Investigations presented here are (a) the study of reorientational dynamics and internal rotation in transition metal complexes by NMR relaxation experiments, and (b) the study of ligand exchange dynamics in transition metal complexes by exchange NMR experiments.

The phenyl ring rotation in $\text{Ru}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-NPh})$ and $\text{Re}(\text{Co})_2(\text{CO})_{10}(\mu_3\text{-CPh})$ was monitored by $^{13}\text{C}$ NMR relaxation experiments to probe intramolecular electronic and/or steric interactions. It was found that the rotation is relatively free in the first complex, but is restrained in the second one. The steric interactions in the complexes were ascertained by the measurement of the closest approach intramolecular distances. The rotational energy barriers in the two complexes were also calculated by using both the Extended Hückel and Fenske-Hall methods. The study suggests that the barrier is due mainly to the steric interactions.

The exchange NMR study revealed two carbonyl exchange processes in both $\text{Ru}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-NPh})$ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)(\mu_3\text{-CO})(\mu_3\text{-NPh})$. The lower energy process is a tripodal rotation of the terminal carbonyls. The higher energy process, resulting in the exchange between the equatorial and bridging carbonyls, but not between the axial and bridging carbonyls, involves the concerted formation of edge-bridging $\mu_2\text{-CO}$ moieties. The effect of the $\text{PPh}_3$ ligand on the carbonyl exchange rates

Investigations presented here are (a) the study of reorientational dynamics and internal rotation in transition metal complexes by NMR relaxation experiments, and (b) the study of ligand exchange dynamics in transition metal complexes by exchange NMR experiments.

The phenyl ring rotation in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh) and Re(Co)$_2$(CO)$_{10}$(μ$_3$-CPh) was monitored by $^{13}$C NMR relaxation experiments to probe intramolecular electronic and/or steric interactions. It was found that the rotation is relatively free in the first complex, but is restrained in the second one. The steric interactions in the complexes were ascertained by the measurement of the closest approach intramolecular distances. The rotational energy barriers in the two complexes were also calculated by using both the Extended Hückel and Fenske-Hall methods. The study suggests that the barrier is due mainly to the steric interactions.

The exchange NMR study revealed two carbonyl exchange processes in both Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh) and Ru$_3$(CO)$_9$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh). The lower energy process is a tripodal rotation of the terminal carbonyls. The higher energy process, resulting in the exchange between the equatorial and bridging carbonyls, but not between the axial and bridging carbonyls, involves the concerted formation of edge-bridging μ$_2$-CO moieties. The effect of the PPh$_3$ ligand on the carbonyl exchange rates
has been discussed.

A combination of relaxation and exchange NMR found that PPh$_3$ ligand rotation about the Ru-P bond is slow on the exchange NMR time scale and the phenyl rotation about the P-C$_{ipso}$ bond is fast on the exchange NMR time scale but is slow on the NMR relaxation time scale.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. THE DYNAMICS OF NUCLEAR SPIN SYSTEMS</td>
<td></td>
</tr>
<tr>
<td>A. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>B. Qualitative Description of Exchange NMR</td>
<td>2</td>
</tr>
<tr>
<td>C. Quantitative Description of Dynamics in NMR</td>
<td>7</td>
</tr>
<tr>
<td>1. Classical Description of Spin Systems Without</td>
<td></td>
</tr>
<tr>
<td>Spin-Spin Couplings</td>
<td>7</td>
</tr>
<tr>
<td>2. Density Operator Description of Spin Systems With</td>
<td>10</td>
</tr>
<tr>
<td>Spin-Spin Couplings</td>
<td></td>
</tr>
<tr>
<td>D. One-Dimensional Exchange NMR Methods</td>
<td>11</td>
</tr>
<tr>
<td>1. Bandshape Analysis</td>
<td>11</td>
</tr>
<tr>
<td>2. Magnetization Transfer Methods</td>
<td>12</td>
</tr>
<tr>
<td>E. Two-Dimensional Exchange NMR Methods</td>
<td>14</td>
</tr>
<tr>
<td>1. Exchange in Systems Without Resolved Couplings</td>
<td>15</td>
</tr>
<tr>
<td>2. Exchange in Coupled Spin Systems</td>
<td>19</td>
</tr>
<tr>
<td>3. Future Trends</td>
<td>20</td>
</tr>
<tr>
<td>F. Relaxation and Molecular Dynamics</td>
<td>21</td>
</tr>
<tr>
<td>1. Semi-Classical Relaxation Theory</td>
<td>22</td>
</tr>
<tr>
<td>2. Relaxation Mechanisms</td>
<td>23</td>
</tr>
<tr>
<td>3. Correlation Functions and Diffusion Coefficients</td>
<td>24</td>
</tr>
<tr>
<td>II. NMR STUDY OF REORIENTATIONAL DYNAMICS IN</td>
<td></td>
</tr>
<tr>
<td>TRANSITION METAL COMPLEXES</td>
<td>29</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>29</td>
</tr>
<tr>
<td>B. Experimental</td>
<td>31</td>
</tr>
<tr>
<td>1. Synthesis</td>
<td>31</td>
</tr>
<tr>
<td>2. NMR Experiments</td>
<td>31</td>
</tr>
<tr>
<td>3. Computations</td>
<td>32</td>
</tr>
<tr>
<td>C. The Results of NMR Studies</td>
<td>32</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$^{13}$C Relaxation Times in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>34</td>
</tr>
<tr>
<td>2.</td>
<td>Rotational Correlation Times and Diffusion Coefficients in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>37</td>
</tr>
<tr>
<td>3.</td>
<td>$^{13}$C Relaxation Times, Rotational Correlation Times and Diffusion Coefficients in $\text{ReCo}<em>2(\text{CO})</em>{10}(\mu_5-\text{CPh})$</td>
<td>46</td>
</tr>
<tr>
<td>4.</td>
<td>The Closest Approach Distances in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$ and $\text{ReCo}<em>2(\text{CO})</em>{10}(\mu_5-\text{CPh})$</td>
<td>53</td>
</tr>
<tr>
<td>5.</td>
<td>The Free Angle $\phi_{\text{free}}$ in Complexes</td>
<td>54</td>
</tr>
<tr>
<td>6.</td>
<td>Temperature Dependence of Carbonyl Exchange Rate Constants in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>73</td>
</tr>
<tr>
<td>7.</td>
<td>Mixing Time Dependence of the Intensity Ratio, $I_{eb}/I_{eb}$ in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>76</td>
</tr>
<tr>
<td>8.</td>
<td>2D-EXSY Intensities and Rate Constants in $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>79</td>
</tr>
<tr>
<td>9.</td>
<td>The Terminal Carbonyl Exchange Rate Constants in $\text{Ru}_3(\mu_3-\text{NPh})(\text{CO})_6(\mu_3-\text{CO})(\text{PPh}_3)$</td>
<td>83</td>
</tr>
<tr>
<td>10.</td>
<td>The Exchange Rate Constants Between the Terminal and Bridging Carbonyl in $\text{Ru}_3(\mu_3-\text{NPh})(\text{CO})_6(\mu_3-\text{CO})(\text{PPh}_3)$</td>
<td>86</td>
</tr>
<tr>
<td>11.</td>
<td>2D-EXSY Intensities and Rate Constants for PPh$_3$ Rotation in $\text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>91</td>
</tr>
<tr>
<td>12.</td>
<td>$^{13}$C NMR Data (Phenyl Region) for $\text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>92</td>
</tr>
<tr>
<td>13.</td>
<td>The Rotation Rate of PPh$_3$ Ligand in $\text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>95</td>
</tr>
</tbody>
</table>
14. $^{13}$C Relaxation Times (Phenyl Region) and Diffusion Coefficients in
   Ru$_3$(CO)$_6$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh) .................................................. 97
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Exchanging NMR Spectra for a Pair of Nuclei AB With Different Exchange Rates</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>Vector Diagram for Magnetization Transfer Experiment</td>
<td>5</td>
</tr>
<tr>
<td>3.</td>
<td>A Typical 2D-EXSY Spectrum for an ABCD System</td>
<td>6</td>
</tr>
<tr>
<td>4.</td>
<td>Temperature Dependence of the Perpendicular “Tumbling”</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Diffusion Coefficient in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_1$-NPh)</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Temperature Dependence of the &quot;Spinning&quot; Diffusion Coefficient</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh)</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Temperature Dependence of the &quot;Spinning&quot; Diffusion Coefficient</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>in ReCo$<em>2$(CO)$</em>{10}$(μ$_3$-CPh)</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Energy and Distance Dependence Upon Phenyl Group Dihedral</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Angle in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_1$-NPh)</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Energy and Distance Dependence Upon Phenyl Group Dihedral</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Angle in ReCo$<em>2$(CO)$</em>{10}$(μ$_3$-CPh)</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>Structures of the Clusters Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_1$-NPh) and</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Ru$_3$(CO)$_9$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh)</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>The Experimental and Calculated $^{13}$C NMR Bandshapes of</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh) in the Carbonyl Region</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Temperature Dependence of the Equatorial/Axial Exchange Rate</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Constants of Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh)</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Carbonyl region $^{13}$C 2D-EXSY Spectrum of</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh)</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Terminal Carbonyl Region $^{13}$C 2D-EXSY Spectrum of</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Ru$_3$(CO)$_9$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh)</td>
<td></td>
</tr>
</tbody>
</table>
14 Temperature Dependence of the Equatorial/Axial Exchange Rate Constants of Ru$_3$(CO)$_8$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh) ........................................ 84

