shown in Figure 5.18, the average $\text{HMn(CO)}_5$ concentration is highest for the CP=5 ml experiments, which also has the fastest product formation rate. In contrast, the average $\text{HMn(CO)}_5$ concentration is lowest in the CP=2 ml experiments, which also has the lowest product formation rate.
5.4.3.4.3 TOF analyses

The effect of initial concentrations of cyclopentene on TOF is shown in Figure 5.23. The average turnover frequencies were $0.16\pm0.04\text{min}^{-1}$, $0.23\pm0.02\text{min}^{-1}$ and $0.21\pm0.03\text{min}^{-1}$ in the three experiments starting with $X_{CP}=0.01,0.025,0.05$ respectively.

![Figure 5.23 The effect of CP on TOF](image)

It seems that the influence of initial concentration of cyclopentene on the turnover frequencies is very small. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate.

When comparing the HMn(CO)$_5$ concentration profiles in the three experiments, it is not difficult to see the contribution of HMn(CO)$_5$ to the small differences between TOF. Indeed, as described in Figure 5.18, the average HMn(CO)$_5$ concentration is highest in the CP=5 ml experiments, which has the highest TOF. The average HMn(CO)$_5$ concentration is lowest at CP=2 ml, which is related to the smallest TOF.
The present results are consistent with the findings for the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of 33DMB.

5.4.3.5. Changing CO pressure

The initial concentration of CO was systematically varied in four hydroformylation experiments performed at 289.7K, 2.0MPa hydrogen in 300 ml n-hexane. The pressures of carbon monoxide were 1.0, 2.0, 3.0 and 4.0 MPa. Accordingly, the concentrations of CO in mole fractions were $X_{CO} = 0.0257$, 0.0504, 0.0739 and 0.0964.

The corresponding concentration of dissolved H$_2$ was circa 0.0198. Circa 50 mg Rh$_4$(CO)$_{12}$ was used and the calculated initial concentrations of Rh$_4$(CO)$_{12}$ in mole fractions were circa $3.0 \times 10^{-5}$. The initial loading of cyclopentene was 5ml and the mole fraction was $X_{CP} = 0.025$. The initial loading of Mn$_2$(CO)$_{10}$ was circa 100 mg and the corresponding initial concentrations of HMn(CO)$_5$ were circa $2 \times 10^{-5}$ to $4 \times 10^{-5}$ mole fraction. This is because of the irreproducibility of the photo-irradiation of Mn$_2$(CO)$_{10}$ with H$_2$.

5.4.3.5.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HMn(CO)$_5$ and Mn$_2$(CO)$_{10}$, and the only observable intermediate RCORh(CO)$_4$ are shown in Figures 5.24-5.27.
Figure 5.24 Time dependent mole fractions of Rh₄(CO)₁₂

Figure 5.25 Time dependent mole fractions of HMn(CO)₅
Figure 5.26 Time dependent mole fractions of Mn$_2$(CO)$_{10}$

Figure 5.27 Time dependent mole fractions of acyl
It can be observed again, that in the Rh₄(CO)₁₂ catalyzed hydroformylation promoted with Mn₂(CO)₁₀/HMn(CO)₅, a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occur.

The half-lives at the present conditions for Rh₄(CO)₁₂ in the mixed Rh/Mn system were circa 300, 80, 40 and 20 minutes respectively when X_CO = 0.0257, 0.0504, 0.0739 and 0.0964. Accordingly, the final concentrations of RCORh(CO)₄ were 4.7×10⁻⁵, 9.1×10⁻⁵, 1.1×10⁻⁴, and 1.1×10⁻⁴. This indicates that increased CO partial pressures led to faster transformation of Rh₄(CO)₁₂ to RCORh(CO)₄.

Figure 5.27 (CO=4.0MPa) also indicates that the rhodium acyl RCORh(CO)₄ begun to appear in the first spectrum (at this point, there were only n-hexane, cyclopentene, Rh₄(CO)₁₂, HMn(CO)₅/Mn₂(CO)₁₀ and CO in the autoclave). This again clearly supports that HMn(CO)₅ alone can attack Rh₄(CO)₁₂ to produce RCORh(CO)₄.

The concentrations of HMn(CO)₅ slightly decreased and the concentrations of Mn₂(CO)₁₀ correspondingly increased in three of the hydroformylation reactions, while in one of the experiments (CO=3.0MPa), there was a fast decline of HMn(CO)₅.

5.4.3.5.2 Product formation

The transient concentrations of the reagent cyclopentene and the hydroformylation product aldehyde are shown in Figures 5.28 and 5.29.
Figure 5.28 Time dependent mole fractions of CP

Figure 5.29 Time dependent mole fractions of aldehyde
It is clear that the variation in the concentration of dissolved CO strongly influences the formation of aldehyde. Generally, the rate of hydroformylation tended to decrease with increasing liquid carbon monoxide concentrations. This is again consistent with Garland’s work (Garland et al, 1991, 1993, 1999). As mentioned in Chapter 4, in the pure rhodium catalyzed hydroformylation system there exists a one-to-one relationship between $[\text{RCORh(CO)}_4]_t$ and the rate of aldehyde formation $(\text{d}[\text{aldehyde}]/\text{dt})_t = k[\text{RCORh(CO)}_4]_t[\text{CO}]^{-1}[\text{H}_2]$. The present results in part support the negative effect of CO on the product formation rate.

As described in Figure 5.29, during the last 270 minutes, the reaction rates are constants and they are circa $1.4 \times 10^{-5}$, $1.6 \times 10^{-5}$, $9.6 \times 10^{-6}$, and $8.7 \times 10^{-6}$ (mol fraction)/min respectively for $X_{\text{CO}} = 0.0257$, 0.0504, 0.0739, and 0.0964 respectively.

Like the Rh/Mn/33DMB system, the above data clearly show the complications of the present bimetallic system with $\text{Rh}_4(\text{CO})_{12}$ and $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$. It is interesting to note that the product formation rate at 2.0MPa CO is even faster than the reaction rate at 1.0 MPa CO. This is apparently in contrast to the classic hydroformylation kinetics.

The possible reason could be again traced to the difference of the $\text{HMn(CO)}_5$ concentration profiles in these two experiments. Figure 5.25 indicates that the average $\text{HMn(CO)}_5$ concentration at 2.0MPa CO is much higher than the $\text{HMn(CO)}_5$ concentration at 1.0MPa CO. The very different $\text{HMn(CO)}_5$ concentration profiles at 3.0 and 4.0 MPa CO could also be a plausible explanation of the two similar time-dependent product concentrations for these two experiments. All of this implies that the $\text{HMn(CO)}_5$ shall play a significant role in the catalytic pathway to produce aldehyde.
5.4.3.5.3 TOF analyses

The effect of loading of CO on TOF is shown in Figure 5.30. The average turnover frequencies were were 0.48±0.11 min\(^{-1}\), 0.23±0.02 min\(^{-1}\), 0.10±0.02 min\(^{-1}\) and 0.08±0.01 min\(^{-1}\) in the four experiments starting with X\(_{CO}\) = 0.0257, 0.0504, 0.0739 and 0.0964 respectively.

![Figure 5.30](image)

**Figure 5.30** The effect of CO on TOF

The TOF results suggest that the influence of CO concentrations on the turnover frequencies is very big. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate.

However, close inspection of the two experiments at CO=3.0 and 4.0 MPa, shows that although the general trend is consistent with the pure unmodified rhodium catalyzed
hydroformylation system, the TOF difference is very small. This could be again traced to the effect of HMn(CO)$_5$ concentration differences in the two experiments (Figure 5.25), namely the average HMn(CO)$_5$ concentration at 4.0MPa CO is higher than the HMn(CO)$_5$ concentration at 3.0MPa CO.

The current results again agree with those found in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of 33DMB system.

5.4.3.6. Changing H$_2$ pressure

Three experiments were performed to study the influence of hydrogen. The experiments were conducted at 289.7K, 2.0MPa CO, and 5ml cyclopentene in 300 ml n-hexane. The corresponding concentrations of CO were circa 0.0504. The initial input of cyclopentene was 5 ml and the concentration was 0.016 mole fraction. The initial loading of Rh$_4$(CO)$_{12}$ was circa 50 mg and $X_{Rh4(CO)_{12}}$ was circa $3.0 \times 10^{-5}$. The initial loading of Mn$_2$(CO)$_{10}$ was circa 100 mg and the corresponding initial concentrations of HMn(CO)$_5$ were circa $2 \times 10^{-5}$ to $4 \times 10^{-5}$ mole fraction. This is because of the irreproducibility of the photo-irradiation of Mn$_2$(CO)$_{10}$ with H$_2$. The pressures of hydrogen were 1.0, 2.0, 3.0 and 4.0 MPa. The corresponding concentrations of H$_2$ in mole fractions were $X_{H2}$= 0.0101, 0.0198, 0.0292 and 0.0383 respectively.

5.4.3.6.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HMn(CO)$_5$ and Mn$_2$(CO)$_{10}$, and the only observable intermediate RCorh(CO)$_4$ are shown in Figures 5.31-5.34. Some errors can be observed in the first 9 spectra at $H_2$=1.0 MPa. This is again due to the circulation pump and mixing problems in the experiment.
Figure 5.31 Time dependent mole fractions of Rh₄(CO)₁₂

Figure 5.32 Time dependent mole fractions of HMn(CO)₅
Figure 5.33 Time dependent mole fractions of Mn$_2$(CO)$_{10}$

Figure 5.34 Time dependent mole fractions of acyl
It can be observed again, upon addition of Mn$_2$(CO)$_{10}$, HMn(CO)$_5$ and H$_2$, that a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occurs. Generally, the rate of fragmentation of Rh$_4$(CO)$_{12}$ to RCORh(CO)$_4$ increases with increased dissolved hydrogen concentrations.

The half-lives at the present conditions for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system were circa 80, 80, 75 and 40 minutes for the four experiments when X$_{H2}$ = 0.0101, 0.0198, 0.0292 and 0.0383 respectively.

The concentrations of HMn(CO)$_5$ monotonically decreased and the concentrations of Mn$_2$(CO)$_{10}$ correspondingly increased in the four hydroformylation reactions.

5.4.3.6.2 Product formation

The time-dependent concentrations of the reagent cyclopentene and the hydroformylation product aldehyde are shown in Figures 5.35 and 5.36.
Figure 5.35 Time dependent mole fractions of CP

Figure 5.36 Time dependent mole fractions of aldehyde
It appears that the variation in the initial concentration of H$_2$ has a strong effect on the formation of aldehyde. Except for the first 100 minutes, the product formation rates in the four experiments are more-or-less constants, namely $8.0 \times 10^{-6}$, $1.6 \times 10^{-5}$, $2.2 \times 10^{-5}$ and $2.9 \times 10^{-5}$. The reaction rate increases with increasing H$_2$ concentration. This is in part consistent with the classic product formation kinetics, i.e.,

$$(d[\text{aldehyde}]/dt)_r = k[R\text{CORh(CO)}_4][\text{CO}]^{-1}[\text{H}_2]$$

for hydroformylation of alkenes catalyzed by unmodified Rh$_4$(CO)$_{12}$ alone. However, using the above function alone, we can not get a good fit to the present data obtained in the Rh/Mn bimetallic system. This suggests that there exists another pathway contributing to the product formation.

5.4.3.6.3 TOF analyses

The effect of H$_2$ on TOF is shown in Figure 5.37. The average turn over frequencies were $0.12 \pm 0.08\text{min}^{-1}$, $0.23 \pm 0.02\text{min}^{-1}$, $0.31 \pm 0.03\text{min}^{-1}$ and $0.42 \pm 0.01\text{min}^{-1}$ in the four experiments starting with $X_{H_2} = 0.0101, 0.0198, 0.0292$ and $0.0383$ respectively.
The TOF results suggest that the influence of H$_2$ concentration on the turnover frequencies is strong. The higher H$_2$ concentrations result in higher TOFs. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate.

As described before, the TOF at 2.0MPa H$_2$ with pure Rh$_4$(CO)$_{12}$ catalyzed hydroformylation of cyclopentene is 0.12min$^{-1}$. The present result shows that with the Rh/Mn bimetallic system, a similar TOF is obtained at 1.0MPa H$_2$ (all the other conditions are the same). This proves the catalytic activity of HMn(CO)$_5$ in the hydroformylation of cyclopentene with the Rh/Mn bimetallic system.
The present results for the Rh/Mn/Cyclopentene system are also in good agreement with that observed in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of 33DMB system.

5.4.3.7. Changing temperature

Five experiments were performed at 281.5K, 289.7K, 293.7, 299.4K and 308.9K respectively. Each experiment was conducted in a similar manner to the standard experiment. The reaction conditions were 2.0MPa hydrogen, 2.0MPa carbon monoxide, 5ml cyclopentene, circa 50mg Rh$_4$(CO)$_{12}$ and circa 100mg Mn$_2$(CO)$_{10}$. Accordingly, the initial concentration of cyclopentene was 0.025 mole fraction, the initial X$_{Rh4(CO)12}$ was circa 3.0×10$^{-5}$ and the initial concentrations of HMn(CO)$_5$ were circa 2.2×10$^{-5}$ to 4×10$^{-5}$ mole fraction. This small variation in the HMn(CO)$_5$ concentrations was again due to the irreproducibility of the photo-irradiation of Mn$_2$(CO)$_{10}$ with H$_2$.

5.4.3.7.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HMn(CO)$_5$ and Mn$_2$(CO)$_{10}$, and the only observable intermediate RCORh(CO)$_4$ are shown in Figures 5.38-41. Again, some errors could be observed in the first data points due to the mixing problems.
Figure 5.38 Time dependent mole fractions of \( \text{Rh}_4(\text{CO})_{12} \)

Figure 5.39 Time dependent mole fractions of \( \text{HMn}(\text{CO})_5 \)
**Figure 5.40** Time dependent mole fractions of Mn$_2$(CO)$_{10}$

**Figure 5.41** Time dependent mole fractions of acyl
As shown in the Figures 5.38 and 5.41, the concentrations of Rh$_4$(CO)$_{12}$ monotonically declined in the three experiments at low temperature (T=281.5, 289.7 and 293.7K) and the concentration of RCORh(CO)$_4$ monotonically increased. However, in other two experiments with higher temperature (T=299.4 and 308.9K), it can be noted that RCORh(CO)$_4$ reached maxima at circa 70 and 200 minutes and then began to decrease. This is quite similar to the results obtained in the Rh$_4$(CO)$_{12}$ and HMn(CO)$_5$ catalyzed hydroformylation of 33DMB at high temperature. One possible reason is that at high temperature the hydroformylation of alkene is very fast and consequently the alkene is at low concentration, which implies a faster back reaction of rhodium to form Rh$_4$(CO)$_{12}$.

Figure 5.38 shows that higher temperature leads to a faster disappearance of Rh$_4$(CO)$_{12}$. The half-lives are circa 100, 80, 70, 60 and 30 minutes in the five experiments when T= 281.5K, 289.7K, 293.7, 299.4K and 308.9K respectively.

The concentrations of HMn(CO)$_5$ monotonically decreased and the concentrations of Mn$_2$(CO)$_{10}$ slightly increased in the three low-temperature hydroformylation reactions.

5.4.3.7.2 Product formation

The time-dependent concentrations of the reagent cyclopentene and the hydroformylation product aldehyde are shown in Figures 5.42 and 5.43.
Figure 5.42 Time dependent mole fractions of CP

Figure 5.43 Time dependent mole fractions of aldehyde
The temperature has a strong effect on the formation of the organic product aldehyde. Generally, the rate of hydroformylation tended to be faster with higher reaction temperature. At low temperature (T=281.5, 289.7, 293.7 and 299.4 K), the hydroformylation rates are constants except for the first 90 minutes. The rates are circa $4.5 \times 10^{-6}$, $1.6 \times 10^{-5}$, $2.8 \times 10^{-5}$, and $4.6 \times 10^{-5}$ (mol fraction)/min when the temperature is 281.5, 289.7, 293.7 and 299.4 K respectively.

At high temperature (T=308.9K), the reaction rate is constant for the first 100 minutes. It is circa $1.3 \times 10^{-4}$. After that, the product formation rate becomes slow. This is consistent with the rhodium acyl concentration profile as described in Figure 5.41.

5.4.3.7.3 TOF analyses

The effect of temperature on TOF is shown in Figure 5.44. The average turnover frequencies were $0.1 \pm 0.05 \text{min}^{-1}$, $0.23 \pm 0.02 \text{min}^{-1}$, $0.35 \pm 0.01 \text{min}^{-1}$, $0.54 \pm 0.07 \text{min}^{-1}$ and $1.54 \pm 0.2 \text{min}^{-1}$ in the five experiments starting with T= 281.5, 289.7, 293.7, 299.4 and 308.9 K respectively. This suggests that the influence of temperature on the turnover frequencies is strong. The TOF is higher with higher temperature. This result is consistent with previous kinetic studies of unmodified rhodium catalyzed hydroformylation of alkenes and it is also in agreement with the present results obtained in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of 33DMB.
5.5 Catalysis and kinetics

5.5.1 Pre-catalytic

From the above six sub-series of experiments performed at different loadings of precursors $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$ and $\text{Rh}_4(\text{CO})_{12}$, substrate cyclopentene, different dissolved concentrations of CO and H$_2$, and at different reaction temperatures, the effect of the $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$ on the disappearance of $\text{Rh}_4(\text{CO})_{12}$ is apparent.

Like the $\text{HMn(CO)}_5/\text{Mn}_2(\text{CO})_{10}$ bimetallic catalyzed hydroformylation of 33DMB system, the kinetic results again indicate that the decrease of $\text{Rh}_4(\text{CO})_{12}$ and increase of $\text{RCORh(CO)}_4$ are not simple monotonic functions at initial reaction times. In fact, upon addition of $\text{Mn}_2(\text{CO})_{10}$, $\text{HMn(CO)}_5$ and H$_2$, a very rapid decline in the catalyst precursor...
concentration and increase in acyl complex concentration were also observed. Compared to the 120 mins half-life of pure Rh system under similar reaction conditions, the half-life for Rh$_4$(CO)$_{12}$ in the mixed Rh/Mn system was circa 60 minutes when 229 mg Mn$_2$(CO)$_{10}$ was used. This atypical initial time behavior again supports 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)$_{12}$. Indeed, as described in Section 5.3, the manganese hydride facilitated Rh$_4$(CO)$_{12}$ fragmentation to produce rhodium acyl was clearly observed when the reactor had only Rh/Mn/alkene/CO without any presence of added H$_2$.