15 Temperature Dependence of the Equatorial/Bridging Exchange Rate Constants of Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) .................. 87

16 The Variable-Temperature $^{13}$C{¹H} NMR Spectrum of Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) ........................................ 88

17 Phenyl Region $^{13}$C 2D-EXSY Spectrum of Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) ........................................ 90

18 The Experimental and Calculated $^{13}$C{¹H} NMR Bandshapes for the Phenyl ortho Carbons of the PPh$_3$ Ligand in Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) ........................................ 94

19 Temperature Dependence of the Rotation Rate of the PPh$_3$ Ligand About the P-Ru Bond in Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) ................. 96

20 Temperature Dependence of the Phenyl Rotational Diffusion Constants in Ru$_3$(CO)$_8$(PPh$_3$)(μ$_1$-CO)(μ$_3$-NPh) ........................................ 99
CHAPTER I

THE DYNAMICS OF NUCLEAR SPIN SYSTEMS

A. Introduction

The dynamics of nuclear spin systems can be classified as relaxation and exchange processes. The relaxation of a spin system is caused by the interactions with its surroundings. The exchange is through a nuclear site exchange process. Nuclear magnetic resonance (NMR) is especially well suited to the studies of both relaxation and exchange processes, because it contains information about molecular reorientation, molecular structure and chemical exchange.

The $^{13}$C-$^1$H systems we studied do not have resolved scalar coupling. Therefore, the dynamics of isolated nuclear spins can be understood in terms of the motion of classical magnetization vectors, $M(t)$. To interpret the relation between NMR relaxation parameters and molecular reorientation dynamics, however, it is necessary to have recourse to a quantum mechanical formalism where the state of the system is expressed by a state function or, more generally, by a density operator $\sigma(t)$.\textsuperscript{1}

In this chapter, we will give a detailed description for exchange dynamics based on classical vectors, and a brief view of relaxation dynamics in the quantum mechanical formalism to show the relation between NMR relaxation times and molecular reorientation dynamics.
B. Qualitative Description of Exchange NMR

NMR is an important technique for the investigation of chemical-exchange processes, which is based on two points: (a) the nuclei in different chemical environments have separated NMR peaks with different chemical shifts, and (b) exchanges among the nuclei will cause changes in the NMR spectrum, such as peak widths, peak positions and coupling constants. The application of the resultant spectral changes to the study of kinetics is often called dynamic NMR (DNMR). The most commonly used DNMR methods are the classical band-shape analysis,\textsuperscript{2} 1D magnetization transfer,\textsuperscript{3} and the recently developed two-dimensional exchange spectroscopy\textsuperscript{4} (2D-EXSY). DNMR is specially powerful for the study of exchange dynamics because of (a) its sensitivity to the dynamic equilibrium, where the exchange reaction is proceeding at a detectable rate even though there is no net reaction and products are identical to reactants, and (b) its unique ability to resolve and assign the separate signals due to nuclei in different chemical environments. Its ability to trace the exchange pathways offers valuable information on the exchange mechanism. In this section, a brief glance of typical DNMR methods is given. More mathematical description is given in next sections.

Band shape analysis is the oldest and simplest DNMR method. Let us consider the simplest AB case: an intramolecular nucleus exchanging between two sites with equal populations. Figure 1 shows how the 1D NMR is affected by the exchange between the two sites.\textsuperscript{5} When the exchange is slow, there are two equally intense and narrow NMR peaks from the nuclei at the two different sites. As the exchange rate is
Figure 1. Exchanging NMR spectra for a pair of nuclei AB with different exchange rates. The difference in resonance frequencies of the two sites, $\delta v$, is 50 Hz. The peak widths in the absence of exchange are 1 Hz.
increased, the two peaks first broaden and shift towards each other, then merge into a single, wide, flat-topped peak which is called coalescence. Further increase in the exchange rate produces a sharp peak. Experimentally, the exchange rate is increased by increasing the temperature. The exchange rate can be measured from the peak width, coalescence temperature, complete band shape (CBS) analysis and other methods.  

A typical magnetization transfer method is the selective inversion experiment. Figure 2 demonstrates the way it works for an AB case. First, both spins at site A and B are at equilibrium position and are aligned with the external magnetic field $H_0$, which is pointing in the +z direction. Then, if the spin at site A is selectively inverted to the -z direction at $t = t_0$, it will relax back to the equilibrium position through the relaxation matrix $R$, and exchange with the spin at site B through the exchange matrix $K$, as time goes on. Therefore, it will transfer the negative $z$-component to the spin at site B. The $z$-component of the spin at site B first decreases, then relaxes back to its equilibrium position. The exchange information can be extracted from the curves.

2D-EXSY is a two-dimensional version of the magnetization transfer method. A typical 2D-EXSY spectrum is shown in Figure 3. If there are four peaks, A, B, C and D, in a normal 1D-NMR spectrum, there will be four corresponding peaks on the diagonal line of the 2D-EXSY spectrum. The exchange between sites A and C transfers magnetization between them, and produces cross peaks at the cross positions of sites A and C. Normally, there are no cross peaks at the cross positions of sites A and B if there is no direct exchange between them. (Note: it is possible that there are
Figure 3. A typical 2D-EXSY spectrum for ABCD system. There are exchanges between sites A and C and between sites B and D, but no other exchanges.
weak cross peaks caused by indirect exchange). The 2D-EXSY spectrum gives a visual mapping of exchange paths. Quantitative exchange rates can be obtained by analyzing the diagonal and off-diagonal peak intensities.

C. Quantitative Description of Dynamics in NMR

1. Classical Vector Description of Spin Systems Without Spin-Spin Couplings

In the absence of chemical exchange, the relaxation of the magnetization $M_i$ of spin at site $i$ obeys the conventional Bloch equation:

$$\frac{d}{dt} M_i(t) = \gamma (1 - \sigma) M_i(t) \times B(t) - R_i (M_i(t) - M_{eq})$$  \hspace{1cm} (1)

with the chemical shielding constant $\sigma$, gyromagnetic ratio $\gamma$, and relaxation matrix

$$R_i = \begin{pmatrix} 1/T_{2i} & 0 & 0 \\ 0 & 1/T_{2i} & 0 \\ 0 & 0 & 1/T_{1i} \end{pmatrix}$$  \hspace{1cm} (2)

In the presence of chemical exchange, the time-dependence of the concentrations $[A_i]$ is then given by

$$\frac{d}{dt} [A_i(t)] = (\sum_{j=1}^{n} k_{ij} [A_j(t)] + \sum_{j=1}^{n} k_{ji} [A_j(t)]$$  \hspace{1cm} (3)

with the exchange rate constant from site $i$ to $j$ given by $k_{ij}$. Defining

$$K_{ij} = k_{ij}, \quad i \neq j,$$

$$K_n = \sum_{j=1}^{n} k_{ij},$$  \hspace{1cm} (4)

equation (3) can be written in the form as
If we assume that the magnetization $M_i$ is proportional to concentration $[A_i]$, then the chemical exchange dynamics, governed by equation (5), leads to the modified Bloch equation

$$\frac{d}{dt} [A_i(t)] = \sum_j K_{ij} [A_j(t)]$$  \hspace{1cm} (5)$$

$$\frac{d}{dt} M_i(t) = \gamma (1 - \sigma_i) M_i(t) \times B(t) - R_i [M_i(t) - M_{io}] + \sum_j K_j M_j(t)$$  \hspace{1cm} (6)$$

where the matrix elements $K_{ij}$ are related through equation (4) to chemical rate constants $k_{ij}$ but not to $k_y$.

In the context of one- and two-dimensional Fourier spectroscopy, the chemical exchange and relaxation processes normally occur in the absence of r.f. fields in the course of one or several free precession periods. The transverse and longitudinal magnetization components, described in a frame rotating with the radio-frequency $\omega_{1\omega}$, evolve independently in these intervals

$$\frac{d}{dt} M_i^* = (i \Omega_i - \frac{1}{T_2^*}) M_i^*(t) + \sum_j K_{ij} M_j^*,$$  \hspace{1cm} (7a)$$

$$\frac{d}{dt} M_i^* = -\frac{1}{T_1^*} (M_i^* - M_{io}(t)) + \sum_j K_{ij} M_j^*,$$  \hspace{1cm} (7b)$$

with $M_i^* = M_{io} + iM_{io}$ and the chemical shift frequency $\Omega_i = -\gamma (1 - \sigma_i) B_0$. The z-magnetization component in magnetic equilibrium, $M_{io}(t)$, is proportional to the instantaneous concentration $[A_i(t)]$. In the equilibrium exchange case, the $[A_i(t)]$ and, thus, $M_{io}(t)$ are constants. Due to microscopic reversibility, the term $\sum K_{ij} M_{io}$ summed
over i is zero. Thus, these equations are conveniently written in matrix form:

\[
\frac{d}{dt} M(t) = \mathbf{L}^* M(t) \tag{8}
\]

\[
\frac{d}{dt} \Delta M_i(t) = \mathbf{L} \Delta M_i(t) \tag{9}
\]

where \( \Delta M_z = M_z - M_0 \), and vector \( M \) comprises the magnetization components \( M_i \) of spin \( i \) for \( i = 1 \) to \( n \). The dynamic matrices \( \mathbf{L}^* \) and \( \mathbf{L} \) describe precession, relaxation, and chemical kinetics

\[
\mathbf{L}^* = i\Omega - \mathbf{A} + \mathbf{K} \tag{10}
\]

\[
\mathbf{L} = -\mathbf{R} + \mathbf{K}. \tag{11}
\]

The elements of the diagonal matrix \( \Omega \) correspond to the chemical shift frequencies \( \Omega \), the transverse relaxation matrix \( \mathbf{A} \) is also diagonal (in the absence of degenerate transitions) with elements \( \lambda_{ij} = \delta_{ij} T_2^{-1} \), the elements of matrix \( \mathbf{K} \) are \( K_{ij} \) as defined in equation (4), and the matrix \( \mathbf{R} \) contains the longitudinal relaxation information.

Cross-relaxation between nuclei associated with different chemical species is represented by off-diagonal elements of the longitudinal relaxation matrix \( \mathbf{R} \). Detailed studies\(^1\) showed that cross-relaxation in the study of relaxation and exchange is negligible when the correlation time for molecular reorientation, \( \tau_c \), is much smaller than \( 1/\omega_0 \), where \( \omega_0 \) is the nuclear Larmor frequency. Thus, matrix \( \mathbf{R} \) can be treated as a diagonalized matrix when we study the relaxation and chemical exchange in small molecules in non-viscous solutions. An ingenious method, NOESY-ROESY, has been proposed\(^6\) for eliminating the cross-relaxation from the 2D exchange spectrum of
macromolecules.

2. Density Operator Description of Spin Systems With Spin-Spin Couplings

In systems containing several nuclear spins that interact through scalar couplings, the classical treatment based on the modified Bloch equations is no longer valid. We have to return to a full density-matrix treatment, which is complicated by the presence of several molecular species and their chemical interconversion. The density-matrix treatment can describe the cross-relaxation, cross-correlation, and the multiple-quantum coherence caused by coupling.

A general density operator equation for "n" spin sites involved in both relaxation and exchange processes has been derived by Kühne et al.\textsuperscript{7} Detailed mathematical descriptions are skipped here, and a simplified equation for dynamics including relaxation and first-order chemical exchange in equilibrium is\textsuperscript{1}

\[
\frac{d}{dt}\sigma_i = -i[H,\sigma_i] - \Gamma_i[\sigma_i,\sigma_i] + \sum_{j=1}^{n} k_{ij} [R_p^j,\sigma_i] - \sigma_i
\]  

where $\sigma$ is the density operator, $H$ is the corresponding Hamiltonian superoperator, $\Gamma$ is the relaxation superoperator, and $R$ is the rearrangement operator which transforms the reactant density operator into the density operator of the product.

The density-matrix calculation is so complicated that the calculation performed by hand normally is limited to a two-spin system. Fortunately, progress in computer computation makes this kind of matrix calculation possible for spin systems of moderate size. Programs, such as DNMR5\textsuperscript{8} and ANTOPE,\textsuperscript{9} are written for this purpose.
D. One-dimensional Exchange NMR Methods

The one-dimensional exchange NMR methods can be classified as band-shape analysis and magnetization transfer studies. Band-shape methods are based on the analyses of normal one-dimensional NMR spectra, which include the complete band-shape (CBS) fitting method, methods based on bandwidths, methods based on peak separations, methods based on peak heights, etc. Magnetization transfer methods include selective saturation and selective inversion.

1. Bandshape Analysis

The simple one-pulse one-dimensional NMR experiment measures the transverse magnetization \( M^+ \). For systems without resolved coupling, \( M^+(t) \) obeys equation (8), and its solution is given by

\[
M(t) = e^{L^+ t} M(0). \tag{13}
\]

Fourier transformation converts it to an NMR spectrum, which is a function of frequency.

\[
S(\omega) = \int e^{L^+ \omega t} M(0) dt \tag{14}
\]

Note again that the \( L^+ \) is a matrix and \( M^+ \) is a vector. There is no simple analytical solution of equation (14) except in special cases. An analytical formula for the \( A_nB_n \) two-site case has been presented by Sandstrom.

The density matrix method is required for systems with resolved couplings. The general relation of density matrix \( \sigma \) for a first-order exchange process is given by equation (12). What the one-pulse one-dimensional NMR experiment observes is the
coherence of order -1, \( \sigma^{-1} \), which is responsible for the transverse magnetization, \( M^+ \). More mathematical descriptions are given by Ernst and Sandstrom.\(^{10}\)

Programs, such as DNMR5\(^8\), solve the exchange problem using a density matrix method. They iteratively optimize the fitting between the theoretical and experimental spectra by adjusting parameters. This procedure is called "the Complete Band-Shape method" (CBS). It is possible to determine false minima by using these programs, especially for complex spectra that have many variable parameters. It is thus always advisable to plot the final calculated spectrum and make a visual comparison with the experimental one.

The common way to obtain rate constants by band shape analysis is the CBS method, but some simple methods exist which are still useful for obtaining straightforward results for uncoupled, equally populated, two-site systems. These methods are based either on bandwidth or on coalescence.\(^{10}\)

2. Magnetization Transfer Methods

The deviation from thermal equilibrium, \( \Delta M(t) = M(t) - M_e \), at one spin site caused by selective inversion or selective saturation can transfer to other spin sites through the chemical exchange network \( K \), or relax back through the relaxation network \( R \). Therefore, chemical exchange rates \( K \), that are of comparable magnitude to the relaxation rate \( R \), are suitably measured by selective saturation or selective inversion methods.

2.1 Selective Saturation

The pulse sequence for selective saturation is:
During selective saturation, the $M_{z}$ of the selected site $i$ is zero, and $M_{z}$ for $j \neq i$ is affected according to equation (9). The hard $\pi/2$ pulse converts the $M_z$ to the transverse magnetization $M^+$ that is acquired.