As discussed in Chapter 4, mononuclear hydride attack and subsequent opening of metal clusters is well documented in the literature (Churchill et al, 1986). In the present case, and in the presence of numerous organic reactants, a sequence of steps leading to the rapid formation of RCORh(CO)$_4$ occurs.

Similar to the HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB system, under the present experimental conditions, the following two term equation again provided a good fit for the observable kinetics of the acyl formation at 289.7K. The first term represents the fragmentation mechanism in the pure rhodium system, while second term represents the second parallel precatalytic pathway for the transformation of Rh$_4$(CO)$_{12}$ to RCORh(CO)$_4$ by the HMn(CO)$_5$ attack.

$$\frac{d[RCORh(CO)\_4]}{dt} = k\_1\' [Rh\_4(CO)\_12][CO]\_2[H\_2] + k\_2\' [Rh\_4(CO)\_12][CO]\_2[HMn(CO)\_5] \quad (5.2)$$

The regressed numerical values of the rate constants were

$$k\_1\' = (4.0 \pm 0.8) \times 10^2 \text{ min}^{-1}$$
\[ k_2' = (1.1 \pm 0.6) \times 10^5 \text{ min}^{-1}. \]

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The rate constant \( k_1' \) is consistent with our previous studies.

Temperature was systematically varied in five unmodified rhodium catalyzed hydroformylation experiments of cyclopentene promoted with \( \text{HMn(CO)}_5 \) at 2.0MPa CO and 2.0MPa \( \text{H}_2 \) to regress the reaction activation parameters. The five temperatures are 281.5, 289.7, 293.7, 299.4 and 308.9 K. The activation parameters are regressed using the following definitions.

\[
d[Rh_4(CO)_{12}]/dt = k_1'[Rh_4(CO)_{12}][CO]^2[H_2]+k_2'[Rh_4(CO)_{12}][CO]^2[HMn(CO)_5] \quad (5.3)
\]

where

\[
k_1' = \kappa T/h \times \exp(-\Delta H^\neq/RT+\Delta S^\neq/R)
\]

\[
k_1' = A \times \exp(-\Delta E_a/RT)
\]

\[
k_2' = \kappa T/h \times \exp(-\Delta H^\neq/RT+\Delta S^\neq/R)
\]

\[
k_2' = A \times \exp(-\Delta E_a/RT)
\]

The definitions are the same as that of Chapter 4.

With respect to the rhodium acyl \( \text{RCORh(CO)}_4 \) formation, the above two term linear-bilinear form was used to regress the kinetic data at four temperatures. Table 5.4 lists the regressed constants \( k_1' \) and \( k_2' \) at different reaction temperatures, where the regressions failed at high temperatures (\( T=299.4 \text{K} \) and 308.9K). This could be due to the very fast reactions at high temperature.
Table 5.4  Regressed k values at different temperatures

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Temperature (K)</th>
<th>$k'_1$ (1/min)</th>
<th>$k'_2$ (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1</td>
<td>281.5</td>
<td>288</td>
<td>$0.6 \times 10^5$</td>
</tr>
<tr>
<td>T-2</td>
<td>289.7</td>
<td>399</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td>T-3</td>
<td>293.7</td>
<td>440</td>
<td>$1.4 \times 10^5$</td>
</tr>
</tbody>
</table>

The reaction constants $k'_1$ and $k'_2$ as shown in Table 5.4 for the 3 temperature variation series were analyzed by using Eq 5.3 to get $\Delta E_a$, $\Delta H^\ne$ and $\Delta S^\ne$.

For $k'_1$,

$\Delta E_a=24\pm29$ KJ/mol

$\Delta H^\ne=22\pm29$ KJ/mol

$\Delta S^\ne=-154\pm103$ J/(mol·K)

For $k'_2$,

$\Delta E_a=46\pm79$ KJ/mol

$\Delta H^\ne=44\pm79$ KJ/mol

$\Delta S^\ne=-31\pm280$ J/(mol·K )

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The regressed results show that some errors are incurred, especially for the entropies. With respect to the $k'_1$, the first term in the Eq 5.3, which represents the classic unicycle hydroformylation mechanism, the present activation parameters are consistent with previous work (Garland and Pino, 1991).
The activation parameters are also consistent with activation parameters obtained with 33DMB as substrate in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation system.

5.5.2 Hydroformylation

A total of 23 kinetic experiments in six sub-series 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. The strong effect of HMn(CO)$_5$ on the product formation rate and TOF was clearly demonstrated.

Like the HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB system, with respect to the catalysis or product formation, the following two term linear-bilinear form in organometallic species provided an excellent fit for the observable kinetics of the aldehyde formation.

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

Circa 1200 sets of mole fraction data at 289.7K 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 non-linear regression program (Matlab), the regressed numerical values of the rate constants at 289.7 K were

\[ k_1 = 0.314 \pm 0.08 \text{ min}^{-1} \]

\[ k_2 = 37 \pm 15 \text{ min}^{-1} \]
x = -1.6 ± 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 constant $k_2$ and the exponent for CO are in agreement with the results of HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB system.

In most experiments, the contributions of these two terms at the reference reaction conditions of this experimental study were circa 1:1. In particular, according to the above kinetics, at 289.7 K, 2.0MPa CO, 2.0MPa H$_2$, 5 ml cyclopentene, circa 50mg Rh$_4$(CO)$_{12}$ and 229.0 mg Mn$_2$(CO)$_{10}$ ($X_{MnH(CO)5}=4\times10^{-5}$), the contribution of CBER to the final product formation is 51%.

Rearrangement of the two terms $k_1[CO]^{-1}/k_2[CO]^{-1.6}$ leads to the conclusion that under 2.0 MPa CO, HMn(CO)$_5$ is circa 520 times more efficient than H$_2$, for the hydrogenolysis of the acyl-rhodium bond, on a mole-to-mole basis. As discussed in Chapter 4($x=1.5\pm0.1$), the exponent $x = -1.6\pm0.01$ suggests that coordinative unsaturation may occur in both metal carbonyl complexes.

Temperature was systematically varied in five unmodified rhodium catalyzed hydroformylation of cyclopentene promoted with HMn(CO)$_5$ at 2.0MPa CO and 2.0MPa H$_2$ to regress the reaction activation parameters. The five temperatures are 281.5, 289.7, 293.7, 299.4 and 308.9K. The activation parameters are regressed using the following definitions.

$$r_{Total}=k_1[RCORh(CO)_4][H_2][CO]^{-1}+k_2[RCORh(CO)_4][HMn(CO)_5][CO]^{-1.6} \quad (5.5)$$

where
\[ k_1 = \kappa \frac{T}{h} \exp(-\Delta H^\circ/RT + \Delta S^\circ/R) \]

\[ k_1 = A \times \exp(-\Delta E_a/RT) \]

\[ k_2 = \kappa \frac{T}{h} \exp(-\Delta H^\circ/RT + \Delta S^\circ/R) \]

\[ k_2 = A \times \exp(-\Delta E_a/RT) \]

The parameters definitions are the same as that of Chapter 4.

With respect to the product aldehyde formation, the above two term linear-bilinear form was used to regress the kinetic data at four temperatures. Table 5.5 lists the regressed constants \( k_1 \) and \( k_2 \) at different reaction temperatures.

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Temperature (K)</th>
<th>( k_1 ) (1/min)</th>
<th>( k_2 ) (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1</td>
<td>281.5</td>
<td>0.095</td>
<td>21</td>
</tr>
<tr>
<td>T-2</td>
<td>289.7</td>
<td>0.314</td>
<td>37</td>
</tr>
<tr>
<td>T-3</td>
<td>293.7</td>
<td>0.524</td>
<td>44</td>
</tr>
<tr>
<td>T-4</td>
<td>299.4</td>
<td>0.995</td>
<td>71</td>
</tr>
<tr>
<td>T-5</td>
<td>308.9</td>
<td>3.02</td>
<td>137</td>
</tr>
</tbody>
</table>

The reaction constants \( k_1 \) and \( k_2 \) as shown in Table 5.5 for the 5 temperature variation series were analyzed by using Eq 5.5 to get \( \Delta E_a, \Delta H^\circ \) and \( \Delta S^\circ \).

For \( k_1 \),

\[ \Delta E_a = 91 \pm 6 \text{ KJ/mol} \]

\[ \Delta H^\circ = 88 \pm 6 \text{ KJ/mol} \]

\[ \Delta S^\circ = 15 \pm 20 \text{ J/(mol·K)} \]
For $k_2$,

$$\Delta E_a = 49 \pm 8 \text{ KJ/mol}$$

$$\Delta H^\circ = 47 \pm 8 \text{ KJ/mol}$$

$$\Delta S^\circ = -88 \pm 28 \text{ J/(mol·K)}$$

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The regressed results show that some errors are incurred. This could be in part due to the temperature dependencies of the solubilities. With respect to the $k_1$, the first term in the equation 5.5, which represents the classic unicycle hydroformylation mechanism, the present activation parameters are consistent with previous work (pure rhodium system (Garland et al, 1991) and HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB system, Chapter 4). As for $k_2$, the enthalpy indicates that the Rh/Mn bimetallic CBER is an exothermic reaction. The negative entropy clearly indicates that the degrees of freedom have decreased for the system.

### 5.6 Discussion

#### 5.6.1 Further evidence for existence of CBER

Like the Rh$_4$(CO)$_{12}$/HMn(CO)$_3$ bimetallic catalyzed hydroformylation of 33DMB system the present 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.
As mentioned before, 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 an 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 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 coordinately unsaturated bimetallic rhodium manganese dinuclear complex with probable stoichiometry RhMn(CO)$_8$ (or possibly RhMn(CO)$_7$). However, such a species (or its coordinatively saturated analog) was un-observable in these experiments. Similar to the discussion in Chapter 4, this could be again traced 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 (James, 1982), is known to occur exceptionally rapidly, even at low temperatures, on heterometallic dinuclear carbonyl complexes - where CoRh(CO)$_7$ is perhaps the best example (Garland and Pino, 1990).

Similar to the HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB system, a proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Mn CBER hydroformylation reactions is shown in Figure 5.45. All intermolecular transformations in the unicyclic topology are 1st order in the mononuclear metal complexes. Two elementary steps in Figure 5.45 are highlighted by the labels $\alpha$ and $\beta$. These labels are used to identify the key mechanisms which give rise
to the existence of the bimetallic CBER. The $\alpha$ 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 $\beta$ step is the binuclear elimination step. The steps –$\alpha$ and $\beta$ are bimolecular in metal complexes. The binuclear elimination step has been drawn as if the process proceeds through a concerted 4-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 4-center transition state, but instead through 2 or more simpler transition states, additional intermediates exist on the reaction pathway.

Figure 5.45. The proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Mn CBER hydroformylation reactions.
Concerning other details in Figure 5.45, 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 5-coordinate rhodium structures, namely, axially substituted trigonal bipyramid geometries.

The interconnected topology of a unicyclic mechanism and a CBER mechanism as shown in Figure 5.45 supports the complex linear-bilinear form of the observed kinetics of product formation shown as Eq. 5.5.

5.6.2 Initial reaction times and pre-catalytic steps

In the present bimetallic system, a two term equation providing a good fit was again obtained from the 21 experiments at 289.7K.

\[
\frac{d[RCORh(CO)_4]}{dt} = k_1' [Rh_4(CO)_{12}] [CO]^2 [H_2] + k_2' [Rh_4(CO)_{12}] [CO]^2 [HMn(CO)_5] \quad (5.6)
\]

The functional form used for the first term is that which was previously shown to arise in simple monometallic rhodium hydroformylations. The common factor \([Rh_4(CO)_{12}] [CO]^2\) suggests a rate limiting step involving a pre-equilibrated open polyhedron intermediate \(\{Rh_4(CO)_{14}\}\). Kinetic evidence for open polyhedron clusters as intermediates in cluster fragmentation reactions is readily available (Bor et al, 1978). 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 Figures 5.6 and 5.7, the Mn$_2$(CO)$_{10}$ concentration declines somewhat from its initial value at \( t=0 \) and the HMn(CO)$_5$ concentration increases from its non-zero initial value. The manganese carbonyl concentrations then remain essentially constant for the remainder of the experiment. In some other experiments, the HMn(CO)$_5$ concentration monotonically decreased and the Mn$_2$(CO)$_{10}$ concentration correspondingly increased. But the HMn(CO)$_5$ concentration never reached zero in any of the 5 hour hydroformylations.

As discussed in Chapter 4, redistribution of Mn$_2$(CO)$_{10}$ and HMn(CO)$_5$ in the bimetallic system may occur for many reasons, including hydrogen activation on Mn$_2$(CO)$_{10}$ (i.e. equilibrium of Mn$_2$(CO)$_{10}$/HMn(CO)$_5$), reaction of HMn(CO)$_5$ with the trace impurities in the 300 ml reaction autoclave solution. It is well known that the manganese hydride is extremely 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.

**5.7 Conclusions**

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 in-situ FTIR spectroscopic data were analyzed using the total system identification algorithm.
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 statistically significant contribution to aldehyde formation from the bimetallic catalytic binuclear elimination of manganese hydride complexes with acyl rhodium tetracarbonyl. This is the further evidence on the existence of bimetallic CBER.

As secondary effects, manganese carbonyl hydride leads to a reduction in the induction period (promotes the pre-catalytic transformation of rhodium precursor to rhodium intermediates) and retards or even reverses, deactivation due to cluster formation. However, due to the instability of the mixed rhodium and manganese complexes under hydrogen, there is no IR spectral data showing the presence of mixed dinuclear Rh-Mn intermediates under our reaction conditions for both of the 33DMB and cyclopentene systems.

In the next step, it might be advantageous to try another metal hydrides HM*Lx in the unmodified rhodium catalyzed hydroformylation to find out whether we can observe a new Rh-M*Ly intermediate. If such a new dinuclear species is observable during catalysis, the description of the CBER kinetics will be considerably more complicated. One selected candidate, namely HRe(CO)₅ will be tried in the unmodified rhodium catalyzed hydroformylation to find further evidence for bimetallic elimination in catalysis. Cyclopentene will continue to be the substrate used.
CHAPTER 6 THE Rh₄(CO)₁₂ CATALYZED HYDROFORMYLATION OF CYCLOPENTENE PROMOTED WITH HRe(CO)₅

6.1 Introduction

In Chapter 4 and Chapter 5, Rh₄(CO)₁₂/HMn(CO)₅ was used in the homogeneous catalyzed hydroformylation of 33DMB and cyclopentene respectively. In both systems, the high activity of HMn(CO)₅ was observed and similar linear-bilinear equations were obtained to express the product formation rate. The spectroscopic and kinetic analyses produced strong evidence of the existence of bimetallic CBER in these two systems. However, the expected dinuclear complex was not observed. This chapter will use a second metal carbonyl hydride HRe(CO)₅ (in the same group as Mn) to search for the further evidence of bimetallic CBER, in which the dinuclear complex might be identified. HRe(CO)₅ has been used in many stoichiometric binuclear elimination reactions.

The liquid reactions of HRe(CO)₅ and Rh₄(CO)₁₂ solutions in n-hexane under CO and or H₂ will be studied first.

6.2 The identification of RhRe(CO)₉

6.2.1 Experiments

An experimental design was planned, which would utilize the semi-batch approach and algorithm. All the experiments were performed in a similar manner. For example, first, single beam background spectra of the IR sample chamber were recorded. Then 150 ml 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 the set CO pressure, 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 Rh₄(CO)₁₂ dissolved in 50ml 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 Rh₄(CO)₁₂ /CO/ n-hexane / solution in the high-pressure cell were recorded. A solution of HRe(CO)₅ dissolved in 50ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO and then added to the autoclave. In the following steps, the semi-batch experiment methodology was used, namely, the CO/H₂ pressures were varied in each semi-batch step. The spectra were taken every 10-20 minutes in the range of 1000-2500 cm⁻¹ with a resolution of 4 cm⁻¹ at each step. Two consecutive spectra were checked to see if equilibrium had been obtained. If the system reached equilibrium, the CO/H₂ pressures were varied to conduct next semi-batch step. The detailed experimental design is shown in Table 6.1.
<table>
<thead>
<tr>
<th>Expt</th>
<th>Step</th>
<th>$P_{H_2}$ MPa</th>
<th>$P_{CO}$ MPa</th>
<th>Rh$<em>4$(CO)$</em>{12}$ mg</th>
<th>HRe(CO)$_5$ µL</th>
<th>Hexane mL</th>
<th>T K</th>
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<td>0.4</td>
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<td>0.4</td>
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<td>1.6</td>
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<td>250</td>
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<td>1.6</td>
<td>124.9</td>
<td>64.5</td>
<td>250</td>
<td>308.2</td>
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<tr>
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<td>2.0</td>
<td>2.2</td>
<td>124.9</td>
<td>64.5</td>
<td>250</td>
<td>308.2</td>
</tr>
</tbody>
</table>
6.2.2 Spectral analyses

The total system identification method will be employed for the spectral analyses.

One of the raw experimental spectra before any spectral pre-processing is shown in Figure 6.1.

Similar to the previous section (Chapter 4), only two spectral windows with the region of 1000 – 1300 cm\(^{-1}\) and 1550 – 2500 cm\(^{-1}\) are used for spectral reconstruction. The first region only contains information for the solvent n-hexane, while the second region contains the spectroscopic information for the organometallic species.

As shown in Figure 6.1, in addition to the spectral features of the solvent n-hexane, the dissolved CO and the added Rh\(_4\)(CO)\(_{12}\) and HRe(CO)\(_5\), a new peak at 2027 cm\(^{-1}\) is easily identified from the raw reaction spectrum. This could be a new species formed in the Rh\(_4\)(CO)\(_{12}\) / HRe(CO)\(_5\) system under CO/H\(_2\).
A total of 751 spectra were obtained in the equilibrium experiments. Singular value decomposition (SVD) was employed first to decompose the experimental absorbance data matrix $A_{751 \times 2951}$ to give the orthonormal matrices $U_{751 \times 751}$ and $V^T_{2951 \times 2951}$.