The calculation is straightforward for uncoupled two-site AB systems. Assume that the populations of site A and B are $M_{0a}$ and $M_{0b}$, the exchange rates are $k_{ab} = (M_{0b}/M_{0a}) k_{ba}$, the relaxation times are $T_{1a}$ and $T_{1b}$, and the intensities of site B in the absence and presence of saturation at site A are $M_{ob}$ and $M_{b}$, respectively. Then equation (9) becomes

$$\frac{d}{dt} \begin{pmatrix} M_{oa} \\ M_{ob} \end{pmatrix} = \begin{pmatrix} -1/T_{1a} - k_{ab} & k_{ba} \\ k_{ab} & -1/T_{1b} - k_{ba} \end{pmatrix} \begin{pmatrix} M_{oa} - M_{0a} \\ M_{ob} - M_{0b} \end{pmatrix}$$

The solution of equation (15) is

$$k_{ba} = (M_{ob} - M_{b}) / (T_{1b} M_{b}).$$

Thus, $k_{ba}$ can be calculated through the measurement of $M_{ob}$, $M_{b}$, and $T_{1b}$.

2.2 Selective Inversion

The pulse sequence for selective inversion is:

{selective $\pi$} - {mixing time $\tau$} - {hard $\pi/2$} - {acquisition}

The selective $\pi$ pulse can be generated using the DANTE pulse sequence. The sequence is most effective when it consists of more than 30 pulses. Since most spectrometers do not permit the accurate setting of pulse widths much below one microsecond, it is usually necessary to attenuate the transmitter output. If this
attenuation is not available, a $\pi/2 - t_D - \pi/2$ sequence can be used as a selective $\pi$ pulse when Larmor frequency difference between the two vectors is $\Delta = 1/(2t_D)$.\cite{12}

The magnetization exchange occurs during the mixing time $\tau$, and obeys equation (9) when the system is uncoupled. Because the final hard $\pi/2$ pulse converts the $M_z$ to detectable signals $M^t$, we need solve the equation only for $M_z$ during mixing time $\tau_m$. The general solution is given by equation (24).

$$\Delta M_z(t) = \exp\{-Lt\} \Delta M_z(0)$$

(17)

A standard procedure to calculate the right side of equation (17) is to diagonalize matrix $L$ into $XAX^{-1}$ form, and then perform normal matrix multiplication.

$$\Delta M_z(t) = X e^{Lt} X^{-1} \Delta M_z(0)$$

(18)

Matrix calculations are performed by computer programs.\cite{13} For a $n$-site exchange system, there are $n(n-1)/2$ exchange rates and $n$ longitudinal relaxation rates to be evaluated. Fitting a series of experimentally measured magnetizations $\Delta M_z(t)$ using these exchange and relaxation rates by a nonlinear least squares procedure is then required. The case is complicated if the pulse is not completely selective. Even though there are suggested ways\cite{14} to deal with this, such a problem may be handled more efficiently by 2D-EXSY.

E. Two-dimensional Exchange NMR Methods

The extension of NMR methodology from one- to two- frequency regimes has been of very great importance in the investigation of molecular dynamics. Here, we give a theoretical description of the 2D-exchange spectroscopy (2D-EXSY), and a brief view of higher-dimensional methods.
The basic 2D-EXSY pulse sequence based on the 2D-NOESY pulse sequence consists of three hard $\pi/2$ pulses,

$$\{\pi/2\} - t_1 - \{\pi/2\} - \tau_m - \{\pi/2\} - \{\text{acquisition}\}.$$  

For a $n$-site spin system, the first $\pi/2$ pulse converts the longitudinal magnetization $M_z$ into the transverse one, $M^*$. The $M^*$ are labeled by their individual frequencies during the evolution period $t_1$, and are converted into $M_z$ again by the second $\pi/2$ pulse. The exchange processes among $M_z$ occur during the mixing period $\tau_m$. Finally, the third $\pi/2$ pulse converts the $M_z$ into $M^*$, which are labeled by the second dimensional frequency during the acquisition period $t_2$. So, the fundamental idea of 2D exchange spectroscopy is the "frequency-labelling" of the $M_z$ before and after exchange takes place, such that after exchange the pathways of $M_z$ can be traced back to their origins. Detailed descriptions are given in the next section.

1. Exchange in Systems Without Resolved Couplings

Consider a $n$-site system without resolved couplings. The dynamics can be described in terms of modified classical Bloch equations (8) and (9). Because only $M^*$ is detected during the $t_2$ period, we need to consider only the $M^*$ dynamics during periods $t_1$ and $t_2$, and $M_z$ during the $\tau_m$ period.

The equilibrium $z$-magnetizations of the $n$ sites are collected in the vector $M_0$ with elements $M_{0i} = n_i x_i M_0$, that are proportional to the number of equivalent nuclei $n_i$ in site $i$, to the mole fraction $x_i$ in chemical equilibrium, and to the equilibrium magnetization $M_0$ per mole of spins. If we put the $M_0$ into the normalization factor, then the elements $M_{0i}$ of vector $M_0$ can be represented by an initial population $p_i = n_i x_i$. 


The first $\pi/2$ pulse converts $M_0$ into $M^*$

$$M^*(t_1 = 0) = M_0. \quad (19)$$

The evolution of $M^*$ is governed by equation (8), with the solution

$$M^*(t_1) = \exp \{ L^* t_1 \} M_0. \quad (20)$$

The second $\pi/2$ pulse then converts $M^*(t_1)$ into $M_z$

$$M_z(\tau_m = 0) = M^*(t_1). \quad (21)$$

The dynamics of $M_z$ is governed by equation (9) with $\Delta M_z(\tau_m) = M_z(\tau_m) - M_0$, and its solution is expressed as

$$M_z(\tau_m) = M_0 + \exp \{ L \tau_m \} \Delta M_z(\tau_m = 0). \quad (22)$$

Finally, the last $\pi/2$ pulse converts $M_z(\tau_m)$ into $M^*$ again

$$M^*(t_2 = 0) = M_z(\tau_m). \quad (23)$$

The overall time dependence can be summed up by combining the above equations into the expression

$$M^*(t_1, \tau_m, t_2) = \exp \{ L^* t_2 \} [1 - \exp \{ L \tau_m \} (1 + \exp \{ L^* t_1 \})] M_0. \quad (24)$$

Terms which do not depend on $t_1$ give the so-called "axial peaks" at $\omega_1 = 0$. They are usually eliminated by alternation of the phase of the first $\pi/2$ pulse and of the receiver reference phase. The remainder take the form

$$M^*(t_1, \tau_m, t_2) = \exp \{ L^* t_2 \} \exp \{ L \tau_m \} \exp \{ L^* t_1 \} M_0 \quad (25)$$

Before we Fourier transform equation (25) from the time-domain to the frequency-domain, we need to make another assumption, that of slow exchange, to simplify it. The matrix $L^*$, as expressed in equation (10) $L^* = i\Omega - \Lambda + K$, contains the exchange matrix $K$. The slow exchange assumption assumes that the elements $k$ of
$K$ are not large, so that the lineshapes are not noticeably affected by $K$ - the transport of transverse magnetization from one site to another. Mathematically, it can be expressed as

$$L^* = i\Omega - \Lambda.$$  \hspace{1cm} (26)

As a result, matrix $L^*$ is diagonal and equation (25) can be simplified to

$$M^*(t_1, \tau_m, t_2) = \sum \exp\{(i\Omega - \lambda_i)t_1\} \exp\{iL\tau_m\} \exp\{(i\Omega - \lambda_j)t_i\} M_{ij}.$$  \hspace{1cm} (27)

After 2D Fourier transformation, the integrated amplitude of a signal with frequency coordinates $(\omega_1, \omega_2) = (\Omega, \Omega)$ is

$$I_j(\tau_m) = \exp\{iL\tau_m\} M_j.$$  \hspace{1cm} (28)

This can been written in matrix form

$$I(\tau_m) = \exp\{iL\tau_m\} P$$  \hspace{1cm} (29)

where $I$ is the intensity matrix, and the element $P_n$ of diagonal matrix $P$ is $M_n$ that corresponds to the population $p_n$. Equation (29) is the master equation of 2D-EXSY.