The significant spectral extrema in the first few right singular vectors were inspected and were used as targets in the BTEM algorithm. Four significant bands (indicated by numbers in Figure 6.2) were selected for the reconstructions. Table 6.2 lists the parameters used for BTEM.

![Figure 6.2. Four significant spectral extrema used to recover pure spectra](image)
Figure 6.3 The recovered pure component spectra of the organometallic species
Table 6.2 Spectral Reconstruction Parameters and Species Identities

<table>
<thead>
<tr>
<th># Species</th>
<th># Vᵀ vectors, z</th>
<th>Wavenumber region</th>
<th>Maximum Abs, α</th>
<th>Species identification</th>
</tr>
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<tr>
<td>1</td>
<td>25</td>
<td>1885 – 1887</td>
<td>1</td>
<td>Rh₄(CO)₁₂</td>
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<tr>
<td>2</td>
<td>25</td>
<td>2006 – 2008</td>
<td>1</td>
<td>HRe(CO)₅</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>2025.4 – 2027.4</td>
<td>1</td>
<td>Unknown X</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>1815-1819</td>
<td>5</td>
<td>Rh₆(CO)₁₆</td>
</tr>
</tbody>
</table>

The reconstructed pure component spectra via BTEM are presented in Figure 6.3.

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.

As shown in Figure 6.3, in addition to the precursors Rh₄(CO)₁₂ and HRe(CO)₅ and the cluster Rh₆(CO)₁₆ which were recovered via BTEM, a new species was also identified. The new species has peaks at 1985.6(s), 2012.2(w), 2026.6(vs, br), 2075(s) and 2127.2(w) cm⁻¹.

In the present Rh/Re system, since the IR spectrum of the new species has no features indicating bridging C-O groups, a higher nuclearity cluster involving 2 or more Rh atoms is unlikely. Indeed, all known mixed Rh-M clusters having 2 or more Rh atoms have bridging carbonyls. Good examples include Co₂Rh₂(CO)₁₂, CoRh₃(CO)₁₂, Rh₂Ir₂(CO)₁₂, and Rh₃Ir(CO)₁₂(Horvath et al, 1986; Garland and Pino, 1991). Consequently, a low nuclearity mixed rhodium and rhenium carbonyl is suspected. The
simplest example would be a dinuclear complex with a single metal-metal bond and moieties Rh(CO)₄ and Re(CO)₅ for coordinative saturation.

It is known that the local symmetry of Rh(CO)₄ group is $C_{3v}$ and the local symmetry of Re(CO)₅ group is $C_{4v}$ (Braterman, 1976). Figure 6.4 presents the IR spectra of HRh(CO)₄ (Li et al, 2002) and BrRe(CO)₅ obtained in our lab. As shown in Figure 6.4, HRh(CO)₄ has three metal-carbonyl vibrations at 2041.6 (vs), 2071.8 (m) and 2123.6 (w) cm⁻¹ while BrRe(CO)₅ has three vibrations at 1986 (s), 2016.4 (w) and 2046 (vs) cm⁻¹. Therefore, if it is assumed that the two “local symmetries” (Cotton et al, 1956) is the rule that governs the structure of the observed new complex, we would expect six bands, three $(2A_1 + 1E)$ for the Rh(CO)₄ part of the molecule and another three $(2A_1 + 1E)$ for the Re(CO)₅ part of the molecule. Accordingly, two very strong bands ($E$) should be found in the spectrum. The intensity ratio of the two very strong bands ($E$) should be circa $\frac{3}{4}$ and they should represent circa $\frac{7}{9}$ of the total CO stretching intensities.
Indeed, the new complex appears to meet the above assumptions. The two bands 2075(s) and 2127.2(w) cm\(^{-1}\) are quite close to the \(2\Delta_1\) belonging to Rh(CO)\(_4\) part, while the other two bands 1985.6(s) and 2012.2(w) cm\(^{-1}\) are quite close to \(2\Delta_1\) belonging to Re(CO)\(_5\) part. Furthermore, close inspection of the spectrum indicates that the peak at
2026.6 cm\(^{-1}\) is very strong and broad (the half-width is circa 10 cm\(^{-1}\)) and it could be the combinations of the two required strong bands \((E)\). Integrated intensities at this position accounts for circa 74% of the total CO stretching intensities.

On the other hand, Bor. et al (Sbrignadello et al, 1972) reported the similar dinuclear complex ReCo(CO)\(_9\) which has six peaks at 1971.7(w, br), 1990(s), 2007(w), 2032.8(vs), 2059.8(s) and 2133.9(w) cm\(^{-1}\). Except for the weak broad peak at 1971.7 cm\(^{-1}\), all the other peaks are quite similar to the present new complex. In their assignment, a “free rotational model” was employed and the peak at 1971.7 cm\(^{-1}\) was assigned to the degenerate vibration \(\nu_6\). It should be noted the spectrum was taken 30 years ago and some impurities in the complex ReCo(CO)\(_9\) could contribute to the peak at 1971.7 cm\(^{-1}\). Bor et al also reported that the presence of the isotopic satellite (1956 cm\(^{-1}\)) from natural \(^{13}\)C. The similar \(^{13}\)C isotopic satellite was also found in our new complex at 1944.8 cm\(^{-1}\).

![Figure 6.5 Spectral assignment](image)

In summary, the new species is tentatively assigned as RhRe(CO)\(_9\). The proposed structure is shown in Figure 6.5. The following mole number concentration profiles (Figures 6.6-6.8) and the thermodynamics calculations (Section 6.2.3) will further support the above-mentioned assignment.
A procedure similar to that described in Chapter 3 was used to calculate the mole numbers of all the observed species. The re-normalization of the spectroscopic data was performed first using the solvent n-hexane as the reference in order to eliminate the dependence on variable reaction volume and variable path length of cell. Next, the reaction invariant model was set up using the mole balances on Rh and Re. Accordingly, the proposed chemical group matrix is as follows.

\[
\begin{bmatrix}
0 & 1 & 0 \\
4 & 0 & 0 \\
1 & 1 & 0 \\
\end{bmatrix}
\] (6.1)

Sequentially the rows of this matrix are associated with HRe(CO)\(_5\), Rh\(_4\)(CO)\(_{12}\), and RhRe(CO)\(_9\) species. Since the signal of Rh\(_6\)(CO)\(_{16}\) is very weak, which means a very low concentration, Rh\(_6\)(CO)\(_{16}\) was not included in the chemical group balance.

As described in Chapter 3, a diagonal weighting matrix \(d_{i \times f}\) was determined to calculate the real magnitudes of the reconstructed pure component spectra. The maxima of these three pure component spectra are shown in Table 6.3.

**Table 6.3** The maximum absorptivities for each pure component spectral estimate

<table>
<thead>
<tr>
<th>Species</th>
<th>Max Peak, cm(^{-1})</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRe(CO)(_5)</td>
<td>2016.6</td>
<td>16200</td>
</tr>
<tr>
<td>Rh(<em>4)(CO)(</em>{12})</td>
<td>2070</td>
<td>18145</td>
</tr>
<tr>
<td>RhRe(CO)(_9)</td>
<td>2026.6</td>
<td>21500</td>
</tr>
</tbody>
</table>

Upon obtaining the real magnitudes of the absorptivities, the time series of moles for the observable organometallic components in all the experiments can be directly
generated. Figures 6.6-6.8 show the time-dependent mole numbers of Rh₄(CO)₁₂, HRe(CO)₅ and RhReCO)₉ respectively for experiment 6 (Table 6.1). As all the peaks of the HRe(CO)₅ are overlapped with other species, its calculation is somewhat sensitive.

**Figure 6.6** Time dependent moles of HRe(CO)₅

**Figure 6.7** Time dependent moles of Rh₄(CO)₁₂
As shown in Figures 6.6-6.8, in step 1, with only $\text{Rh}_4(\text{CO})_{12} / \text{HRe}(\text{CO})_5 / \text{CO}$ in the system, the mole numbers of both $\text{Rh}_4(\text{CO})_{12}$ and $\text{HRe}(\text{CO})_5$ have a very rapid decline, while the mole numbers of $\text{RhRe}(\text{CO})_9$ increased rapidly. This means that with no or a bit of molecular hydrogen in the system, the reaction $\text{Rh}_4(\text{CO})_{12} + 4\text{HRe}(\text{CO})_5 + 4\text{CO} \leftrightarrow 4 \text{RhRe}(\text{CO})_9 + 2\text{H}_2$ goes very fast to the right side. In step 2, when the molecular hydrogen was added (0.11Mpa), it can be seen that $\text{RhRe}(\text{CO})_9$ mole numbers began to decrease, and accordingly the mole numbers of both $\text{Rh}_4(\text{CO})_{12}$ and $\text{HRe}(\text{CO})_5$ increased until they reached equilibrium. This is irrefutable evidence for the rapid and reversible molecular hydrogen activation by the heterometallic dinuclear carbonyl $\text{RhRe}(\text{CO})_9$. In the following steps, with more hydrogen introduced in the reactor, similar trends can be observed in Figures 6.6-6.8.
6.2.3 Thermodynamics

Six series of experiments were conducted at three temperatures to determine the equilibrium constants for the reaction

$$\text{Rh}_4(\text{CO})_{12} + 4\text{HRe(CO)}_5 + 4\text{CO} \leftrightarrow 4\text{RhRe(CO)}_9 + 2\text{H}_2$$

(6.2)

Where

$$K_{eq} = [\text{RhRe(CO)}_9]^4[\text{H}_2]^2 / ([\text{Rh}_4(\text{CO})_{12}][\text{HRe(CO)}_5]^4[\text{CO}]^4)$$

(6.3)

In the above equations, all the concentrations were used as mole fractions. As shown in Table 6.1, the equilibrium experiments were performed under different partial pressures of CO and H$_2$ with different initial loadings of Rh$_4$(CO)$_{12}$ and HRe(CO)$_5$.

Figures 6.9-6.11 present the data set for the equilibrium experiments at three temperatures. The regression analysis of the data yields the equilibrium constants at different temperatures. At 289.7K, more data points from the kinetic studies (Section 6.3) were included here to get a good regression. The equilibrium constants are listed in Table 6.4. The $R^2$ values indicate the present regressions could be a little better. [It should be noted that difficulties in measuring the equilibria of very reactive organometallics are well known i.e. CoRh(CO)$_7$ (Garland et al, 1991). In addition, it should be noted that the exponents in the equilibrium constant expression are sometimes very large – this can lead to the introduction of significant errors]. The linear relationship between $[\text{RhRe(CO)}_9]^4[\text{H}_2]^2$ and $[\text{Rh}_4(\text{CO})_{12}][\text{HRe(CO)}_5]^4[\text{CO}]^4$ confirms that the overall equilibrium reaction is indeed a stoichiometric reaction. This in part supports the assignment of the new heterometallic dinuclear carbonyl RhRe(CO)$_9$. 

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Figure 6.9 Equilibrium relationship at 308.2K

Figure 6.10 Equilibrium relationship at 298.3K
The equilibrium thermodynamics was regressed using two kinds of models. One is a 2-parameter model which includes enthalpy ($\Delta_r H$) and entropy ($\Delta_r S$). The second 3-parameter model considers the pressure effects and the model covers the enthalpy ($\Delta_r H$), entropy ($\Delta_r S$), and volume of reaction ($\Delta_r V$). The relationship between the equilibrium
constant and the thermodynamic parameters is expressed by the Van’t Hoff equation as follows.

\[
- \ln K_{eq}(P, T) = \frac{\Delta_r G(P, T)}{RT} = \frac{\Delta_r H_{P=1}}{RT} - \frac{\Delta_r S}{R} + \frac{\Delta_r V(P-1)}{RT} \tag{6.4}
\]

\[
- \ln \left\{ \frac{[\text{RhRe}(\text{CO})_9][\text{H}_2]^2}{[\text{Rh}_4(\text{CO})_{12}]^6[\text{HRe}(\text{CO})_3]^4} \right\} = \frac{\Delta_r H}{RT} - \frac{\Delta_r S}{R} + \frac{\Delta_r V(P-1)}{RT} \tag{6.5}
\]

If a 2-parameter expression is implemented, the volume of reaction term (\(\Delta_r V\)) in the right hand side of equation can be eliminated.

The multiple linear regression result using the 2-parameter model provided the thermodynamics parameters

\[
\Delta_r H = -116 \pm 29 \text{ KJ/mole}
\]

\[
\Delta_r S = -312 \pm 99 \text{ J/(mole K)}
\]

The 3-parameter model provided

\[
\Delta_r H = -71 \pm 29 \text{ KJ/mole}
\]

\[
\Delta_r S = -168 \pm 95 \text{ J/(mole K)}
\]

\[
\Delta_r V = -847 \pm 349 \text{ ml / mole}
\]

The negative value of the enthalpy \(\Delta_r H\) is consistent with the observation of higher conversion to the heterometallic dinuclear complex \(\text{RhRe}(\text{CO})_9\) at lower temperatures. In addition, the negative sign of the entropy \(\Delta_r S\) of the reaction is in agreement with the stoichiometric equation for this reaction, namely, nine molecules give only six molecules as products. The negative sign for the volume of reaction is consistent with the loss of the unusually large partial molar volumes of dissolved molecular carbon monoxide of circa 50 ml / mole upon reaction (Asano and Noble, 1978; Handa and
Benson, 1982; Eldik et al, 1989). However, a value smaller than -850 ml / mole is expected (Garland et al, 1991). These results indicates the severe limitation of the atypically small total pressure interval of circa 2 MPa used in this study versus pressure intervals of circa 100 MPa used in traditional reaction volume studies.

### 6.2.4 Discussion

The intrinsic reaction kinetics on the formation and hydrogen activation of RhRe(CO)$_9$ was too rapid to be captured with the present experimental set-up. Indeed, characteristic times for gas-liquid mass transfer as well as liquid-phase mixing were on the order of a few minutes. Therefore, it is possible that transport controlled rather than intrinsic kinetics was observed. Nevertheless, it looks likely that an intermediate such as an unobservable H$_2$RhRe(CO)$_8$ and/or H$_2$RhRe(CO)$_7$ is formed, and it subsequently undergoes fragmentation to give HRe(CO)$_5$ and a very unstable hydridorhodium species such as HRh(CO)$_4$ and/or HRh(CO)$_3$ (Chini and Martinengo, 1969), which rapidly yields Rh$_4$(CO)$_{12}$.

In this section, the chemometric analyses were performed in collaboration with Mr Guo Liangfeng.
6.3 The $\text{Rh}_4(\text{CO})_{12}$ catalyzed hydroformylation of cyclopentene promoted with $\text{HRe} (\text{CO})_5$

In the previous section, the equilibrium of $\text{Rh}_4(\text{CO})_{12} / \text{HRe} (\text{CO})_5$ under $\text{CO}/\text{H}_2$ was studied. The Rh-Re bimetallic dinuclear complex $\text{RhRe} (\text{CO})_9$ was identified and its formation and hydrogen activation were characterized. This provides an opportunity to find another type of bimetallic CBER where the expected dinuclear species could be found. In the following, the $\text{Rh}_4(\text{CO})_{12}$ catalyzed hydroformylation of cyclopentene promoted with $\text{HRe} (\text{CO})_5$ will be systematically studied to check this possibility.

6.3.1 Experimental section

All the experiments were performed in a similar manner. In a typical experiment, first, single beam background spectra of the IR sample chamber were recorded. Then 150 ml 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 4.0 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 5.5 ml cyclopentene (CP) dissolved in 50 ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurized with CO and then added to the autoclave. After equilibration, infrared spectra of the CP/CO/n-hexane solution in the high-pressure cell were recorded. A solution of circa 40 mg $\text{Rh}_4(\text{CO})_{12}$ dissolved in 50 ml n-hexane was prepared, transferred to the high-pressure reservoir under argon, pressurized with CO and then added to the autoclave. After equilibration, infrared spectra of the $\text{Rh}_4(\text{CO})_{12} / \text{CP} / \text{CO} / \text{n-hexane} /$ solution in the high-pressure cell were recorded. A solution of circa 20 µL $\text{HRe} (\text{CO})_5$ dissolved in 50 ml n-
hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO and then added to the autoclave. Then 1.0 MPa hydrogen was added to initiate the hydroformylation. The detailed experimental design for this study is shown in Table 6.5. The spectra were taken every 2 minutes in the range of 1000-7500 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. In each experiment, circa 150 spectra were recorded.

**Table 6.5  Experimental design**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>HRe(CO)$_5$µL</th>
<th>CO, MPa</th>
<th>H$_2$,MPa</th>
<th>CP, ml</th>
<th>Rh$<em>4$(CO)$</em>{12}$,mg</th>
<th>Temperature,K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>42.49</td>
<td>289.7</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>0</td>
<td>289.7</td>
</tr>
<tr>
<td>Pure Rh</td>
<td>0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>49.03</td>
<td>289.7</td>
</tr>
<tr>
<td>Pure Re 1</td>
<td>20.0</td>
<td>2.0</td>
<td>2.0</td>
<td>5.5</td>
<td>0</td>
<td>294.3</td>
</tr>
<tr>
<td>Pure Re 2</td>
<td>35.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>0</td>
<td>289.7</td>
</tr>
<tr>
<td>CO Variation</td>
<td>20.0</td>
<td>3.0</td>
<td>1.0</td>
<td>5.5</td>
<td>37.17</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>5.0</td>
<td>1.0</td>
<td>5.5</td>
<td>37.42</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>6.0</td>
<td>1.0</td>
<td>5.5</td>
<td>39.42</td>
<td>289.7</td>
</tr>
<tr>
<td>H$_2$ Variation</td>
<td>20.0</td>
<td>4.0</td>
<td>0.5</td>
<td>5.5</td>
<td>38.14</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>4.0</td>
<td>1.5</td>
<td>5.5</td>
<td>38.67</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>4.0</td>
<td>2.0</td>
<td>5.5</td>
<td>38.07</td>
<td>289.7</td>
</tr>
<tr>
<td>Cyclopentene Variation</td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>3.0</td>
<td>37.89</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>15.0</td>
<td>40.4</td>
<td>289.7</td>
</tr>
<tr>
<td>Rh$<em>4$(CO)$</em>{12}$ Variation</td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>9.33</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>21.38</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>69.59</td>
<td>289.7</td>
</tr>
<tr>
<td>Temperature Variation</td>
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<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>40.02</td>
<td>282.6</td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>40.43</td>
<td>294.0</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>37.7</td>
<td>298.5</td>
</tr>
<tr>
<td>HReCO)$_5$ variation</td>
<td>5.4</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>39.87</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>39.37</td>
<td>289.7</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>4.0</td>
<td>1.0</td>
<td>5.5</td>
<td>39.9</td>
<td>289.7</td>
</tr>
</tbody>
</table>
The experimental design of the experiments involved 300 ml solvent and the intervals 282.6-298.5K, \( P_{\text{H}_2} = 0.5-2.0 \) MPa, \( P_{\text{CO}} = 3.0-6.0 \) MPa, initial alkene = 3-15ml, initial \( \text{Rh}_4(\text{CO})_{12} = 9.33-69.59 \) mg and initial \( \text{HRe(\text{CO})}_5 = 5.4-40.0 \) \( \mu \)L.

All hydroformylation experiments exhibited product formation rates belonging to infinitely slow reaction compared to gas-liquid mass transfer (category H of the Hatta classifications). Since the maximum rate of the hydroformylation in this study was \( 10^{-7} \) mol/s, the gas-liquid mass transfer can be ignored in all the experiments.

Blank experiments, in the presence of organic reactants but without added complexes, were performed throughout the study.

The in-situ spectra were taken every 2 minutes in the range of 1000-7000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). In each experiment, circa 150 spectra were recorded during the 5 hours experiment and a total of circa 3500 spectra were obtained. For the following analysis, only circa 1/3 of these spectra (each 10 minutes) were used, therefore only 763 spectra were used to do the BTEM reconstruction.

### 6.3.2 Spectral analyses

In this section, the total system identification algorithm is used to analyse the in-situ FTIR data.

One of the raw experimental spectra before any spectral pre-processing is shown in Figure 6.12.
Similar to the previous section (Chapter 4), since the IR transmission in the range of 1300 – 1550 cm\(^{-1}\) is very low, this region was eliminated. In addition, close inspection shows that there is no special spectral features in the range of 2500 – 7000 cm\(^{-1}\) for present system. Accordingly, this region is also excluded for further spectral analyses. Therefore, two spectral windows with the region of 1000 – 1300 cm\(^{-1}\) and 1550 – 2500 cm\(^{-1}\) are obtained. The first region only contains information for the solvent n-hexane, while the second region contains the spectroscopic information for both the organic and organometallic species.

Singular value decomposition (SVD) was firstly employed to decompose the experimental absorbance data matrix \(A_{763 \times 2951}\) to give the orthonormal matrices \(U_{763 \times 763}\) and \(V_{2951 \times 2951}^T\), and the diagonal singular value matrix \(\Sigma_{763 \times 2951}\).

The significant spectral extrema in the first few right singular vectors were inspected and were used as targets in the BTEM algorithm. Six significant bands (indicated by numbers in Figure 6.13) were selected for the reconstructions. Table 6.6 lists

![Raw experimental spectrum](image-url)
the selected wavenumber regions, the maximum peak absorbance, number of $V^T$ vectors taken for spectral reconstruction and the identity of the resolved pure component spectrum.

Figure 6.13 Significant spectral extrema used for BTEM

Table 6.6 Spectral Reconstruction Parameters and Species Identities

<table>
<thead>
<tr>
<th># Species</th>
<th># $V^T$ vectors, $z$</th>
<th>Wavenumber region</th>
<th>Maximum Abs, $\alpha$</th>
<th>Species identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>25</td>
<td>1732 – 1733</td>
<td>1</td>
<td>aldehyde</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>1614 – 1615</td>
<td>1</td>
<td>cyclopetene</td>
</tr>
<tr>
<td>3.</td>
<td>25</td>
<td>1885 – 1887</td>
<td>5</td>
<td>Rh$<em>4$(CO)$</em>{12}$</td>
</tr>
<tr>
<td>4.</td>
<td>25</td>
<td>2110 – 2112</td>
<td>1</td>
<td>RCORh(CO)$_4$</td>
</tr>
<tr>
<td>5.</td>
<td>25</td>
<td>2006 – 2008</td>
<td>1</td>
<td>HRe(CO)$_5$</td>
</tr>
<tr>
<td>6.</td>
<td>25</td>
<td>2025.4 – 2027.4</td>
<td>1</td>
<td>RhRe(CO)$_9$</td>
</tr>
</tbody>
</table>
Reconstructed pure component spectra via BTEM are presented in Figure 6.14.

As shown in Figure 6.14, the quality of the BTEM reconstructions is very high. Flat and smooth baselines are observed in all 6 spectral estimates. 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.

Similar procedures were carried out to calculate the mole numbers of the 6 estimates (refer to Chapter 4). The spectroscopic data were firstly re-normalized to eliminate the dependence on variable reaction volume and variable path length of cell. The standard $A_{\omega}^{std}$ of each reaction spectrum was derived from solvent n-hexane’s absorbance data at a reference wavenumber $\omega = 1137 \text{ cm}^{-1}$. In the next step, a reaction invariant model was set up based on the chemical group balance of Rh-, Org-, and Re-. Accordingly, the proposed chemical group matrix is as follows.

$$
\begin{bmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
4 & 0 & 0 \\
0 & 0 & 1 \\
1 & 0 & 1 \\
1 & 1 & 0
\end{bmatrix}
$$

(6.6)

Sequentially the rows of this matrix are associated with aldehyde, HRe(CO)$_5$, Rh$_4$(CO)$_{12}$, cyclopentene, RCORh(CO)$_4$, and RhRe(CO)$_9$ species.

As described in Chapter 3, a diagonal weighting matrix $d_{s,s}$ is required to calculate the absolute magnitude of the time series of moles for the observable species. This diagonal matrix can be obtained using a reaction invariant / material balance model, in which the sum of squares error minimization between the estimated $\overline{N}_{k\epsilon s E}$ and the initial reaction condition $N_{k\epsilon s E}$ is utilized.
The obtained optimum matrix $d_{sys}$ is employed to calculate the real magnitudes of the reconstructed pure component spectra. The maxima of these six pure component spectra are shown in Table 6.7. The absorptivities of cyclopentene, aldehyde, $\text{Rh}_4(\text{CO})_{12}$ and $\text{RCORh}(\text{CO})_4$ are quite close to those obtained in the $\text{Rh}_4(\text{CO})_{12}/\text{HMn}(\text{CO})_5$ bimetallic catalyzed hydroformylation of cyclopentene system, while the absorptivities of $\text{HReCO})_5$ and $\text{RhReCO})_9$ are close to those obtained in the Rh/Re equilibrium studies (Section 6.2).

**Table 6.7** The maximum absorptivities for the pure component spectra

<table>
<thead>
<tr>
<th>Species</th>
<th>Max Peak, $\text{cm}^{-1}$</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>aldehyde</td>
<td>1732.6</td>
<td>376</td>
</tr>
<tr>
<td>$\text{HReCO})_5$</td>
<td>2016.6</td>
<td>16360</td>
</tr>
<tr>
<td>$\text{Rh}<em>4(\text{CO})</em>{12}$</td>
<td>2070</td>
<td>18340</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>1615</td>
<td>7.4</td>
</tr>
<tr>
<td>$\text{RhReCO})_9$</td>
<td>2026.6</td>
<td>20460</td>
</tr>
<tr>
<td>$\text{RCORh}(\text{CO})_4$</td>
<td>2021.2</td>
<td>3800</td>
</tr>
</tbody>
</table>

After obtaining the real magnitudes of the absorptivities, the time series of moles for the six observable components in all the experiments can be directly generated. These are presented in Figure 6.15.
From all the above time-dependent concentration profiles of both organic and organometallic species, it should be noted that even under reaction conditions of circa 5.0 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 rhenium remained constant.

*In this section, the chemometric analyses were performed in collaboration with Dr Chen Li.*
6.3.3 Catalysis results

6.3.3.1 Spectra aspects

As mentioned in Chapter 4 and Chapter 5, in the previous in-situ FTIR spectroscopic studies of unmodified rhodium catalyzed hydroformylation of alkenes, only 5 observable organometallics have been identified, namely the known species \( \text{RCORh(CO)}_4 \), \( \text{Rh}_2(\text{CO})_8 \), \( \text{Rh}_4(\text{CO})_{12} \), \( \text{Rh}_6(\text{CO})_{16} \), and \( \text{Rh}_4(\sigma-\text{CO})_{12} \), where the last two normally exist at the ppm or sub-ppm level under most catalytic conditions. No evidence for observable quantities of the known rhodium hydride species could be obtained.

In the present \( \text{Rh}_4(\text{CO})_{12} /\text{HRe(CO)}_5 \) bimetallic catalyzed hydroformylation of cyclopentene, the chemometric analyses (Section 6.3.2) of the in situ infrared spectra of the reaction recovered the precursor \( \text{Rh}_4(\text{CO})_{12} \), the precursor \( \text{HRe(CO)}_5 \), the reagent cyclopentene, the rhodium intermediate \( \text{RCORh(CO)}_4 \) and the organic product \( \text{RCHO} \).

In contrast to the \( \text{Rh}_4(\text{CO})_{12} /\text{HMn(CO)}_5 \) bimetallic catalyzed hydroformylation of 33DMB and cyclopentene, a new dinuclear complex \( \text{RhRe(CO)}_9 \) was also observed in the present Rh/Re system.

6.3.3.2 Calculations

The solubilities of \( \text{H}_2 \) and \( \text{CO} \), reactant and product concentrations, and TOF were calculated using the same methods as described in Chapter 4.

6.3.3.3 Hydroformylation with only \( \text{HRe(CO)}_5 \)

To determine the activities of \( \text{HRe(CO)}_5 \), two blank experiments with only \( \text{HRe(CO)}_5 \) as the precursor were carried out. The experimental conditions are listed in

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Table 6.8. The two 6 hour experiments showed that there was no observable reaction under our reaction conditions. Also, there was no degradation of the HRe(CO)\textsubscript{5} to Re\textsubscript{2}(CO)\textsubscript{10}.

<table>
<thead>
<tr>
<th>No</th>
<th>HRe(CO)\textsubscript{5} (µL)</th>
<th>Cyclopentene (mL)</th>
<th>T (K)</th>
<th>CO (MPa)</th>
<th>H\textsubscript{2} (MPa)</th>
<th>n-Hexane (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>5.5</td>
<td>291.6</td>
<td>2.0</td>
<td>2.0</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>5.5</td>
<td>289.7</td>
<td>4.0</td>
<td>1.0</td>
<td>350</td>
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</tbody>
</table>

6.3.3.4 Hydroformylation with Rh\textsubscript{4}(CO)\textsubscript{12} and HRe(CO)\textsubscript{5} : Changing HRe(CO)\textsubscript{5} initial loadings

In the following, the kinetic results of the hydroformylation of cyclopentene with Rh\textsubscript{4}(CO)\textsubscript{12} and HRe(CO)\textsubscript{5} will be presented in detail. A total of six sub-series experiments have been carried out with variations of HRe(CO)\textsubscript{5} loading, Rh\textsubscript{4}(CO)\textsubscript{12} loading, cyclopentene loading, CO pressure, hydrogen pressure and reaction temperature. Here the effect of HRe(CO)\textsubscript{5} loading on the rhodium catalyzed hydroformylation of cyclopentene will be discussed first.

The initial concentration of the precursor HRe(CO)\textsubscript{5} was systematically varied in five hydroformylations. The five kinetic experiments were performed at 289.7K, 4.0MPa CO and 1.0MPa H\textsubscript{2} to investigate the effect of HRe(CO)\textsubscript{5} on the unmodified rhodium catalyzed hydroformylation. The corresponding concentrations of H\textsubscript{2} and CO were 0.0097 and 0.0986 respectively. The initial input of cyclopentene was 5.5 ml and the concentration was 0.027mole fraction. The initial loadings of HRe(CO)\textsubscript{5} were 0, 5.4, 15.0,
20.0 and 40.0 µL while the initial loadings of Rh₄(CO)₁₂ were between 39.4-42.9 mg. Accordingly, the initial concentrations of HRe(CO)₅ in mole fraction were \( X_{HRe(CO)5}=0 \), \( 1.72 \times 10^{-5} \), \( 4.78 \times 10^{-5} \), \( 6.38 \times 10^{-5} \) and \( 1.28 \times 10^{-4} \) respectively. The corresponding initial concentrations of Rh₄(CO)₁₂ were circa \( 2.3 \times 10^{-5} \) mole fraction.

### 6.3.3.4.1 Initial reaction times

The time-dependent concentrations of the precursors Rh₄(CO)₁₂, HRe(CO)₅, and the only observable intermediates RhRe(CO)₉ and RCORh(CO)₄ are shown in Figures 6.16-6.19.

![Figure 6.16](image)

**Figure 6.16** The time dependent mole fractions of Rh₄(CO)₁₂
Figure 6.17 The time dependent mole fractions of HRe(CO)₅

Figure 6.18 The time dependent mole fractions of acyl
From Figure 6.16, it can be noted that after the simultaneous addition of the rhenium carbonyl hydride HRe(CO)$_5$ and hydrogen to the systems initially containing Rh$_4$(CO)$_{12}$, cyclopentene, hexane and CO, the concentrations of Rh$_4$(CO)$_{12}$ monotonically declined in all the five experiments. The data presented in Figure 6.16 indicate that a very rapid decline in the catalyst precursor concentration occurs when HRe(CO)$_5$ and Rh$_4$(CO)$_{12}$ are added simultaneously. Indeed, under the present conditions, the half-life of Rh$_4$(CO)$_{12}$ in the Rh/Re bimetallic system is less than 10 minutes, while the half-life of Rh$_4$(CO)$_{12}$ in the pure system is circa two hours under the similar reaction conditions. However, the addition of 5-40 micro-liters of HRe(CO)$_5$ has little effect on the time-dependent transformation of Rh$_4$(CO)$_{12}$. This may be due to a shift in the rate limiting
step. For example, the presence of HRe(CO)₅ may seriously deplete the concentration of \{Rh₄(CO)₁₄\} and the reaction Rh₄(CO)₁₂ to \{Rh₄(CO)₁₄\} may become rate determining.

Figure 6.18 shows that the concentration of RCORh(CO)₄ monotonically increased in all the five experiments. As in the Rh₄(CO)₁₂/HMn(CO)₅ bimetallic catalyzed hydroformylation system, relative to the pure Rh₄(CO)₁₂ system, a faster increase in acyl complex concentration occurs. This is due to rhenium hydride attack that facilitates the Rh₄(CO)₁₂ fragmentation. Figure 6.18 also indicates that the rhodium acyl concentration generally decreases when increasing the HRe(CO)₅ concentrations. The final concentrations of RCORh(CO)₄ were 6.7×10⁻⁵, 5.7×10⁻⁵, 6.1×10⁻⁵ and 3.3×10⁻⁵ when the initial loadings of HRe(CO)₅ were 5.4, 15.0, 20.0 and 40.0 µL respectively.

The concentration profiles of HRe(CO)₅ and RhRe(CO)₉ are shown in Figures 6.17 and 6.19. The RhRe(CO)₉ concentration generally increases and the HRe(CO)₅ concentration generally decreases during the initial reaction period and pseudo steady-state is reached in all the four experiments with both HRe(CO)₅ and Rh₄(CO)₁₂ present. However, in two of the experiments (HRe(CO)₅=15.0, 20.0 µL), a redistribution of HRe(CO)₅ and RhRe(CO)₉ was observed at initial reaction times. As described in the Rh₄(CO)₁₂ and HRe(CO)₅ equilibrium experimental results, this could be traced to the effect of adding molecular hydrogen to the system. Its presence will influence the ratio between HRe(CO)₅ and RhRe(CO)₉.

The presence of HRe(CO)₅ in the pure Rh₄(CO)₁₂ experiment is most likely a numerical artifact. The reactor was always cleaned thoroughly between experiments, and HRe(CO)₅ is very easy to clean from the reactor (as compared to the rhodium clusters). The presence of a non-zero amount of HRe(CO)₅ in the pure Rh₄(CO)₁₂ experiment is due
to the fact that the spectrum of HRe(CO)$_5$ is almost entirely imbedded / overlapping with RhRe(CO)$_9$. The presence of HRe(CO)$_5$ will therefore be indicated from the calculations when in fact there is none there.

Figure 6.19 indicates that the final concentration of RhRe(CO)$_9$ increases with increasing initial loading of HRe(CO)$_5$. Indeed, the final mole fractions of RhRe(CO)$_9$ were $6.1 \times 10^{-6}, 1.6 \times 10^{-5}, 2.1 \times 10^{-5}$ and $4.1 \times 10^{-5}$ when the initial loadings of HRe(CO)$_5$ were 5.4, 15.0, 20.0 and 40.0 µL respectively. This supports the Rh$_4$(CO)$_{12}$ and HRe(CO)$_5$ equilibrium experimental results, i.e., the higher HRe(CO)$_5$ concentration results in higher RhRe(CO)$_9$ concentration.

6.3.3.4.2 Effect of HRe(CO)$_5$ on the product formation

The concentration profiles of the product aldehyde are shown in Figure 6.20. The concentrations of the product aldehyde monotonically increase in all the five experiments. The production of aldehyde could be identified within the first few minutes when HRe(CO)$_5$ /Rh$_4$(CO)$_{12}$ were used simultaneously.
A very significant increase in aldehyde formation was observed in the experiments when both rhodium carbonyl and rhenium carbonyl complexes were used. Generally speaking, increased concentrations of HRe(CO)$_5$ lead to increased hydroformylation rates. The product formation rates were circa $1.28 \times 10^{-6}$, $6.87 \times 10^{-6}$, $7.96 \times 10^{-5}$, $1.41 \times 10^{-5}$, and $1.45 \times 10^{-5}$ (mol fraction)/min in the last 280 minutes when the initial loadings of HRe(CO)$_5$ were 0, 5.4, 15.0, 20.0 and 40.0 µL respectively. When 20 µL HRe(CO)$_5$ was used with Rh$_4$(CO)$_{12}$, the rate of hydroformylation was as great as 800% of the rate that was anticipated from the rhodium loading alone. Since HRe(CO)$_5$ is nearly inert towards transformations of alkenes under the present reaction conditions, this result implies that HRe(CO)$_5$ gets involved in the rhodium catalytic pathway to produce aldehyde.
It is interesting to note that when more HRe(CO)₅ (40.0µL) was used in the HRe(CO)₅ /Rh₄(CO)₁₂ bimetallic catalyzed hydroformylation of cyclopentene, the aldehyde formation rate is almost the same as that of 20.0µL HRe(CO)₅. One of the possible reasons is that at higher loading of HRe(CO)₅, there would be higher RhRe(CO)₉ concentration and accordingly a lower RCORh(CO)₄ concentration (as described in the Rh₄(CO)₁₂ and HRe(CO)₅ equilibrium experimental results). RCORh(CO)₄ is the key intermediate to produce the organic product in the unmodified Rh₄(CO)₁₂ catalyzed hydroformylation.