Several mathematical results, which can be formally proved, are given below.

1. If the matrix $I$ is multiplied by an arbitrary normalization factor $\alpha$, the $K_{ij}$ obtained from equation (29) will not be affected; only $T_{ij}$ will be affected.

2. The matrix $I$ is always symmetric, i.e. $I = I^\top$. Therefore spectra can been symmetrized prior to analysis.

3. $I_j / I_k = K_{ij}p_j / K_{ik}p_k$ if $\tau_m$ is small, and $I_j / I_k = p_j / p_k$ if $\tau_m$ is large for $j \neq i,k$.

Rate constants can been extracted from 2D-EXSY spectra through equation (29). Three strategies have been employed to tackle the problem.
1. Linear approximation. When $\tau_m$ is small, equation (29) can be simplified as a linear matrix equation

$$I(\tau_m) = (1 + L\tau_m)M_0$$

(30)

which can be easily solved.

2. Direct matrix transformation.\textsuperscript{15} If matrix $IP^t$ is diagonalized into $XAX^{-1}$, then equation (29) can be written as

$$L\tau_m = \ln\{IP^t\} = \ln\{XAX^{-1}\} = X\{\ln\Lambda\}X^{-1}.$$ \hspace{1cm} (31)

For a $n$-site system, $n(n+1)/2$ unknowns ($n(n-1)/2$ rate constants and $n$ relaxation constants) in the $n \times n$ $L$ matrix can be determined by $n(n+1)/2$ independent intensity elements in the $I$ matrix. Thus, it is possible to extract the complete $K$ information from the complete $I$ data at only one optimized mixing time, $\tau_m$. When the dynamic range of $K$ is too large, an iterative fitting with several $\tau_m$ will improve the results.

3. Iterative fitting.\textsuperscript{16} In this case, several $I(\tau_m)$ matrices at different $\tau_m$ points are used to calculate one $L$ matrix through iterative fitting. This, of course, will improve the results. The fitting is driven by a program that finds a minimum of a function of several variables. The equation (29) is solved by diagonalizing the $L$ matrix. A careful intensity normalization is important for fitting, because the intensities at different $\tau_m$ are compared.

With the development of numerical calculation and NMR technology, the matrix calculation and the data collection of 2D NMR spectra are no longer difficult problems. 2D-EXSY NMR has advantages over 1D NMR. It can handle a complicated exchange system with a large number of spin sites and with a large dynamic range,
because of its complete information and its sensitivity. It is also possible to study partially overlapping spectra, where selective excitation is not possible.

2. Exchange in Coupled Spin Systems

In systems with resolved couplings, not only chemical exchange and relaxation, but also coherence transfer caused by couplings, contribute to the spin dynamics. A density operator treatment based on equation (12) is required, and has been presented\textsuperscript{17} by Ernst in detail. The zero-, single- and multiple-order coherences cause J cross-peaks in 2D-EXSY spectra. Different methods have been used to eliminate the J cross-peaks caused by different order coherences.

1. J cross-peaks caused by single-, double- and higher-order coherences can be suppressed either by applying a magnetic field gradient pulse or by phase-cycling techniques. A magnetic field gradient pulse applied in the course of the mixing period defocuses single- and higher-order coherences and thus suppresses them. However, it does not affect longitudinal magnetization nor does the zero-quantum coherence. This pulse may interfere with the NMR system. It is often more convenient to apply phase-cycling techniques.

Phase-cycling techniques add the responses to the phase-cycling pulse sequence to eliminate undesired responses. For example, the 16 phase-cycling pulse sequence\textsuperscript{18} can eliminate the single- and higher-order coherences, eliminate the axial peaks with \( \omega_1 = 0 \), and achieve phase sensitive spectra with high resolution. Another phase-cycling pulse sequence involving time-proportional phase increments (TPPI)\textsuperscript{19} also functions in the same way.
2. Zero-order J cross-peaks can be suppressed either by variation of mixing time $\tau_m$ or by partial refocusing. The partial refocusing technique inserts a $\pi$ pulse into the mixing period at a random position to eliminate the zero-order coherence by addition of a sufficient number of experiments. Random variation of $\tau_m$ in a range or random variation of $\tau_m$ with $t_1$ can also suppress zero-order coherence.

For practical realizations of 2D-EXSY, the phase-cycling pulse sequences are often used in combination with randomized $\tau_m$. J cross-peaks can be eliminated by these techniques, except for systems with strong couplings. After the elimination of the J cross-peaks, the system with resolved couplings has been reduced to a system without resolved couplings. Its 2D-EXSY data thus can be described by equation (29), and the data analysis is the same for the system without resolved coupling.

3. Future Trends

The progress in NMR and computer techniques not only gives 2D-EXSY advantages over 1D-DNMR, but also makes higher-dimensional NMR possible. 3D NMR experiments have gradually emerged in recent years. One reported 3D-EXSY-EXSY experiment involves a study of heptamethylbenzenonium sulphate in sulphuric acid, where the 1,2-methyl group commutations round the ring were monitored. Many 3D-NOESY-NOESY experiments, which have the same pulse sequence as 3D-EXSY-EXSY, have been used to elucidate macro-molecular structures. The 3D-NOESY-NOESY NMR can give more direct and well resolved information than the 1D and 2D experiments.
Sorensen\textsuperscript{23} has speculated about the potential feasibility and practical importance of higher-dimensional NMR. He has argued that two is a natural number of dimensions in time-domain spectroscopy, and a higher-dimensional spectrum, in principle, does not contain any information that can not be extracted from a set of individual 2D spectra.

For studies of chemical exchange in lower-molecular-weight species, 2D-EXSY methods are not likely to be superseded in the near future. One single 2D-EXSY spectrum at optimized mixing time $\tau_m$ will give all exchange information in most cases. If the dynamic range of the exchange matrix is large, several 2D-EXSY spectra at different $\tau_m$ will improve the result through data fitting.

F. Relaxation and Molecular Dynamics

The relaxation of isolated nuclear spin systems can be described by the Bloch equation (1). The relaxations times, $T_1$ and $T_2$, have been introduced on purely phenomenological grounds, and can be measured by experiments. To understand the relation between relaxation times and molecular dynamics, a detailed relaxation mechanism study should be performed by a quantum mechanical formalism. There are three different levels of quantum-mechanical descriptions:\textsuperscript{24,25} transition probabilities, semi-classical relaxation theory and quantum-mechanical relaxation theory. The transition probabilities theory, like the absorption theory in optics, calculates the transition probabilities between different energy levels with second-order perturbation theory. Therefore, it can easily describe the spin-lattice relaxation, but not the transverse relaxation, which requires a more fundamental density operator treatment.
The semi-classical relaxation theory, which is the most useful approach, describes the evolution of the spin system with density operators, but treats the influence of the surroundings as fluctuating random processes. Quantum-mechanical relaxation theory describes both the spin system and surroundings quantum mechanically. It can lead to a detailed understanding of the origin of the relaxation, but is usually too complicated to be applied. The results of the semi-classical relaxation theory are summarized below.

1. Semi-classical Relaxation Theory

The interactions between the spin system and the surroundings are described as fluctuating random processes, and are written in the irreducible tensor form

$$H(t) = \sum F^{(q)}(t) A^{(q)}$$

where $A^{(q)}$ are operators acting on the spin system only, and $F^{(q)}(t)$ are random processes representing the lattice dynamics. The random processes $F^{(q)}(t)$ are characterized by the spectral density functions

$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} d\tau F^{(q)}(0)F^{(q)}(\tau) \exp(-i\omega \tau) = \int_{-\infty}^{\infty} d\tau g^{(q)}(\tau) \exp(-i\omega \tau)$$

where $g^{(q)}(\tau)$ are correlation functions. These functions for small molecules can be correctly described with a single correlation time $\tau_c$, while the ones for macromolecules can only be described with more than one correlation time. After considerable assumption and manipulation, one finds the expression for the relaxation superoperator $\Gamma(\sigma^*)$ as
\[
\frac{d}{dt} \sigma^* = \Gamma(\sigma^* - \sigma_0) = \frac{1}{2} \sum_i \sum_p J^{(q)(p)}(\omega_i) [A_p^{(q)}, [A_p^{(q)}, \sigma^* - \sigma_0]]
\]  \tag{34}

where \(\sigma^*\) is the transformed density matrix, \(\sigma_0\) is the equilibrium density matrix, and operators \(A^{(q)}\) are expressed by the eigenoperators \(A_p^{(q)}\) of the Hamiltonian superoperator.