6.3.3.4.3 TOF analyses

The effect of loading of HRe(CO)₅ on the TOF is shown in Figure 6.21. The turnover frequencies (TOF) based on rhodium acyl were 0.03±0.01 min⁻¹, 0.11±0.01min⁻¹, 0.15±0.01min⁻¹, 0.25±0.02min⁻¹ and 0.44±0.06 min⁻¹ when the initial loading of HRe(CO)₅ were 0, 5.4, 15.0, 20.0 and 40.0 µL respectively. The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The monometallic rhodium TOF value obtained in this study is consistent with our previous studies in Chapter 5.
The TOF values demonstrate that HRe(CO)$_5$ is very active with Rh$_4$(CO)$_{12}$ for the hydroformylation of cyclopentene. The TOF increases when increasing the loading of HRe(CO)$_5$. When the initial concentration of HRe(CO)$_5$ was 20.0 µL, the TOF is as great as 800% of that anticipated from the rhodium loading alone. This is a clear-cut quantitative confirmation that HRe(CO)$_5$ contributes significantly to the rate of product formation and that ReH(CO)$_5$ must be involved in at least one step of the catalytic cycle for the hydroformylation. The most likely situation is that HRe(CO)$_5$ interacts with the most active rhodium intermediate RCORh(CO)$_4$.

6.3.3.5 Changing Rh$_4$(CO)$_{12}$ concentration
The initial concentration of Rh₄(CO)₁₂ was systematically varied in four hydroformylation experiments performed at 289.7K, 4.0MPa carbon monoxide, 1.0MPa hydrogen and circa 20 µL HRe(CO)₅ in 300 ml n-hexane. The corresponding concentrations of H₂ and CO were 0.0097 and 0.0986 respectively. The initial input of cyclopentene was 5.5 ml and the concentration was 0.027 mole fraction. The initial loadings of Rh₄(CO)₁₂ were 9.33, 21.38, 42.49 and 69.59 mg. Accordingly, the calculated initial concentrations of Rh₄(CO)₁₂ in mole fractions were \( X_{Rh_4(CO)_{12}} = 5.4 \times 10^{-6} \), \( 1.2 \times 10^{-5} \), \( 2.5 \times 10^{-5} \), and \( 4.0 \times 10^{-5} \) respectively. For easy comparison, the concentration profiles of pure rhodium catalyzed hydroformylation were also included in the figures.

### 6.3.3.5.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HRe(CO)₅, and the only two other observable intermediates RCORh(CO)₄ and RhRe(CO)₉ are shown in Figures 6.22-25.
**Figure 6.22** The time dependent mole fractions of Rh$_4$(CO)$_{12}$

**Figure 6.23** The time dependent mole fractions of HRe(CO)$_5$
Figure 6.24 The time dependent mole fractions of acyl

Figure 6.25 The time dependent mole fractions of RhRe(CO)$_9$
As shown in Figure 6.22, compared to the pure Rh₄(CO)₁₂ catalyzed hydroformation of cyclopentene, a faster decline of Rh₄(CO)₁₂ was observed when both HRe(CO)₅ and Rh₄(CO)₁₂ were used simultaneously. Indeed, the half-life of Rh₄(CO)₁₂ were circa 5-20 minutes in the Rh₄(CO)₁₂/HRe(CO)₅ bimetallic system, while the half-life for the pure Rh₄(CO)₁₂ system was circa 2 hours.

Figure 6.24 demonstrates that the concentration of RCORh(CO)₄ monotonically increased in all the four experiments. Compared to the pure Rh₄(CO)₁₂ catalyzed hydroformation of cyclopentene, there exists a faster increase of RhCORh(CO)₄ at the initial reaction times when both HRe(CO)₅ and Rh₄(CO)₁₂ were used simultaneously. This implies that there could be a rhenium hydride attack on the Rh₄(CO)₁₂ to give RCORh(CO)₄. This is consistent with the results as observed in Rh₄(CO)₁₂ /HMn(CO)₅ bimetallic catalyzed hydroformylation of 33DMB and cyclopentene.

As indicated in Figure 6.24, the initial loading of Rh₄(CO)₁₂ appears to have a strong effect on the final concentrations of RCORh(CO)₄. Indeed, the final concentrations of RCORh(CO)₄ were 9.7×10⁻⁶, 2.9×10⁻⁵, 6.2×10⁻⁵, and 9.7×10⁻⁵ when the initial loading of Rh₄(CO)₁₂ was 5.4×10⁻⁶, 1.2×10⁻⁵, 2.5×10⁻⁵, and 4.0×10⁻⁵ respectively.

From Figure 6.23 and Figure 6.25, it can be seen again that the RhRe(CO)₉ concentration generally increases and the HRe(CO)₅ concentration generally decreases during the initial reaction. A pseudo steady-state is reached in all the four experiments with both HRe(CO)₅ and Rh₄(CO)₁₂ present along with RhRe(CO)₉. Figure 6.25 indicates that increased initial Rh₄(CO)₁₂ concentrations lead to increased pseudo-state concentrations of RhRe(CO)₉ and accordingly the decreased pseudo-state concentrations of HRe(CO)₅. The final concentrations of RhRe(CO)₉ were 8.2×10⁻⁶, 1.3×10⁻⁵, 2.1×10⁻⁵,
and $2.4 \times 10^{-5}$, while the final concentrations of HRe(CO)$_5$ were $5.1 \times 10^{-5}$, $4.3 \times 10^{-5}$, $3.8 \times 10^{-5}$, and $3.2 \times 10^{-5}$ when the initial loadings of Rh$_4$(CO)$_{12}$ were $5.4 \times 10^{-6}$, $1.2 \times 10^{-5}$, $2.5 \times 10^{-5}$, and $4.0 \times 10^{-5}$ respectively. This is consistent with the results obtained in the Rh$_4$(CO)$_{12}$ and HRe(CO)$_5$ equilibrium experiments.

### 6.3.3.5.2 Product formation

In the interest of completeness, the time-dependent concentrations of both the reagent cyclopentene and the hydroformylation product aldehyde are shown in Figures 6.26 and 6.27. However, it should be noted that the concentrations of aldehyde are much more reliable than those for cyclopentene. Indeed, as listed in Table 6.7, cyclopentene has a smaller maximal absorptivity than aldehyde (7 versus 376). Some numerical problems arise.

![Figure 6.26](image)

**Figure 6.26** The time dependent mole fractions of CP
Figure 6.27 The time dependent mole fractions of aldehyde

The variation in the initial concentration of Rh₄(CO)₁₂ has a big effect on the formation of aldehyde. The product formation rates were circa $3.6 \times 10^{-6}$, $8 \times 10^{-6}$, $1.5 \times 10^{-5}$, and $1.8 \times 10^{-5}$ (mol fraction)/min when the initial loadings of Rh₄(CO)₁₂ were 9.33, 21.38, 42.49 and 69.59 mg respectively. One obvious reason is that the higher concentration of Rh₄(CO)₁₂ gives rise to a higher concentration of RCORh(CO)₄, which produces the final product.

However, Figure 6.27 also shows that the bimetallic system has much higher activity than the pure rhodium system. At the same loading of Rh₄(CO)₁₂ (circa 40 mg), the hydroformylation rate of the Rh/Re system was circa 10 times faster than that of pure rhodium system. When 9.33 mg Rh₄(CO)₁₂ was used with HRe(CO)₅, the
hydroformylation reaction was much faster (circa 3 times) than when 49.03 mg Rh$_4$(CO)$_{12}$ was used alone.

6.3.3.5.3 TOF analyses

The effect of loading of Rh$_4$(CO)$_{12}$ on TOF is shown in Figure 6.28.

The average turnover frequencies were $0.30 \pm 0.01 \text{min}^{-1}$, $0.25 \pm 0.02 \text{min}^{-1}$, and $0.19 \pm 0.03 \text{min}^{-1}$ in the three experiments starting with $X_{\text{Rh}_4(\text{CO})_{12}}=1.2 \times 10^{-5}$, $2.5 \times 10^{-5}$, and $4.0 \times 10^{-5}$ respectively.

It seems that the influence of the initial concentration of Rh$_4$(CO)$_{12}$ on the turnover frequencies is very small. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate (Garland and
Pino, 1991) and the previous results obtained in the Rh/Mn bimetallic hydroformylation of 33DMB (Chapter 4) and cyclopentene (Chapter 5). The small TOF differences could be traced to the effect of HRe(CO)₅ concentration differences in the three experiments. Indeed, as shown in Figure 6.23, the concentration of HRe(CO)₅ is lower when the rhodium loading is higher. This result suggests that HRe(CO)₅ is the active species contributing to the final organic product formation.

6.3.3.6 Changing CP initial loadings

The initial concentration of substrate cyclopentene was systematically varied in three hydroformylation experiments performed at 289.7K, 4.0MPa carbon monoxide and 1.0MPa hydrogen in 300 ml n-hexane. The corresponding concentrations of H₂ and CO were 0.0097 and 0.0986 respectively. The initial loadings of Rh₄(CO)₁₂ in mole fractions were circa 2.4×10⁻⁵. The initial loadings of cyclopentene were 3.0, 5.5 and 15.0 ml. Accordingly, the calculated initial concentrations in mole fractions were X₇ = 0.015, 0.027, and 0.074 respectively. The initial loading of HRe(CO)₅ was circa 20 µL and the corresponding initial concentrations of HRe(CO)₅ were circa 6.4×10⁻⁵ mole fraction.

6.3.3.6.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HRe(CO)₅, and the only other two observable intermediates RCorh(CO)₄ and RhRe(CO)₉ are shown in Figures 6.29-6.32.
Figure 6.29 The time dependent mole fractions of $\text{Rh}_4(\text{CO})_{12}$

Figure 6.30 The time dependent mole fractions of $\text{HRe(CO)}_5$
Figure 6.31 The time dependent mole fractions of acyl

Figure 6.32 The time dependent mole fractions of RhRe(CO)\textsubscript{9}
As shown in Figure 6.29, the rapid disappearance of \( \text{Rh}_4(\text{CO})_{12} \) was again observed. The half-life of \( \text{Rh}_4(\text{CO})_{12} \) was less than 10 minutes in all the three experiments. It appears that the influence of cyclopentene loading on the initial reaction time is small. However, some differences among the final \( \text{Rh}_4(\text{CO})_{12} \) concentrations occurred. The final \( \text{Rh}_4(\text{CO})_{12} \) concentration decreases with increasing initial loading of cyclopentene.

Figure 6.31 describes the concentration of \( \text{RCORh(CO)}_4 \) as a function of time. The rhodium acyl \( \text{RCORh(CO)}_4 \) mole fraction generally increases in the initial reaction time and then reaches a pseudo steady state. It appears that the initial concentration of cyclopentene has a small effect on the \( \text{RCORh(CO)}_4 \) concentration at the pseudo steady state. When the initial loadings of cyclopentene were 5.5 and 15.0 ml, the final concentrations of \( \text{RCORh(CO)}_4 \) were quite close (6.1\times10^{-5} and 5.6 \times10^{-5} ). However, when the initial loading of cyclopentene was only 3 ml, a slight decrease of \( \text{RCORh(CO)}_4 \) was observed and the final concentration of \( \text{RCORh(CO)}_4 \) was 4.2\times10^{-5}.

The concentration profiles of \( \text{HRe(CO)}_5 \) and \( \text{RhRe(CO)}_9 \) are shown in Figure 6.30 and Figure 6.32. The rhodium rhenium dinuclear complex \( \text{RhRe(CO)}_9 \) concentration generally increases at initial reaction times and then reaches a pseudo steady state, while the rhodium rhenium hydride \( \text{HRe(CO)}_5 \) concentration generally decreases at the initial reaction times and then reaches a pseudo steady state. It appears that initial loading of cyclopentene is somewhat correlated with the time-dependent concentration profiles of \( \text{RhRe(CO)}_9 \) and \( \text{HRe(CO)}_5 \). In particular, the \( \text{HRe(CO)}_5 \) concentrations at pseudo steady state were 2.6\times10^{-5}, 3.7\times10^{-5} and 3.7\times10^{-5}, while the \( \text{RhRe(CO)}_9 \) concentrations at
pseudo steady state were $2.7 \times 10^{-5}$, $2.1 \times 10^{-5}$ and $1.7 \times 10^{-5}$ with the initial loading of cyclopentene 3.0, 5.5 and 15.0 ml respectively.

### 6.3.3.6.2 Product formation

The time-dependent concentrations of the hydroformylation product aldehyde are shown in Figure 6.33. It appears that the variation in the initial concentration of cyclopentene has a small effect on the formation of aldehyde. This is again consistent with pure rhodium catalyzed hydroformylation and previous results obtained for the Rh/Mn bimetallic hydroformylation of 33DMB (Chapter 4) and cyclopentene (Chapter 5). The rates of product formation are circa $1.0 \times 10^{-5}$, $1.4 \times 10^{-5}$, and $1.3 \times 10^{-5}$ (mol fraction)/min starting with initial loadings of cyclopentene of 3.0, 5.5 and 15.0 ml respectively.

![Figure 6.33](image-url) The time dependent mole fractions of aldehyde

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*Figure 6.33* The time dependent mole fractions of aldehyde
6.3.3.6.3 TOF analyses

The effect of loading of cyclopentene on TOF is shown in Figure 6.34. The average turnover frequencies were $0.23\pm0.05\text{min}^{-1}$, $0.25\pm0.02\text{min}^{-1}$ and $0.26\pm0.04 \text{min}^{-1}$ in the three experiments starting with the initial loading of cyclopentene 3.0, 5.5 and 15.0 ml respectively.

![Figure 6.34](image)

**Figure 6.34** The effect of cyclopentene on TOF

It seems that the influence of initial concentration of cyclopentene on the turnover frequencies is very small. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate. The present results are also consistent with the kinetic studies of Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylations of 33DMB(Chapter 4) and cyclopentene (Chapter 5).
6.3.3.7 Changing CO pressure

The initial concentration of CO was systematically varied in four hydroformylation experiments performed at 289.7K, 1.0MPa hydrogen in 300 ml n-hexane. The pressures of carbon monoxide were 3.0, 4.0, 5.0 and 6.0 MPa. Accordingly, the concentrations of CO in mole fractions were $X_{CO} = 0.0755$, 0.0986, 0.1205 and 0.1415.

The corresponding concentration of H$_2$ was circa 0.0097. Circa 40 mg Rh$_4$(CO)$_{12}$ was used and the calculated initial concentrations of Rh$_4$(CO)$_{12}$ in mole fractions were circa $2.4 \times 10^{-5}$. The initial loading of cyclopentene was 5.5 ml and the mole fraction was $X_{CP} = 0.027$. The initial loading of HRe(CO)$_5$ was circa 20 µL.

6.3.3.7.1 Initial reaction times

The instantaneous concentrations of the precursors Rh$_4$(CO)$_{12}$, HRe(CO)$_5$, and the only other two observable intermediates RCORh(CO)$_4$ and RhRe(CO)$_9$ are shown in Figures 6.35-6.38.
Figure 6.35 The time dependent mole fractions of Rh₄(CO)₁₂

Figure 6.36 The time dependent mole fractions of HRe(CO)₅
**Figure 6.37** The time dependent mole fractions of acyl

**Figure 6.38** The time dependent mole fractions of RhRe(CO)$_9$
As shown in Figure 6.35, a rapid disappearance of Rh₄(CO)₁₂ occurred during the initial reaction periods. The half-life was less than 10 minutes in all four experiments. Figure 6.35 also indicates that the fragmentation of Rh₄(CO)₁₂ became faster with higher CO pressure.

As shown in Figure 6.37, the concentration of RCORh(CO)₄ monotonically increased in all four experiments and a rapid increase of RCORh(CO)₄ was observed at the initial reaction times. Unlike the pure Rh₄(CO)₁₂ catalyzed hydroformylation of alkene, the effect of the dissolved carbon monoxide concentration on the time-dependent rhodium acyl concentrations is not straightforward. Indeed, the final mole fractions of RCORh(CO)₄ were 5.0×10⁻⁵, 6.1×10⁻⁵, 5.0×10⁻⁵ and 6.2×10⁻⁵ starting with 3.0, 4.0, 5.0 and 6.0 MPa CO respectively. This complexity could be due to the other reactions involved in HRe(CO)₅ / RCORh(CO)₄ / Rh₄(CO)₁₂ / RhRe(CO)₉ / CO / H₂.

As shown in Figure 6.36, the HRe(CO)₅ concentrations decrease in the first circa 90 minutes and the rate of decrease is generally faster with higher CO pressure. The final HRe(CO)₅ concentrations are slightly dependent on the dissolved CO concentrations. In fact, the final HRe(CO)₅ mole fractions were 3.9×10⁻⁵, 3.8×10⁻⁵, 3.5×10⁻⁵ and 3.3×10⁻⁵ starting with 3.0, 4.0, 5.0 and 6.0 MPa CO respectively. This result is consistent with the results obtained in the Rh₄(CO)₁₂ and HRe(CO)₅ equilibrium experiments.

As for the RhRe(CO)₉, the time-dependent mole fractions increase in the first circa 90 minutes and the rate of increase is generally faster with higher CO pressure. Similar to the rhodium acyl RCORh(CO)₄, the effect of the dissolved carbon monoxide concentration on the time-dependent dinuclear complex RhRe(CO)₉ concentrations is not straightforward. Indeed, the final mole fractions of RhRe(CO)₉ were 1.9×10⁻⁵, 2.1×10⁻⁵,
2.0×10^{-5} and 1.8×10^{-5} starting with 3.0, 4.0, 5.0 and 6.0 MPa CO respectively. This complexity could also be due to the other reactions (Rh-Re equilibrium and HRe(CO)\textsubscript{5} attack on Rh\textsubscript{4}(CO)\textsubscript{12} etc.) involved in the system.

6.3.3.7.2 Product formation

The time-dependent concentrations of the hydroformylation product aldehyde are shown in Figure 6.39.

![Aldehyde Mole Fractions vs Reaction Time](image)

**Figure 6.39** The time dependent mole fractions of aldehyde

It appears that the CO pressure influence on the product formation rate is quite complicated. Indeed, the hydroformylation rates were 1.4×10^{-5}, 1.5×10^{-5}, 9.1×10^{-6} and 8.5×10^{-6} (mole fraction/minute) starting with 3.0, 4.0, 5.0 and 6.0 MPa CO respectively. The general trend, i.e., the higher CO pressure with the higher reaction rate, is consistent
with previous kinetic studies of both pure rhodium and Rh/Mn catalyzed hydroformylation of 33DMB and cyclopentene. However, as shown in Figure 6.39, the product formation rates at 3.0MPa and 4.0MPa are quite close and the hydroformylation rate at 4.0MPa is even a bit higher than that of 3.0MPa. All of this appears to be associated with the above mentioned complicated concentration profiles of $\text{RCORh(CO)}_4$ and $\text{RhRe(CO)}_9$.

### 6.3.3.7.3 TOF analyses

The effect of CO pressure on TOF is shown in Figure 6.40. The average turnover frequencies were $0.31 \pm 0.02 \text{ min}^{-1}$, $0.25 \pm 0.02 \text{ min}^{-1}$, $0.18 \pm 0.02 \text{ min}^{-1}$ and $0.14 \pm 0.01 \text{ min}^{-1}$ in the four experiments starting with $X_{\text{CO}} = 0.0755$, 0.0986, 0.1205 and 0.1415 respectively.

![Figure 6.40](image_url) The effect of CO on TOF
The TOF results suggest that the influence of CO concentration on the turnover frequencies is big, namely, the TOF increases with decreasing CO pressure. This is consistent with the previous kinetic study with unmodified rhodium catalyzed hydroformylation with 33DMB as substrate. It is also consistent with the kinetic results obtained in the Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylations of 33DMB and cyclopentene.

**6.3.3.8 Changing H₂ pressure**

Four experiments were performed to study the influence of hydrogen. The experiments were conducted at 289.7K and 4.0MPa CO in 300 ml n-hexane. The corresponding concentrations of CO were 0.0986. The initial input of cyclopentene was 5.5 ml and the concentration was 0.027 mole fraction. The initial loading of Rh₄(CO)₁₂ was circa 40 mg and X_{Rh₄(CO)₁₂} was circa 2.4×10⁻⁵. The initial loading of HRe(CO)₅ was circa 20 µL. The pressures of hydrogen were 0.5, 1.0, 1.5 and 2.0 MPa and the corresponding concentrations of H₂ in mole fractions were X_{H₂}= 0.0049, 0.0097, 0.0145, and 0.0191 respectively.

**6.3.3.8.1 Initial reaction times**

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HRe(CO)₅ and the only other two observable intermediates RCORh(CO)₄ and RhRe(CO)₉ are shown in Figures 6.41-6.44.
Figure 6.41 The time dependent mole fractions of Rh₄(CO)₁₂

Figure 6.42 The time dependent mole fractions of HRe(CO)₅
**Figure 6.43** The time dependent mole fractions of acyl.

**Figure 6.44** The time dependent mole fractions of RhRe(CO)$_9$. 
As shown in Figure 6.41, again, a rapid decline of Rh$_4$(CO)$_{12}$ during the initial reaction time was observed. The fragmentation rate of Rh$_4$(CO)$_{12}$ is generally faster with higher molecular hydrogen concentration. The half lives were less than 10 minutes in all the four experiments and the conversion of Rh$_4$(CO)$_{12}$ is more than 90% in the circa five hour experiments.

Figure 6.43 shows that the time-dependent concentrations of RCORh(CO)$_4$ monotonically increased in all experiments during the initial reaction times and then reached pseudo steady states. It seems that the effect of dissolved hydrogen is not straightforward. The final mole fractions of RCORh(CO)$_4$ were $5.3 \times 10^{-5}$, $6.0 \times 10^{-5}$, $6.0 \times 10^{-5}$ and $5.4 \times 10^{-5}$ starting with $X_{H_2}$= 0.0049, 0.0097, 0.0145, and 0.0191 respectively. A possible reason could be that HRe(CO)$_5$ plays an important role in the transformation of Rh$_4$(CO)$_{12}$ to the rhodium acyl RCORh(CO)$_4$ hiding the effect of molecular hydrogen.

As shown in Figure 6.42 and Figure 6.44, the transient mole fractions of HRe(CO)$_5$ monotonically decreased and the mole fractions of RhRe(CO)$_9$ monotonically increased during the initial reaction times. After circa 100 minutes, both HRe(CO)$_5$ and RhRe(CO)$_9$ reached a pseudo steady state. The final concentrations of HRe(CO)$_5$ were $3.2 \times 10^{-5}$, $3.7 \times 10^{-5}$, $3.8 \times 10^{-5}$ and $4.2 \times 10^{-5}$ starting with $X_{H_2}$= 0.0049, 0.0097, 0.0145, and 0.0191 respectively. Accordingly, the final concentrations of RhRe(CO)$_9$ were $2.1 \times 10^{-5}$, $2.0 \times 10^{-5}$, $1.7 \times 10^{-5}$ and $1.5 \times 10^{-5}$. This suggests that with higher hydrogen pressure, the conversion of HRe(CO)$_5$ to RhRe(CO)$_9$ is lower. The present results are consistent with the results obtained in the HRe(CO)$_5$/Rh$_4$(CO)$_{12}$ equilibrium experiments.
6.3.3.8.2 Product formation

The time-dependent concentrations of the hydroformylation product aldehyde are shown in Figure 6.45.

![Graph showing time-dependent mole fractions of aldehyde](image)

**Figure 6.45** The time dependent mole fractions of aldehyde

The hydroformylation rates were $9.9 \times 10^{-6}$, $1.3 \times 10^{-5}$, $1.5 \times 10^{-5}$ and $1.5 \times 10^{-5}$ starting with $X_{H2} = 0.0049, 0.0097, 0.0145$, and $0.0191$ respectively. The general trend of the effect of hydrogen on the product formation rates is consistent with the kinetic studies with pure rhodium catalyzed hydroformylation of alkene.

However, the relationship is more complicated in the present Rh/Re bimetallic case. Particularly, as shown in Figure 6.45, the aldehyde concentration profiles at 1.0 and 2.0 MPa hydrogen are almost the same. This could be traced back to the different HRe(CO)$_5$ concentration profiles (Figure 6.42) in these two experiments. In other words,
the present results re-affirm that HRe(CO)$_5$ plays a big role in the final product formation.

6.3.3.8.3 TOF analyses

The effect of H$_2$ loading on TOF is shown in Figure 6.46. The average turnover frequencies were 0.20±0.03min$^{-1}$, 0.25±0.02min$^{-1}$, 0.24±0.01min$^{-1}$, and 0.28±0.01min$^{-1}$ in the four experiments starting with $X_{H_2}$= 0.0049, 0.0097, 0.0145, and 0.0191 respectively.

![Figure 6.46 The effect of H$_2$ on TOF](image)

The TOF results are generally consistent with the previous studies with unmodified rhodium catalyzed hydroformylation, namely, TOF increases with increasing hydrogen pressure. However, the relationship is apparently not proportional (as is observed in the pure rhodium system). Indeed, the differences of TOF are very small for
the four experiments. It appears that there should be another important catalytic pathway (H₂ is not involved) which plays an important role in the product formation.

6.3.3.9 Changing temperature

Four experiments were performed at 282.6, 289.7K, 294.0K and 298.5K respectively. Each experiment was conducted in a similar manner to the standard experiment. They were at 1.0MPa hydrogen, 4.0MPa carbon monoxide, 5.5 ml cyclopentene, circa 40mg Rh₄(CO)₁₂ and circa 20 μL HRe(CO)₅. Accordingly, the initial concentration of cyclopentene was 0.027 mole fraction, the initial Xₐ₄(CO)₁₂ was circa 2.4×10⁻⁵ and the initial concentration of HRe(CO)₅ was 6.4×10⁻⁵ mole fraction.

6.3.3.9.1 Initial reaction times

The instantaneous concentrations of the precursors Rh₄(CO)₁₂, HRe(CO)₅ and the only other two observable intermediates, RCRh(CO)₄ and RhRe(CO)₉, are shown in Figures 6.47-6.50.
Figure 6.47 The time dependent mole fractions of \( \text{Rh}_4(\text{CO})_{12} \)

Figure 6.48 The time dependent mole fractions of \( \text{HRe}(	ext{CO})_5 \)
Figure 6.49 The time dependent mole fractions of acyl

Figure 6.50 The time dependent mole fractions of RhRe(CO)₉
As shown in Figure 6.47, the concentrations of \( \text{Rh}_4(\text{CO})_{12} \) monotonically declined in all the four experiments during the initial reaction times. It should be noted that the approximate initial concentrations were \( 2.4 \times 10^{-5} \) mole fraction. The half-life of \( \text{Rh}_4(\text{CO})_{12} \) was less than 10 minutes in all of the four experiments. The disappearance rate of \( \text{Rh}_4(\text{CO})_{12} \) in the initial reaction time is generally faster with higher temperature. However, after initial reaction time, the final \( \text{Rh}_4(\text{CO})_{12} \) concentration profiles are entirely different from the results obtained during both of \( \text{Rh}_4(\text{CO})_{12} \) and \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(\text{CO})}_5 \) catalyzed hydroformylation of 33DMB and cyclopentene. In the present case, the \( \text{Rh}_4(\text{CO})_{12} \) concentrations at pseudo steady state are higher with higher temperatures. The reasonable explanation is that the \( \text{HRe(\text{CO})}_5/\text{Rh}_4(\text{CO})_{12} \) equilibrium has a big contribution at the present reaction conditions. As shown in the \( \text{HRe(\text{CO})}_5/\text{Rh}_4(\text{CO})_{12} \) equilibrium experiment results, the equilibrium coefficient \( \text{RhRe(\text{CO})}_9 \) \([\text{H}_2]_2/\text{HRe(\text{CO})}_5\) \([\text{Rh}_4(\text{CO})_{12}][\text{CO}]^4 \) is smaller at higher temperature.

The concentration profiles of \( \text{RCORh(\text{CO})}_4 \) are shown in (Figure 6.49). It can be seen that \( \text{RCORh(\text{CO})}_4 \) monotonically increased during the initial reaction time and reached a pseudo steady state after circa 100 minutes in all of the four experiments. The formation rate of \( \text{RCORh(\text{CO})}_4 \) during the initial period is generally faster with higher temperature. However, there is not a big difference in the final \( \text{RCORh(\text{CO})}_4 \) concentrations in the experiments, except for the one at low temperature (282.6K).

Figure 6.48 and Figure 6.50 describe the time dependent mole fractions of \( \text{HRe(\text{CO})}_5 \) and \( \text{RhRe(\text{CO})}_9 \). During the initial reaction times, the \( \text{HRe(\text{CO})}_5 \) monotonically decreased and the \( \text{RhRe(\text{CO})}_9 \) monotonically increased. Some errors are observed for the data set at 282.6K. Figure 6.50 indicates that after the initial reaction
time, the RhRe(CO)$_9$ concentration is higher with decreasing temperature. This is consistent with the Rh$_4$(CO)$_{12}$ concentration profile (Figure 6.47).

### 6.3.3.9.2 Product formation

The time-dependent concentrations of the hydroformylation product aldehyde are shown in Figure 6.51.

![Figure 6.51](image)

**Figure 6.51** The time dependent mole fractions of aldehyde

The temperature has a strong effect on the formation of aldehyde. The hydroformylation rates were $4.6 \times 10^{-6}$, $1.5 \times 10^{-5}$, $1.7 \times 10^{-5}$, and $2.9 \times 10^{-5}$ (mol fraction)/min when the temperature was 282.6, 289.7, 294.0 and 298.5 K respectively. This is consistent with the previous kinetic study of the unmodified rhodium catalyzed hydroformylation of alkenes (Garland et al, 1991, 1993, 1999). It is also consistent with the kinetic results.
obtained in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ catalyzed hydroformylations of 33DMB and cyclopentene.

### 6.3.3.9.3 TOF analyses

The effect of temperature on TOF is shown in Figure 6.52. The average turnover frequencies were 0.18±0.05min$^{-1}$, 0.25±0.02min$^{-1}$, 0.30±0.02min$^{-1}$ and 0.51±0.03min$^{-1}$ in the four experiments starting with T= 282.6, 289.7, 294.0 and 298.5K respectively. This suggests that the influence of temperature on the turnover frequencies is strong. The TOF is higher with higher temperature. The present results are consistent with the previous kinetic study of the unmodified rhodium catalyzed hydroformylation of alkenes. It is also consistent with the kinetic results obtained in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ catalyzed hydroformylations of 33DMB and cyclopentene.

![Figure 6.52 The effect of temperature on TOF](image_url)
6.3.4 Catalysis and kinetics

6.3.4.1 Pre-catalytic

From the above six sub-series of experiments performed at different loadings of precursors HRe(CO)\(_5\) and Rh\(_4\)(CO)\(_{12}\), substrate cyclopentene, different dissolved concentrations of CO and H\(_2\), and at different reaction temperatures, the effect of the HRe(CO)\(_5\) on the disappearance of Rh\(_4\)(CO)\(_{12}\) is apparent. As in the Rh\(_4\)(CO)\(_{12}\)/HMn(CO)\(_5\) bimetallic catalyzed hydroformylations of 33DMB and cyclopentene, a very rapid decline in the catalyst precursor concentration and increase in acyl complex concentration occurs upon addition of HRe(CO)\(_5\) and H\(_2\). This atypical initial time behavior implies that there exists a second parallel precatalytic pathway for the transformation of Rh\(_4\)(CO)\(_{12}\) to RCORh(CO)\(_4\) in the presence of rhenium carbonyl hydride, namely, the hydride facilitated degradation of the cluster Rh\(_4\)(CO)\(_{12}\).

In the present the rhodium/rhenium bimetallic system, and under the present experimental conditions which are similar to Rh\(_4\)(CO)\(_{12}\)/HMn(CO)\(_5\) bimetallic catalyzed hydroformylations of 33DMB and cyclopentene, the following two term equation provided a good fit for the observable kinetics of the acyl formation at 289.7K. The first term represents the fragmentation mechanism in the pure rhodium system, while the second term represents the second parallel precatalytic pathway for the transformation of Rh\(_4\)(CO)\(_{12}\) to RCORh(CO)\(_4\) by HRe(CO)\(_5\) attack. Different integer values of the exponent for CO in the second term were tested, but an exponent equal to two gave the best results.

\[
d[RCORh(CO)_{4}]/dt = k_1'[Rh_4(CO)_{12}][CO]^2[H_2]+k_2'[Rh_4(CO)_{12}][CO]^2[HRe(CO)_{5}] \quad (6.7)
\]

The regressed numerical values of the rate constants were

\[k_1' = (3.0 \pm 0.5) \times 10^2 \text{ min}^{-1}\]
\[ k_2' = (0.62 \pm 0.15) \times 10^5 \text{ min}^{-1}. \]

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 for the pure rhodium catalyzed hydroformylation system. (Garland and Pino, 1991)

The obtained values of \( k_1' \) and \( k_2' \) are also in good agreement with the results of \( \text{Rh}_4(\text{CO})_{12} /\text{HMn}(\text{CO})_5 \) bimetallic catalyzed hydroformylation of cyclopentene at 289.7 K.

With respect to the temperature dependence, the reaction temperature was systematically varied at 4.0MPa CO and 1.0MPa H\(_2\) to regress the reaction activation parameters. The five temperatures were 281.5, 289.7, 293.7, 299.4 and 308.9 K. However, the regression was not successful, as very large errors in the activation parameters are obtained. More data over a larger temperature range are required to get a good result.

### 6.3.4.2 Hydroformylation

From the above six sub-series of experiments performed at different loadings of precursors HRe(CO)\(_5\) and \( \text{Rh}_4(\text{CO})_{12} \), substrate cyclopentene, different dissolved concentrations of CO and H\(_2\), and at different reaction temperatures, the strong effect of the HRe(CO)\(_5\) on the product formation was shown. Similar to the \( \text{Rh}_4(\text{CO})_{12} /\text{HMn}(\text{CO})_5 \) bimetallic catalyzed hydroformylation of 33DMB and cyclopentene system, a dramatic increase in the product formation rate and TOF was observed when HRe(CO)\(_5\) and \( \text{Rh}_4(\text{CO})_{12} \) were used simultaneously. This suggests that HRe(CO)\(_5\) plays an important role in the product formation pathways.

As discussed in Chapter 4 and Chapter 5, hydroformylation of alkenes in the presence of tetrarhodium dodecacarbonyl alone has been extensively studied at low
temperatures. Analysis of the in-situ spectroscopic measurements provide very clean kinetics, where the rate of aldehyde formation is

\[ r = k_1 [\text{RCORh(CO)}_4][\text{CO}]^{-1}[\text{H}_2][\text{alkene}]^0. \]  

(6.8)

The rate expression is consistent with the equilibrium generation of a coordinatively unsaturated intermediate \( \text{RCORh(CO)}_3 \) followed by the subsequent activation of molecular hydrogen. The kinetics support the widely accepted unicyclic catalytic reaction mechanism where all intermediates are mononuclear. The reactions and kinetics are very reproducible.

As shown in \( \text{Rh}_4(\text{CO})_{12}/\text{HMn(} \text{CO})_5 \) bimetallic catalyzed hydroformylation of 33DMB and cyclopentene system, the bimolecular reaction of \([\text{RCORh(CO)}_3]\) with molecular hydrogen is not the only mechanism available for the hydrogenolysis of \( \text{RCORh(CO)}_4 \). In the present \( \text{Rh}_4(\text{CO})_{12}/\text{HRe(} \text{CO})_5 \) bimetallic catalyzed hydroformylation of cyclopentene system, there is also the possibility that some aldehyde formation occurs via a bimolecular elimination reaction.

Under the present experimental conditions, there maybe exists several active species, which could be involved in the product formation. These active species are \( \text{RCORh(CO)}_3, \text{RCORh(CO)}_4, \text{HRe(} \text{CO})_4, \text{HRe(} \text{CO})_5 \) and \( \text{RhRe(} \text{CO})_9 \).