If a given operator \(Q\) acts on the variables of the spin system, the quantity observed in an experiment performed on a macroscopic sample containing a collection of the systems can be expressed in transformed form

\[
\langle Q \rangle^* = \text{tr}\{\sigma^*(t)Q\}.  \tag{35}
\]

From equations (34) and (35), we get

\[
\frac{d}{dt} \langle Q \rangle^* = -\{\text{tr}\{\Gamma(\sigma) \sigma^*\}^* - \text{tr}\{\Gamma(\sigma) \sigma_0\}\}.  \tag{36}
\]

The \(T_1\) and \(T_2\) in the Bloch equation (1) can be calculated for a specific relaxation mechanism from the above equation, when \(Q\) is \(M_z\) and \(M_{xy}\), respectively.

2. Relaxation Mechanisms

Relaxation mechanisms can be classified as either first- or second-rank according to the rank of operator \(A\) in the Hamiltonian \(H_i(t)\). First-rank interactions include Zeeman, spin-rotation, scalar coupling and intermolecular dipole interactions. Second-rank interactions include intramolecular dipole (D), quadrupole (Q) and chemical shielding anisotropy (CSA) interactions. All these interactions may contribute to the overall relaxation process, and the experimental relaxation rate is usually assumed to be a simple summation of the specific rates of all the mechanisms.
involved, which is equivalent to the assumption that the $H_i$ of different interactions are orthogonal to each other. The expressions for the relaxation rate caused by different mechanisms have been reviewed. They have differing dependence on temperature, magnetic field strength and other parameters. Therefore, the relaxation caused by different mechanisms can be separated in some cases.

The cross-correlation caused by the mechanisms which have the same rank and comparable intensities is not negligible, especially when the molecular reorientation is not in the fast-motion limit. The studies of cross-correlation, which mainly includes D-D and D-CSA cross-correlation, are now being reported in ever increasing numbers.

3. Correlation Functions and Diffusion Coefficients

If random processes are characterized by the same correlation time, then the correlation functions are related to each other by

$$g^{(q)}(\tau) g^{(q')}(\tau) = \overline{F^{(q)}} \overline{F^{(q')}}.$$  \hspace{1cm} (37)

It is further assumed that the dependence of $g(\tau)$ on $\tau$ can be expressed as

$$g(\tau) \propto \exp(-|\tau|/\tau_c)$$  \hspace{1cm} (38)

where $\tau_c$ is the correlation time.

The theory relating $\tau_c$ to the diffusion coefficients was developed in the 1960's by Shimizu, Woessner and Huntress. The rotational diffusion of a rigid symmetric-top molecule can be described by perpendicular and parallel diffusion coefficients, $D_\perp$ and $D_\parallel$, which measure the rates of rotation perpendicular and parallel to the principle
axis, respectively. If the reorienting vector is oriented at an angle $\theta$ relative to the symmetry axis of the molecule, the correlation time $\tau_c$ will be given by$^{34}$

$$
\tau_c = \frac{A}{6D_{\perp}} + \frac{B}{5D_{\perp} + D_1} + \frac{c}{2D_{\perp} + 4D_1}
$$

where $A = (3\cos^2\theta - 1)^2/4$, $B = 3\sin^2\theta \cos^2\theta$ and $C = (3\sin^4\theta)/4$. If the reorienting vector has an internal rotation relative to the molecule framework, the internal rotation denoted as $R$ can be incorporated into the above equation to give another relation$^{34}$

$$
\tau_c = \frac{A}{6D_{\perp}} + \frac{B}{5D_{\perp} + D_1 + R} + \frac{c}{2D_{\perp} + 4D_1 + 4R}
$$

For a rigid asymmetric molecule, the anisotropic rotational diffusion can be described by three diffusion coefficients. The relation between the three diffusion coefficients and the correlation time has also been derived and applied with the aid of computer numerical calculations.$^{36}$ However, often we can approximate an asymmetric molecule as a pseudo-symmetric-top. In doing so, the problem will be simplified significantly and the results are still reasonable.
CHAPTER REFERENCES


8. Kleier, D. A.; Binsch, G. Program No. QCPE 365, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.


30. Yuan, P. *Raman and NMR Investigation of Molecular Reorientation and Internal Rotation in Liquids*, 1991, Ph.D. Dissertation, Univ. of North Texas, Denton, TX.


CHAPTER II

NMR STUDY OF REORIENTATIONAL DYNAMICS
IN TRANSITION METAL COMPLEXES

A. Introduction

The use of NMR relaxation measurements in exploring the solution structure of organometallic compounds has been demonstrated by several research groups. Our group has been concerned with the dynamics of internal rotation of capping benzylidyne and phenylphosphinidene groups in polynuclear clusters and the relationship between the adopted solution and solid-state cluster structures. Interestingly enough, no data exist on the barrier to internal rotation of the phenyl group in amido-capped clusters of the form $M_xL_n(\mu_3-NPh)$. Therefore, we decided to investigate the NMR spin-lattice relaxation times of the phenyl and terminal carbonyl $^{13}$C nuclei in $\text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-\text{NPh})$, and to compare the NMR results with those from the isolobally related tricobalt cluster $\text{Co}_3(\text{CO})_9(\mu_3-\text{CPh})$, which we have already studied.

The earlier NMR results showed that the phenyl ring rotation is free in some complexes, but is restrained by the internal rotation energy barrier in others. The origin of the barrier is an interesting subject. Chemists would always like to classify the interactions as either steric or electronic in nature, and then to explain and predict interactions in other systems. It is commonly believed that the internal rotation barrier
is mainly from the orbital interactions between the phenyl ring and the metal skeleton, and much effort has been made to explain the barrier as orbital interactions.\textsuperscript{8,9,10} However, not enough work has been done to explain the barrier as steric interactions.

To study further the internal rotation, we also decided to investigate the phenyl ring rotation in ReCo\textsubscript{2}(CO)\textsubscript{10}(\mu\textsubscript{3}-CPh) by measuring the NMR spin-lattice relaxation times of the phenyl ring. We tried to explain the internal rotation barriers through two different approaches: (a) intramolecular approach distances, (b) molecular orbital calculations. The molecular structures of Ru\textsubscript{3}(CO)\textsubscript{9}(\mu\textsubscript{3}-CO)(\mu\textsubscript{3}-NPh) and ReCo\textsubscript{2}(CO)\textsubscript{10}(\mu\textsubscript{3}-CPh) are shown below.
B. Experimental

1. Synthesis

Both clusters, Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-NPh) and ReCo$_2$(CO)$_{10}$(μ$_3$-CPh), were synthesized in Professor Michael G. Richmond's laboratory.

The amido Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-NPh) was prepared by using the thermolysis conditions reported by Gladfelter. Ru$_3$(CO)$_2$ was synthesized from RuCl$_3$·nH$_2$O using the high-pressure carbonylation procedure of Bruce. Nitrosobenzene and $^{13}$CO were purchased from Aldrich Chemical Co. and Isotec, respectively, and used as received. $^{13}$CO enriched Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-NPh) (ca. 15% enriched) was prepared from $^{13}$CO enriched Ru$_3$(CO)$_2$.

The carbyne ReCo$_2$(CO)$_{10}$(μ$_3$-CPh) was synthesized according to the procedure of Shaposhnikova by using PhCCRe(CO)$_5$ and Co$_2$(CO)$_4$. PhCCRe(CO)$_5$ was synthesized from Re(CO)$_3$Br and PhCCLi reported by Stone. Re(CO)$_3$Br was made by the bromination of Re$_2$(CO)$_{10}$ with bromine in THF.