The most probable binuclear reaction which could be involved in the product formation is listed below.

\[ \text{HRe(} \text{CO})_4 + \text{RCORh(CO)}_3 \leftrightarrow \text{RCHO} + \text{RhRe(} \text{CO})_7 \]  

(6.9)

Substituting for the pseudo-equilibrium concentration of \( \text{HRe(} \text{CO})_4 \) in terms of \( \text{HRe(} \text{CO})_5, \text{RCORh(CO)}_3 \) in terms of \( \text{RCORh(CO)}_4 \) and \( \text{RhRe(} \text{CO})_7 \) in terms of
RhRe(CO)$_9$, the corresponding formation rates of aldehyde by CBER are expressed as follows.

\[ r = k_2[\text{RCORh(CO)}_4][\text{HRe(CO)}_5][\text{CO}]^2 - k_3[\text{RhRe(CO)}_9][\text{RCHO}][\text{CO}]^2 \] (6.10)

Since the reaction rate for the unicyclic hydroformylation mechanism is well defined and reproducible, we adopt an expression where the order for RCORh(CO)$_4$ is 1, the order for CO is –1 and the order for H$_2$ is 1. 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. (6.11).

\[ r_{\text{Total}} = k_1[\text{RCORh(CO)}_4][\text{H}_2][\text{CO}]^{-1} + k_2[\text{RCORh(CO)}_4][\text{HRe(CO)}_5][\text{CO}]^X - k_3[\text{RhRe(CO)}_9][\text{RCHO}][\text{CO}]^Y \] (6.11)

With respect to the catalysis or product formation, the above three term linear-bilinear form in organometallic species provided an excellent fit for the observable kinetics of the aldehyde formation. Circa 750 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 a non-linear regression program (“nlinfit” in Matlab) with 5 degrees of freedom, the regressed numerical values of the rate constants at 289.7 K were

\[ k_1 = 0.35 \pm 0.12 \text{ min}^{-1} \]

\[ k_2 = 56 \pm 26 \text{ min}^{-1} \]
k_3 = 0.64 \pm 1.46 \text{min}^{-1} \\
X = -2.0 \pm 0.16 \\
Y = -2.0 \pm 0.47 

The above k_1 corresponds to the classic unmodified rhodium hydroformylation of cyclopentene. It is quite close to the value obtained in the Rh_4(CO)_{12} /HMn(CO)_5 bimetallic catalyzed hydroformylation of cyclopentene system. As such, the k_1 could be fixed during the next regression with 4 degrees of freedom which produced 

k_1 = 0.35 \text{ min}^{-1} \\
k_2 = 56 \pm 9 \text{ min}^{-1} \\
k_3 = 0.64 \pm 0.9 \text{ min}^{-1} \\
X = -2.0 \pm 0.16 \\
Y = -2.0 \pm 0.47 

Furthermore, the above obtained X and Y values look to be consistent with the indexes shown in Eq 6.11. In this case, we can fix both k_1 and Y to test the regression. The non-linear regressed results are much better. 

k_1 = 0.35 \text{ min}^{-1} \\
k_2 = 56 \pm 9 \text{ min}^{-1} \\
k_3 = 0.64 \pm 0.09 \text{ min}^{-1} \\
X = -2.0 \pm 0.07 \\
Y = -2.0 

The errors are listed as twice the standard deviation, i.e., the 95% confidence limit. The constant k_2 is very similar to the value obtained in the Rh_4(CO)_{12} /HMn(CO)_5 bimetallic catalyzed hydroformylation of cyclopentene. The exponent X = -2 and Y = -2 suggest that coordinative unsaturation in both of the observed acyl RCORh(CO)_4 and
dinuclear complex RhRe(CO)$_9$ is almost certain. This dependence on CO was more ambiguous in the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ system where an exponent $X=-1.5$ was obtained.

In most experiments, after the induction period, the second term was significantly larger than the first - and the contributions of these two terms under the reference reaction conditions of this experimental study were circa 6:1, while the contribution of the third term was circa 1:1 compared to that of the first term. This strongly supports the kinetic results introduced in Section 6.3.3.

The present results show that the binuclear elimination (the second term in the equation 6.11) is the predominant contribution to the product formation. In particular, according to the above kinetics, at 289.7K, 2.0MPa CO, 2.0MPa H$_2$, 5.5 ml CP, 42.49 mg Rh$_4$(CO)$_{12}$ and 20.0 $\mu$L HRe(CO)$_5$ (the reference experiment), the reaction rates in the three terms of Eq. (6.11) (at the reaction time of 200 minutes, equal to an aldehyde concentration of 0.0027) were $2.0\times10^{-6}$, $1.2\times10^{-5}$ and $-1.7\times10^{-6}$ (mole fraction/min) respectively. Accordingly, the contribution of CBER to the final product formation is 80%.

Rearrangement of the first two terms $k_1[CO]^{-1} / k_2[CO]^{-2}$ leads to the conclusion that HRe(CO)$_5$ is circa 1600 times more efficient than H$_2$, for the hydrogenolysis of the acyl-rhodium bond, on a mole-to-mole basis.

With respect to the temperature dependence, the reaction temperature was systematically varied at 4.0MPa CO and 1.0MPa H$_2$ to regress the reaction activation parameters. The four temperatures are 281.5, 289.7, 293.7, 299.4 and 308.9 K. However, the regression was not successful, since large errors were obtained for the activation parameters. More data over a larger temperature range is needed to get a better result.
6.3.5 Discussion

6.3.5.1 Further evidence for existence of bimetallic CBER

The kinetic results strongly suggest the simultaneous existence of one unicyclic catalytic topology and one bimetallic catalytic elimination reaction. The unicyclic catalysis occurs exclusively on mononuclear rhodium intermediates, and the bimetallic CBER occurs on a set of rhodium, rhenium and rhodium-rhenium intermediates.

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 an acyl complex RCORh(CO)₃ is the rate limiting step in the unicyclic rhodium catalysis.

As for the bimetallic CBER, the kinetic results are consistent with the reversible attack of HRe(CO)₄ on RCORh(CO)₃. The exponents of unity for HRe(CO)₅, RCORh(CO)₄ and RhRe(CO)₉ together with X=-2 and Y=-2 provide the strong supporting evidence.

\[
\text{HRe(CO)₄} + \text{RCORh(CO)₃} \leftrightarrow \text{RCHO} + \text{RhRe(CO)⁷} \quad (6.12)
\]

Unlike the HMn(CO)₅/Mn₂(CO)₁₀ bimetallic catalyzed systems for hydroformylation of 33DMB and cyclopentene, the expected transient bimetallic rhodium rhenium dinuclear complex with stoichiometry RhRe(CO)₉ was successfully observed in present Rh/Re system. This is a significant piece of supporting evidence for the existence of bimetallic CBER.
Similar to the one proposed for the HMn(CO)$_5$/Mn$_2$(CO)$_{10}$ bimetallic catalyzed hydroformylation of 33DMB and cyclopentene, a proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Re CBER hydroformylation reactions is shown in Figure 6.53.

All intermolecular transformations in the unicyclic topology are 1$^{st}$ order in the mononuclear metal complexes. Two elementary steps in Scheme 1 are highlighted by the labels $\alpha$ and $\beta$. These labels are used to identify the key mechanisms which give rise to the existence of the bimetallic CBER. The $\alpha$ step denotes the simultaneous generation of the crucial mononuclear hydrides HRh(CO)$_3$ and HRe(CO)$_4$ from the dinuclear complex H$_2$RhRe(CO)$_7$. The $\beta$ step is the binuclear elimination step. The steps –$\alpha$ and $\beta$ are bimolecular in metal complexes. The binuclear elimination step has been drawn as if the process proceeds through a concerted 4-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 4-center transition state, but instead through 2 or more simpler transition states, additional intermediates exist on the reaction pathway. However, it can also be noted that the exponents $X=-2$ and $Y=-2$ lend strong support for a 4-center transition state.
Figure 6.53 The proposed reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Re CBER hydroformylation reactions.

Concerning other details in Figure 6.53, the stereochemistries of the intermediates, (which may exist as a multiplicity of intermediates with different geometries) are not the emphasis of this diagram. Accordingly, we have assumed the most common geometry for 5-coordinate rhodium structures, namely, an axially substituted trigonal bipyramid.

The interconnected topology of a unicyclic mechanism and a CBER mechanism as shown in Figure 6.53 gives rise to the complex linear-bilinear form of the observed kinetics of product formation.

6.3.5.2 Initial reaction times and precatalytic steps
In the present bimetallic system, like the HMn(CO)\textsubscript{2}/Mn\textsubscript{2}(CO)\textsubscript{10} bimetallic catalyzed hydroformylations of 33DMB and cyclopentene, a two term equation again provided a good fit to the kinetic data of the 23 experiments.

\[
d[\text{RCORh(CO)\textsubscript{4}}]/dt = k_1'[\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2[H_2]+k_2'[\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2[\text{HRe(CO)}_5] \quad (6.13)
\]

The functional form used for the first term is that which was previously shown to arise in simple monometallic rhodium hydroformylations. The common factor \([\text{Rh}_4(\text{CO})_{12}][\text{CO}]^2\) again suggests a rate limiting step involving a pre-equilibrated open polyhedron intermediate \{\text{Rh}_4(\text{CO})_{14}\}. Kinetic evidence for open polyhedron clusters as intermediates in cluster fragmentation reactions is readily available (Bor et al, 1978). The second term dominates under rhenium concentrations far lower than the dissolved hydrogen concentrations. In conclusion, the present kinetics support the idea that the pronounced and accelerated rate of cluster fragmentation in the presence of HRe(CO)_5 is due to its efficient attack on \{\text{Rh}_4(\text{CO})_{14}\}.

### 6.4 Conclusions

In this chapter, the equilibrium of Rh\textsubscript{4}(CO)\textsubscript{12} and HRe(CO)_5 under CO/H\textsubscript{2} in n-hexane was firstly studied using in-situ FTIR. The new dinuclear complex RhRe(CO)_9 was identified and further thermodynamic measurements confirmed its existence.

Next, in situ spectroscopic and kinetic measurements were performed for the homogeneous rhodium and rhenium catalyzed hydroformylation of cyclopentene. A series of well-defined experiments were conducted to search for the bimetallic catalytic binuclear elimination. The in-situ FTIR spectroscopic data were analyzed using the total system identification algorithm.
The addition of rhenium carbonyl hydride to the unmodified rhodium catalyzed hydroformylation of cyclopentene leads to a significant increase in system activity. The dinuclear complex RhRe(CO)$_9$ was also observed in this catalytic system. Regression of the kinetic data strongly suggests that there is a reversible bimetallic catalytic binuclear elimination of rhenium hydride complex with acyl rhodium tetracarbonyl, which has a statistically significant contribution to aldehyde formation. In addition, as a secondary effect, it was found that rhenium carbonyl hydride leads to fast fragmentation of Rh$_4$(CO)$_{12}$.

The present results, including the increased system activity with HRe(CO)$_5$, the regressed kinetic equation, and the identification of the dinuclear complex RhRe(CO)$_9$ provide further evidence for the existence of bimetallic CBER.
CHAPTER 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The present work systematically studied three bimetallic homogenous catalyzed hydroformylations, namely Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of 3,3-dimethylbut-1-ene; Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of cyclopentene and Rh₄(CO)₁₂/HRe(CO)₅ catalyzed hydroformylation of cyclopentene. The in situ FTIR spectra were analyzed with the tool of total algebraic system identification. The results provided strong spectroscopic and kinetic experimental evidence for the existence of the bimetallic catalytic binuclear elimination reaction in these three bimetallic hydroformylation reactions.

In Chapter 3, an advanced signal processing technique, i.e., total algebraic system identification, was introduced and successfully developed by including good experimental design. The method was successfully applied to the well studied unmodified rhodium catalyzed hydroformylation of 3,3-dimethylbut-1-ene. Both the major and minor components present in the reaction were successfully reconstructed and their absorptivities were obtained. The results are in good agreement with previous studies and experimental measurements. This methodology was also employed to successfully identify the long sought exclusive rhodium hydride HRh(CO)₄. The algorithm of total algebraic system identification was shown to be a rapid and effective method for spectroscopic system identification of reactive organometallic and homogeneous catalytic systems.

In Chapter 4, the Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of 3,3-dimethylbut-1-ene was studied with in situ FTIR. Circa 710 in situ spectra were analyzed
with the total algebraic system identification method. 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 and the regressed linear-bilinear rate equation indicate that this increase in the rate of product formation is due to the existence of bimetallic catalytic binuclear elimination of manganese hydride complexes with acyl rhodium tetracarbonyl. Accordingly, a reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Mn CBER hydroformylation reactions was proposed, where the unicyclic catalysis occurs exclusively on mononuclear rhodium intermediates, and the bimetallic CBER occurs on a set of rhodium, manganese and rhodium-manganese intermediates. As secondary effects, manganese carbonyl hydride facilitated fragmentation of Rh₄(CO)₁₂ leads to a reduction in the induction period, and manganese carbonyl hydride facilitated fragmentation of Rh₆(CO)₁₆ leads to a retardation in the deactivation.

Chapter 5 presented another example of bimetallic catalytic binuclear elimination in the Rh₄(CO)₁₂/HMn(CO)₅ catalyzed hydroformylation of cyclopentene. The spectroscopic and kinetic analyses showed a significant increase in the product formation and TOF when manganese carbonyl hydride was simultaneously added into the unmodified rhodium catalyzed hydroformylation of cyclopentene. A similar linear-bilinear equation also provided a good fit to the data set of circa 1500 in situ spectra. At the same time, secondary effects such as the manganese hydride attack on Rh₄(CO)₁₂ were also observed.

In Chapter 6, further evidence for the existence of bimetallic CBER was reported in the Rh₄(CO)₁₂/HRe(CO)₃ catalyzed hydroformylation of cyclopentene. A total of circa 4000 in situ spectra were recorded in 28 well designed experiments. In addition to the
observed significant increase in the aldehyde formation rate and TOF, a new dinuclear complex RhRe(CO)$_9$ was also identified in both Rh/Re equilibrium and hydroformylation experiments. Regression of the kinetic data strongly suggests that there is a reversible bimetallic binuclear elimination of rhenium hydride complex with acyl rhodium tetracarbonyl. This step contributes significantly to the overall aldehyde formation. In addition, as secondary effects, it was found that rhenium carbonyl hydride leads to fast fragmentation of Rh$_4$(CO)$_{12}$. Accordingly, a reaction topology for the simultaneous interconnected unicyclic Rh and bimetallic Rh-Re CBER hydroformylation reactions was proposed.

7.2 Implications for future catalytic syntheses


The first area refers to bimetallic catalytic binuclear elimination as the only viable explanation for the observed synergism in the three Rh-Mn and Rh-Re hydroformylation systems. 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 considered 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 observed higher turnover frequency (rate / $[\text{RCORh(CO)}_4]$). 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 which varies with the concentration of the second metal. Accordingly, the present bimetallic CBER is an example of intrinsic non-linear catalytic kinetics and thus higher order catalysis. 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. Furthermore, as introduced in chapter 2, with the application of the Feinberg stability criteria(1989) to generalize bimetallic CBER topologies and numerous permutations, bimetallic CBERs can be expected to be kinetically stable in time and 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 mono-nuclear complexes, at least one elementary reaction step exists which 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 stereo-differentiating 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 stereo-control – 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 the chiral modification $L^*$ in a 2 metal system. The organization in the respective transition states can be expected to vary greatly.

**7.3 Suggestions**

In the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ bimetallic catalyzed hydroformylation of alkenes, the expected transient Rh-Mn dinuclear complex was not identified. A new and better experimental design with more perturbations of HMn(CO)$_5$ and the rhodium complex at low temperature might be useful for the identification of the purported dinuclear species. Such information could provide further valuable evidence in support of the mechanism and interpretation of the kinetic data. It would be also very useful to use other methods (MS, XRD etc.) to confirm RhRe(CO)$_9$.

In the Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ catalyzed hydroformylation of 33DMB and cyclopentene and the Rh/Re equilibrium experiments, the reaction activation parameters $\Delta H^\neq$, $\Delta S^\neq$ and $\Delta V^\neq$ were obtained with some errors. In the Rh$_4$(CO)$_{12}$/HRe(CO)$_5$ catalyzed hydroformylation of cyclopentene, the regressions for $\Delta H^\neq$ and $\Delta S^\neq$ were poor. A new and better experimental design with more perturbations of the reaction conditions (initial loadings of reagents and precursors) and over a larger temperature and pressure range could give new and useful information.

Since Rh$_6$(CO)$_{16}$ had an unusual behavior in Rh$_4$(CO)$_{12}$/HMn(CO)$_5$ catalyzed hydroformylation of 33DMB, it would be interesting to examine the Rh$_6$(CO)$_{16}$/HMn(CO)$_5$ catalyzed hydroformylation of 33DMB.
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Appendix A

COMMUNICATIONS

Rhodium Tetracarbonyl Hydride: The Elusive Metal Carbonyl Hydride**

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Rhodium exhibits considerable activity in a wide range of heterogeneous and homogeneously catalyzed reactions. Accordingly, many large-scale industrial plants, such as those for the synthesis of acetic acid and hydroformylation, have a total inventory of only a few kilograms of rhodium; hydroformylation is one of the five most important homogeneously catalyzed processes worldwide and responsible for about 10^6 t of organic products per year. The activity of rhodium is certainly one of the primary reasons for the enormous number of rhodium complexes developed to date. This activity and industrial utility, together with the rarity of rhodium, are the main reasons for its position as the most expensive precious metal. Undoubtedly, the most well-known rhodium organometallic complexes are the Wilkinson complexes [Rh(CO)(PPPh3)2] and [HRh(CO)2(PPh3)3], which are extensively used in many homogeneously catalyzed reactions, in particular the hydroformylation of alkenes in the presence of molecular hydrogen and carbon monoxide to give aldehydes. One of the primary missing links in the industrial chemistry of rhodium is the identification of the simple, unmodified rhodium carbonyl hydride [HRh(CO)4]. Here we report the spectroscopic identification, thermodynamics, and deuterium substitution of this compound.

In spite of the considerable synthetic effort invested in rhodium organometallic chemistry and the significant historical role played by metal carbonyl chemistry in the chemical process industry, the known chemistry of unmodified rhodium carbonyl complexes is very limited. Notable developments include the synthesis of the clusters [Rh12(CO)20] and [Rh4(CO)12] by Chini and co-workers, and the observation of [Rh2(CO)6] under considerable CO partial pressures by Ottin and Hanack were able to spectroscopically identify [Rh(CO)2], [Rh2(CO)4], [Rh(CO)2], and [Rh(CO)]; however, these were in low-temperature argon matrices. The geometry of the latter species is a distorted tetrahedron, and the infrared spectra accordingly contain two terminal carbonyl vibrations at 192 and 193 cm⁻¹. In terms of simply substituted rhodium carbonyl compounds, only the mononuclear acyl complex [RCORh(CO)4] has been reproducibly observed. Some 17 acyl complexes having aliphatic substituents for R have been characterized under hydroformylation conditions.[9]

In terms of rhodium carbonyl chemistry and homogeneous catalysis, the key species is the mononuclear hydride [HRh(CO)4], which represents the starting point for the catalytic hydrogenation of alkenes to alkanes and aldehydes to alcohols,[6] the catalytic hydroformylation of alkenes to aldehydes,[7] the hydrosilylation of alkenes, and many other reactions. Metal hydrides hold a special place in organocatalytic chemistry[7], and they play a key role in homogeneous catalysis. From a mechanistic perspective, the coordination of unsaturated ligands and subsequent insertion into the metal-hydride bond is the starting point for a wide variety of important and complex transformations.

Given its importance, numerous attempts to synthesize [HRh(CO)4] have been documented. Hieber and Legally described the isolation of a yellow solid, assigned to the tentative formula [HRh(CO)4], at cryogenic temperatures upon reduction of rhodium chloride with molecular hydrogen. Chini and Martinengo made numerous unsuccessful attempts to promote [HRh(CO)4]. Finally, Vidal and Walker reported the treatment of [Rh2(CO)12] with 1300 bars of hydrogen and carbon monoxide and the in situ observation of an infrared spectrum with bands at 2089 (w), 2076 (w), and 2070 (m) cm⁻¹, which they assigned to [HRh(CO)4]; although four bands should be observed in the mid-infrared region. It is important to note that the primary laboratories or groups involved with in situ spectroscopic studies of rhodium carbonyl chemistry and catalysis, namely Whyman at ICI, Reis and Borz in Zürich, and Markó at Budapest[9], never reported a successful attempt.

Recently, we introduced band-target entropy minimization (BTEM)[30] as an advanced and model-free deconvolution technique based on a Shannon entropy criterion.[31] Tests of this novel algorithm with real in situ catalytic spectroscopic data have indicated that it is typically possible to account for more than 99% of the experimental spectroscopic data. Even more striking is the ability to retrieve extremely weak spectra of pure components, for example, corresponding to species with less than 0.07% of the integral intensity of the entire spectroscopic data set. With this tool, we have reinvestigated the [Rh2(CO)12]/H2/CO system in an aliphatic hydrocarbon solvent.

Experiments were conducted in n-hexane in a high-pressure batch reactor system with in situ FT-IR capability. The experiments typically lasted 24 h, and the spectra were taken at ~30 min intervals in the range between 1000 and 2500 cm⁻¹. Details of the equipment and typical experimental procedures used as well as methods of purification and safety issues can be found elsewhere.[31] The experimental design typically involved 300 mL of solvent and other conditions in the following range: T = 285–303 K, P = 1.0–5.0 MPa (or P = 0.5–2.0 MPa), P = 1.0–5.0 MPa, initial concentration of [Rh2(CO)12] = 58–315 mg, and P = 2.0–8.0 MPa. Each experiment was conducted in the semi-batch mode, whereby multiple perturbations in the variables hexane, H2 or D2, CO, and [Rh2(CO)12] could be achieved in any 24-h run. Upon each perturbation of the reactive system, very small changes could be observed in the mid-infrared spectra during the subsequent few minutes. In total, 475 spectra were taken for
reactions involving only molecular hydrogen, and about 200 spectra were recorded with molecular deuterium alone or with deuterium and hydrogen.

A singular value decomposition was performed on the data set. Figure 1 shows some of the right singular vectors from

Figure 1. Several right singular vectors from the singular value decomposition: a) 1st vector, b) 4th vector, c) 5th vector, d) 6th vector, e) 13th vector, f) 17th vector, g) 472nd vector.

the semi-batch experiments involving only molecular hydrogen. The numbers in Figure 1 indicate prominent spectral features in the vectors which were subsequently targeted in the BTEM algorithm. Details of the mathematical constructs and implementation of BTEM can be found in the literature.10,11 The first few vectors represent the primary contributions to signal variance, while the subsequent vectors have increasing contributions from white noise.

Figure 2 presents the reconstructed pure-component spectra of the "major" species present. These spectra were obtained by targeting the features 2 (CO), 3 (hexane), 4 (vapor-phase moisture), and 5 (vapor-phase carbon dioxide) indicated in Figure 1. Figure 3 shows the reconstructed pure-component spectra of the "minor" components, that is, the rhodium organometallic species. These spectra were obtained by targeting the features 1 ([Rh₄(μ-CO)₃(μ- CO)₄], maxima at 1855.8, 2035.8, 2070.2, 2073.8 cm⁻¹), 9 ([Rh₂(μ-CO)₃(μ- CO)₄], maxima at 1845.6, 1861.6, 2062.2, 2084.2 cm⁻¹), 7 ([Rh₃(μ- CO)₃], maxima at 2068.0, 2076.0 cm⁻¹), and 8 ([Rh₄(μ-CO)₃], maxima at 1819.2, 2075.4 cm⁻¹). The concentration of [Rh₄(μ-CO)₃] was typically on the order of ppm or less, and its presence could be detected by unaided visual inspection only in a few experimental spectra.

Figure 2. The reconstructed pure-component spectra of the major component: a) vapor-phase moisture, b) vapor-phase CO, c) hexane, d) dissolved CO.

Figure 3. The reconstructed pure-component spectra of the minor organometallic component: a) [Rh₄(μ-CO)₃(μ- CO)₄], b) [Rh₂(μ-CO)₃(μ- CO)₄], c) [Rh₃(μ-CO)₃], d) [Rh₄(μ-CO)₃].

Most importantly, BTEM was able to reconstruct two new and previously unknown mid-infrared pure-component spectra. One spectrum arose exclusively in the experiments with molecular hydrogen (spectral feature 6 in Figure 1) and the
other arose exclusively in the experiments with molecular deuterium. These pure-component spectra correspond to only about 0.15% of the signals in the respective data sets. In the interest of completeness, it must be mentioned that BTEM also was able to reconstruct only one additional spectrum belonging to [Fe(CO)₄] with bands at 1964.8 (w), 2001.0 (v), 2023.6 (m) cm⁻¹. The presence of [Fe(CO)₄] could be detected in some but not all experiments. It is an omnipresent trace impurity in commercial CO stored in stainless steel cylinders.

Figure 4 reports the entire mid-infrared region from 1550 to 2500 cm⁻¹, where either M–H or M–CO vibrations are expected to occur. Shown are spectra of [HCo(CO)₄] obtained in our laboratory as well as the new spectra recorded upon the use of molecular hydrogen and deuterium. [HCo(CO)₄] is known to have a trigonal-bipyramidal geometry with the hydrogen ligand in an axial position. According to the symmetry of the molecule corresponds to the point group C₃ᵥ. Three metal–carbonyl vibrations are expected and indeed observed at 2029.6 (w), 2052.2 (m), and 2115.6 (w) cm⁻¹ and the metal–hydrogen vibration appears at 1993.0 (w) cm⁻¹. In comparison, the literature values (with relative intensities) in n-heptane are 2029.8 (19), 2052.3 (32), 2116.1 (22), and 1993.0 (0.2) cm⁻¹. The new spectrum observed under molecular hydrogen also has four vibrations in the mid-infrared range, and these occur in the same pattern, namely, a band of minor intensity at 2002.8 (w) cm⁻¹ and three more intense bands at 2041.6 (v), 2071.8 (m), and 2123.6 (w) cm⁻¹. The new spectrum observed under molecular deuterium has only three vibrations in the mid-infrared range at 2041.6 (v), 2063.6 (m), and 2119.6 (w) cm⁻¹.

The new spectra clearly correspond to [HRh(CO)₄] and [DRh(CO)₄]. These molecules have the expected trigonal-bipyramidal geometries with the proton or deuterium ligand in an axial position (Scheme 1). The vibrations at the very high wavenumbers 2123.6 and 2119.6 cm⁻¹ correspond to the totally symmetric mode and are conclusive evidence that the molecules have very high symmetry and are monomeric.\(^{29}\)

Scheme 1. Schematic representation of the trigonal-bipyramidal structures of [HRh(CO)₄] and [DRh(CO)₄].

Furthermore, the shift in metal–carbonyl vibrations and the loss of the metal–hydrogen vibration upon substitution with deuterium is highly analogous to the case of cobalt tetraacetylhydride. Edgell and co-workers reported band at 2043, 2062, 2121, and 1934 cm⁻¹ for [HCo(CO)₄] at 2043, 2055, 2120, and 1396 cm⁻¹ for [DCo(CO)₄].\(^{30}\) The vibration at 2041.6 cm⁻¹ for [HRh(CO)₄][DRh(CO)₄] belongs to the δ mode and is insensitive to substitution, whereas the other two carbonyl vibrations belong to the σ mode and are moderately sensitive to substitution with deuterium. The D–Rh vibration could not be directly observed since the spectral window 1350–1500 cm⁻¹ is opaque due to strong solvent absorption.

The equilibrium thermodynamics were also measured. The concentrations of all reactants were considered in mole fraction units, and the equilibrium was modeled as either a two-parameter expression in enthalpy and entropy of reaction or as a three-parameter expression in enthalpy, entropy, and volume of reaction. The equilibrium constant \(K_e\) is given by Equation (1).

\[
K_e = \frac{[HRh(CO)₄]^2[DRh(CO)₄]^2[CO]^2[Rh]^2}{[HRh(CO)₄][DRh(CO)₄][HRh(CO)₄][DRh(CO)₄]} \quad (1)
\]

Since the overall reaction can be written as \([Rh(μ-CO)₄(CO)] + 2HRh + 4CO ⇌ 4RHr(CO)₄\), at least 39 bonds are broken and formed: six Rh–Rh bonds broken, three μ-CO bonds converted into three σ-CO bonds, two H–H bonds broken, four new Rh–H bonds formed, and four new Rh–CO bonds formed. The two-parameter model provided the thermodynamic parameters \(ΔH = -65.7 ± 19.8 \text{ kJ mol}^{-1}\) and \(ΔS = -0.38 ± 0.27 \text{ kJ mol}^{-1} K^{-1}\). The exothermic nature of the reaction is consistent with the known thermochemistry of rhodium, namely, the low heat of formation of Rh–Rh and Rh–CO bonds and the high heat of formation of Rh–H and Rh–CO bonds. Accordingly, higher conversions into [HRh(CO)₄] are achieved at lower temperatures. Also the negative entropy of reaction is consistent with the reaction of seven molecules to give only four molecules as products. The three-parameter model provided the thermodynamic parameters \(ΔH = -62.4 ± 16.2 \text{ kJ mol}^{-1}\), \(ΔS = -0.44 ± 0.63 \text{ kJ mol}^{-1} K^{-1}\), and \(ΔV = -131 ± 33 \text{ kJ mol}^{-1}\). The negative sign for the volume of reaction is consistent with the loss of the unusually large partial molar volumes of dissolved molecular hydrogen and carbon monoxide of about 60 mL mol⁻¹ upon reaction.\(^{30}\) However, a value on the order of \(-250 \text{ mL mol}^{-1}\) rather than \(-1100 \text{ mL mol}^{-1}\) is expected.\(^{30}\)
These results indicate the severe limitation of the study of the small total pressure interval of ca. 5 MPa used in this study versus pressure intervals of ca. 100 MPa used in traditional reaction volume studies.  

The intrinsic reaction kinetics were too rapid to be captured with the present experimental setup. Indeed, characteristic times for gas-liquid mass transfer as well as liquid-phase mixing were on the order of a few minutes. Therefore, transport-controlled rather than intrinsic kinetics were observed.  

Nevertheless, an informed assumption about the mechanism(s) can be proposed. After each perturbation, hydrogen activation on [Rh$_2$(CO)$_6$] (or equilibrated and unreacted [Rh$_2$(CO)$_6$]) probably occurs very rapidly. After depletion of the dinuclear carbonyl species, the fragmentation of [Rh$_2$(CO)$_6$] (or possibly the equilibrated, open polyhedron structure [Rh$_2$(CO)$_6$]) is likely to be the rate-limiting step. Hence, these kinetics can be anticipated to involve contributions from a number of parallel pathways.  

Finally, the STEM analysis of data from previous and ongoing hydroformylation studies was performed. In these catalytic systems involving [Rh$_2$(CO)$_6$] as catalyst precursor in $n$-hexane with less reactive silicon substrates (i.e., cyclopentane and $m$-xylene) it was possible to recover again the pure-component spectrum of [HRh(CO)$_3$]. The assignment of the fundamental vibrations at 2002.8 (w), 2041.6 (vs), 2071.8 (m) and 2235.6 (w) cm$^{-1}$ is entirely reproducible. In some of these reconstructions, the rhodium-hydrogen vibration at 2002.8 cm$^{-1}$ is better resolved or more pronounced.

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Spontaneous Deposition of Water-Soluble Substances into Micropores: Phenomenon, Mechanism, and Application**

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Novel hollow micropores with sizes ranging from 60 nm to 10 µm have recently been produced by the layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes onto colloidal templates, followed by removal of the template core. Great progress has been made towards optimizing the fabrication conditions for capsules templated onto melanin formaldehyde (MF) particles, with an integrity of 90% having

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Appendix B

HOMOGENEOUS BIMETALLIC CATALYZED
HYDROFORMYLATION OF ALKENES

B.1 Rh₄(CO)₁₂/HMn(CO)₅ bimetallic catalyzed hydroformylation of methylenecyclohexane

Two preliminary experiments were performed at 2.0MPa CO, 2.0 MPa H₂, 289K, with 2.0ml methylenecyclohexane in 300 ml n-hexane. The initial loadings were: 52.28 mg Rh₄(CO)₁₂ for pure rhodium system and 18.08 mg Rh₄(CO)₁₂ and 425.3mg Mn₂(CO)₁₀ for Rh/Mn bimetallic system. In situ FTIR spectral analyses found only four observable organometallic species, namely Rh₄(CO)₁₂, HMn(CO)₅, Mn₂(CO)₁₀ and RCORh(CO)₄. The product formation rate in Rh/Mn (18.08 mg Rh₄(CO)₁₂) bimetallic hydroformylation is circa 20% higher than when 52.28 mg Rh₄(CO)₁₂ was used alone.

B.2 Rh₄(CO)₁₂/HMn(CO)₅ bimetallic catalyzed hydroformylation of styrene

Two preliminary experiments were performed at 5.0MPa CO, 0.5 MPa H₂, 303K, with 25.0 ml styrene in 300 ml n-hexane. The initial loadings were: 96.0 mg Rh₄(CO)₁₂ for pure rhodium system and 99.5 mg Rh₄(CO)₁₂ and 187.5 mg Mn₂(CO)₁₀ for Rh/Mn bimetallic system. In situ FTIR spectral analyses found only four observable organometallic species, namely Rh₄(CO)₁₂, HMn(CO)₅, Mn₂(CO)₁₀ and RCORh(CO)₄. The product formation rate in Rh/Mn bimetallic hydroformylation is circa 90% higher than when Rh₄(CO)₁₂ was used alone.
B.3 \textit{Rh}_4(\textit{CO})_{12}/\textit{HRe(\textit{CO})}_5 \textit{bimetallic catalyzed hydroformylation of styrene}

Two preliminary experiments were performed at 5.0MPa CO, 0.5 MPa H\textsubscript{2}, 303K, with 25.0 ml styrene in 300 ml n-hexane. The initial loadings were: 91.2 mg Rh\textsubscript{4}(\textit{CO})_{12} for pure rhodium system and 82.16 mg Rh\textsubscript{4}(\textit{CO})_{12} and circa 10 \mu L \textit{HRe(\textit{CO})}_5 for Rh/Re bimetallic system. In situ FTIR spectral analyses found four observable organometallic species, namely Rh\textsubscript{4}(\textit{CO})_{12}, HRe(\textit{CO})\textsubscript{5}, RhRe(\textit{CO})\textsubscript{9} and RCORh(\textit{CO})\textsubscript{4}. The product formation rate in Rh/Re bimetallic hydroformylation is circa 150\% higher than when Rh\textsubscript{4}(\textit{CO})_{12} was used alone.

B.4 \textit{Rh}_4(\textit{CO})_{12}/\textit{HRe(\textit{CO})}_5 \textit{bimetallic catalyzed hydroformylation of methylenecyclohexane}

Two preliminary experiments were performed at 2.0MPa CO, 2.0 MPa H\textsubscript{2}, 289.7 K, with 2.0 ml methylenecyclohexane in 300 ml n-hexane. The initial loadings were: 52.28 mg Rh\textsubscript{4}(\textit{CO})_{12} for pure rhodium system and 40.31 mg Rh\textsubscript{4}(\textit{CO})_{12} and circa 20 \mu L \textit{HRe(\textit{CO})}_5 for Rh/Re bimetallic system. In situ FTIR spectral analyses found four observable organometallic species, namely Rh\textsubscript{4}(\textit{CO})_{12}, HRe(\textit{CO})\textsubscript{5}, RhRe(\textit{CO})\textsubscript{9} and RCORh(\textit{CO})\textsubscript{4}. The product formation rate in Rh/Re bimetallic hydroformylation is circa 210\% higher than when Rh\textsubscript{4}(\textit{CO})_{12} was used alone.
LIST OF PUBLICATIONS


Chuanzhao Li, Li Chen, Marc Garland. Bimetallic hydroformylation of cyclopentene with HRe(CO)₅/Rh₄(CO)₁₂: a further evidence on bimetallic CBER. To be submitted.

Chuanzhao Li, Liangfeng Guo and Marc Garland. Deactivation of Rhodium during the hydroformylation of 4VP. In preparation.