2. NMR Experiments

All solvents and NMR tube preparations were carried out by using inert-atmosphere techniques. The solvents, CD$_2$Cl$_2$ and CDC$_1$$_3$, were bulb-to-bulb distilled from P$_2$O$_5$, followed by storage in Schlenk vessels equipped with Teflon stopcocks. All the NMR samples were prepared in 5 mm NMR tubes. The concentration of the $^{13}$C enriched sample of Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-NPh) for the T$_1$ measurements of the carbonyls was about 0.1 M, and the concentrations of non-enriched samples of both clusters for the T$_1$ measurements of the phenyl carbons were about 0.2 M.
$^{13}$C spin-lattice relaxation times were measured by using the standard IRFT pulse sequence, and the NOE were measured by the standard gated-decoupling pulse sequence. All $^{13}$C NMR spectra were recorded either on a Varian VXR-300 NMR spectrometer operating at 75.4 MHz or on a Varian Gemini-200 spectrometer operating at 50.3 MHz. Temperature was regulated by cooled gas flow and measured from the control panel after calibration with a methanol NMR thermometer.

3. Computations

The potential surface characterizing phenyl group internal rotation was calculated by using both the Fenske-Hall and Extended Hückel methods, and the intramolecular distances were measured by using the PC program MOBY. The Fenske-Hall calculations were performed on a DEC VAX 6310 minicomputer using the FORTRAN program FENHALL, and the Extended Hückel calculations were performed on a PC using the FORTRAN program CACAO. Using each method, the magnitude of the rotational barrier was obtained by calculating the energy at regular increments of the phenyl group angle relative to the skeleton, while keeping the other geometric parameters fixed at the values reported in the X-ray crystal structure.

C. Results of the NMR study

1. $\text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-N\text{Ph})$

$^{13}$C spin-lattice relaxation times and nuclear Overhauser enhancements of the ortho, meta and para carbons (at $\delta = 129.5, 126.1$ and 124.9 ppm downfield from TMS) were measured at a number of temperatures spanning the range from 175 K to
293 K in the solvent CD$_2$Cl$_2$. Measurements were performed at two magnetic field strengths: (a) $B_0 = 7.05$ T ($v_0(^{13}\text{C}) = 75.4$ MHz), and (b) $B_0 = 4.70$ T ($v_0(^{13}\text{C}) = 50.3$ MHz), on two different spectrometers, respectively. Additional phenyl group $T_1$ measurements were performed at several temperatures (at $B_0 = 7.05$ T) in the solvent CDCl$_3$. Relaxation times of the six equivalent equatorial carbonyls ($\delta = 192.3$ ppm at 210 K) and the three equivalent axial carbonyls ($\delta = 194.4$ ppm at 210 K) were also measured on both spectrometers at several temperatures in this range. The carbonyl measurements could not be performed at the lowest or highest temperatures due to low sensitivity (line broadening from shortened $T_2$) and peak coalescence of the axial and equatorial resonances (from chemical exchange), respectively. Measurements at several temperatures were repeated to ascertain reproducibility in the calculated diffusion coefficients.

Experimental relaxation times of the phenyl and CO carbons measured at both field strengths are presented in Table 1. Since the ortho and meta C-H bond vectors lie at 60° and 120° relative to the symmetry axis, their relaxation times should be equal. Hence, only the averages of the two measurements are given in the table and used in the analysis. The $T_1$ measurement of the axial carbonyls suffered from the low S/N ratio and is not acceptable. Therefore, only $T_1$ data of equatorial carbonyls was used and is presented in the table.

1.1 Reorientational Correlation Times

To determine the primary relaxation mechanism, the NOE's of the phenyl carbons were measured. It was found that, to within experimental error, the NOE's are
Table 1. \(^{13}\)C Relaxation Times [s] in Ru\(_3\)(CO)\(_6\)(\(\mu_3\)-CO)(\(\mu_3\)-NPh).

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Solvent</th>
<th>(T_{1OM})</th>
<th>(T_{1P})</th>
<th>(T_{1(CO)})</th>
<th>(B_0 = 7.05\ T)</th>
<th>(T_{1OM})</th>
<th>(T_{1P})</th>
<th>(T_{1(CO)})</th>
<th>(B_0 = 4.70\ T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>CD(_2)Cl(_2)</td>
<td>0.31</td>
<td>0.13</td>
<td>--</td>
<td>0.32</td>
<td>0.10</td>
<td>--</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>CD(_2)Cl(_2)</td>
<td>0.30</td>
<td>0.13</td>
<td>--</td>
<td>0.33</td>
<td>0.09</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td></td>
<td>0.38</td>
<td>0.14</td>
<td>--</td>
<td>0.36</td>
<td>0.11</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>184</td>
<td></td>
<td>0.41</td>
<td>0.15</td>
<td>0.36</td>
<td>--</td>
<td>--</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>184</td>
<td></td>
<td>0.40</td>
<td>0.15</td>
<td>0.34</td>
<td>--</td>
<td>--</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>193</td>
<td></td>
<td>0.63</td>
<td>0.18</td>
<td>0.55</td>
<td>--</td>
<td>--</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>205</td>
<td></td>
<td>0.92</td>
<td>0.23</td>
<td>0.82</td>
<td>0.89</td>
<td>0.21</td>
<td>1.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>217</td>
<td></td>
<td>1.25</td>
<td>0.28</td>
<td>1.15</td>
<td>1.20</td>
<td>0.28</td>
<td>2.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>236</td>
<td></td>
<td>2.07</td>
<td>0.44</td>
<td>2.17</td>
<td>2.13</td>
<td>0.48</td>
<td>4.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>268</td>
<td></td>
<td>3.69</td>
<td>0.78</td>
<td>--</td>
<td>3.92</td>
<td>0.78</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td></td>
<td>5.60</td>
<td>1.22</td>
<td>--</td>
<td>4.89</td>
<td>1.24</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td></td>
<td>5.39</td>
<td>1.19</td>
<td>--</td>
<td>4.88</td>
<td>1.23</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>217</td>
<td>CDCl(_3)</td>
<td>0.93</td>
<td>0.22</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>236</td>
<td></td>
<td>1.27</td>
<td>0.29</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td></td>
<td>4.48</td>
<td>1.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
complete \((\eta = \eta_{\text{max}} = 2.0)\), indicating that relaxation results entirely from dipolar coupling with the attached protons (i.e. \(T_1 = T_{1\text{DD}}\)).

The dipolar relaxation time \((T_{1\text{DD}})\) of a \(^{13}\text{C}\) nucleus with one attached proton may be expressed in terms of the rotational correlation time \((\tau_c)\) of the C-H bond vector as:

\[
\frac{1}{T_{1\text{DD}}} = \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{40 \pi^2 R_{CH}^6} \left[ \frac{\tau_c}{1 + (\omega_H - \omega_C)^2 \tau_c^2} + \frac{3 \tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6 \tau_c}{1 + (\omega_H + \omega_C)^2 \tau_c^2} \right].
\]

In this equation, \(\gamma_C\) and \(\gamma_H\) are the magnetogyric ratios of the \(^{13}\text{C}\) and \(^1\text{H}\) nuclei, \(\omega_C\) and \(\omega_H\) are their resonance frequencies, \(R_{CH}\) is the C-H bond length (1.08 \(\text{Å}\)) and \(\hbar\) is Planck's constant.

In the limiting case of complete motional narrowing, where \((\omega_H + \omega_C) \tau_c << 1\) (in which case the denominator, \(1 + (\omega_H + \omega_C)^2 \tau_c^2 \rightarrow 1\), as do the other denominators in the equation), the relaxation time becomes independent of the resonance frequency and equation (1) reduces to:

\[
\frac{1}{T_{1\text{DD}}} \rightarrow \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{4 \pi^2 R_{CH}^6} \tau_c.
\]

Equation (2) may be used to obtain \(\tau_c\) directly from \(T_{1\text{DD}}\) in solutions of small to
medium size molecules at moderate temperatures. However, in systems in which the motional narrowing condition is not satisfied, application of the latter equation results in serious errors (vide infra) in the calculated correlation times and derived diffusion coefficients. In these situations, one must calculate the correlation time by a fit, via non-linear regression, of the experimental data with equation (1). Correlation times for the ortho/meta ($\tau_{OM}$) and para ($\tau_p$) carbons at both magnetic fields, calculated from the former equation, are displayed in Table 2.

The primary relaxation mechanism of the carbonyl carbons is by Chemical Shift Anisotropy ($T_{1CSA}$), with smaller contributions from other mechanisms ($T_{10}$), such as spin-rotation and intermolecular dipole-dipole relaxation. The general equation for the relaxation time of these nuclei is given by:\textsuperscript{26}

$$\frac{1}{T_1} = \frac{1}{T_{1CSA}} + \frac{1}{T_{10}} = \frac{2}{15} \frac{\omega_c^2 \Delta \sigma^2 \tau_c}{1 + \omega_c^2 \tau_c^2} + \frac{1}{T_{10}}. \quad (3)$$

In this equation, $\tau_c$ is the correlation time characterizing rotation of the CO bond vector, and $\Delta \sigma$ is the anisotropy in the chemical shift. For the equatorial carbonyls in Ru$_3$(CO)$_5$(μ$_2$-CO)(μ$_3$-NPh), using standard procedures,$^5$ one finds $\Delta \sigma = 406$ ppm. Equation (3) contains the two unknown quantities, $\tau_c$ and $T_{10}$. Therefore, calculation of the correlation time requires measurement of $T_1$ at two resonance frequencies. One may then solve the two resulting equations iteratively to obtain $\tau_c$ and $T_{10}$. The resulting carbonyl correlation times, $\tau_{CO}$, are presented in Table 2.
Table 2  Rotational Correlation Times and Diffusion Coefficients in Ru₃(CO)₆(μ₁-CO)(μ₁-NPh)

A.  B₀ = 7.05 T

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Solvent</th>
<th>τ_{DOM} [ps]</th>
<th>τ_{IP} [ps]</th>
<th>τ₃(CO) [ps]</th>
<th>Dₛ [ns⁻¹]</th>
<th>χ⁺</th>
<th>Dₛ(MN) [ns⁻¹]</th>
<th>Dₛ [ns⁻¹]</th>
<th>Dₛ(Benz) [ns⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.</td>
<td>CD₂Cl₂</td>
<td>157.</td>
<td>679.</td>
<td>--</td>
<td>0.25</td>
<td>3.6</td>
<td>0.50</td>
<td>--</td>
<td>3.6</td>
</tr>
<tr>
<td>175.</td>
<td>158.</td>
<td>732.</td>
<td>--</td>
<td>0.23</td>
<td>4.0</td>
<td>0.49</td>
<td>--</td>
<td>3.6</td>
<td>7.3</td>
</tr>
<tr>
<td>180.</td>
<td>121.</td>
<td>602.</td>
<td>--</td>
<td>0.28</td>
<td>3.0</td>
<td>0.52</td>
<td>--</td>
<td>4.8</td>
<td>8.7</td>
</tr>
<tr>
<td>184.</td>
<td>117.</td>
<td>479.</td>
<td>581.</td>
<td>0.35</td>
<td>2.3</td>
<td>0.57</td>
<td>0.21</td>
<td>4.7</td>
<td>10.</td>
</tr>
<tr>
<td>184.</td>
<td>111.</td>
<td>487.</td>
<td>679.</td>
<td>0.34</td>
<td>2.3</td>
<td>0.57</td>
<td>0.14</td>
<td>5.1</td>
<td>10.</td>
</tr>
<tr>
<td>193.</td>
<td>71.</td>
<td>316.</td>
<td>349.</td>
<td>0.53</td>
<td>1.6</td>
<td>0.70</td>
<td>0.41</td>
<td>7.9</td>
<td>13.</td>
</tr>
<tr>
<td>205.</td>
<td>48.</td>
<td>228.</td>
<td>234.</td>
<td>0.73</td>
<td>1.3</td>
<td>0.87</td>
<td>0.69</td>
<td>12.</td>
<td>19.</td>
</tr>
<tr>
<td>217.</td>
<td>35.</td>
<td>176.</td>
<td>170.</td>
<td>0.95</td>
<td>1.2</td>
<td>1.1</td>
<td>1.0</td>
<td>17.</td>
<td>25.</td>
</tr>
<tr>
<td>236.</td>
<td>21.</td>
<td>104.</td>
<td>83.</td>
<td>1.6</td>
<td>1.1</td>
<td>1.7</td>
<td>2.7</td>
<td>27.</td>
<td>38.</td>
</tr>
<tr>
<td>268.</td>
<td>12.</td>
<td>57.</td>
<td>--</td>
<td>2.9</td>
<td>1.0</td>
<td>3.0</td>
<td>--</td>
<td>48.</td>
<td>67.</td>
</tr>
<tr>
<td>293.</td>
<td>7.9</td>
<td>36.</td>
<td>--</td>
<td>4.6</td>
<td>1.0</td>
<td>4.6</td>
<td>--</td>
<td>73.</td>
<td>96.</td>
</tr>
<tr>
<td>293.</td>
<td>8.2</td>
<td>37.</td>
<td>--</td>
<td>4.5</td>
<td>1.0</td>
<td>4.6</td>
<td>--</td>
<td>69.</td>
<td>96.</td>
</tr>
</tbody>
</table>

217.  CDCl₄ | 47.3 | 232. | -- | 0.72 | 1.3 | 0.86 | -- | 13. | 17. |
236.  | 34.9 | 165. | -- | 1.0 | 1.2 | 1.1 | -- | 16. | 26. |
293.  | 9.83 | 43.  | -- | 3.9 | 1.0 | 3.9 | -- | 57. | 67. |
Table 2. (Cont'd.)

B. $B_0 = 4.70$ T

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Solvent</th>
<th>$\tau_{\text{comp}}$ [ps]</th>
<th>$\tau_{\text{MP}}$ [ps]</th>
<th>$\tau_{\text{A}}$ (CO) [ps]</th>
<th>$D_1$ [ns$^{-1}$]</th>
<th>$\chi^2$</th>
<th>$D_1$(MN) [ns$^{-1}$]</th>
<th>$D_1$ [ns$^{-1}$]</th>
<th>$D_3$ [ns$^{-1}$]</th>
<th>$D_3$(benz) [ns$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.</td>
<td>CD$_2$Cl$_2$</td>
<td>140.</td>
<td>759.</td>
<td>--</td>
<td>0.22</td>
<td>2.4</td>
<td>0.37</td>
<td>--</td>
<td>4.3</td>
<td>7.3</td>
</tr>
<tr>
<td>175.</td>
<td></td>
<td>137.</td>
<td>824.</td>
<td>--</td>
<td>0.20</td>
<td>2.7</td>
<td>0.36</td>
<td>--</td>
<td>4.5</td>
<td>7.3</td>
</tr>
<tr>
<td>180.</td>
<td></td>
<td>126.</td>
<td>595.</td>
<td>--</td>
<td>0.28</td>
<td>1.9</td>
<td>0.41</td>
<td>--</td>
<td>4.6</td>
<td>8.7</td>
</tr>
<tr>
<td>184.</td>
<td></td>
<td>--</td>
<td>--</td>
<td>581.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>184.</td>
<td></td>
<td>--</td>
<td>--</td>
<td>679.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>193.</td>
<td></td>
<td>--</td>
<td>--</td>
<td>349.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.41</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>205.</td>
<td></td>
<td>50.</td>
<td>228.</td>
<td>234.</td>
<td>0.73</td>
<td>1.1</td>
<td>0.80</td>
<td>0.69</td>
<td>12.</td>
<td>19.</td>
</tr>
<tr>
<td>217.</td>
<td></td>
<td>37.</td>
<td>164.</td>
<td>170.</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
<td>15.</td>
<td>25.</td>
</tr>
<tr>
<td>236.</td>
<td></td>
<td>21.</td>
<td>93.</td>
<td>83.</td>
<td>1.8</td>
<td>1.0</td>
<td>1.8</td>
<td>2.7</td>
<td>27.</td>
<td>38.</td>
</tr>
<tr>
<td>268.</td>
<td></td>
<td>11.</td>
<td>57.</td>
<td>--</td>
<td>2.9</td>
<td>1.0</td>
<td>3.0</td>
<td>--</td>
<td>52.</td>
<td>67.</td>
</tr>
<tr>
<td>293.</td>
<td></td>
<td>9.0</td>
<td>36.</td>
<td>--</td>
<td>4.7</td>
<td>1.0</td>
<td>4.7</td>
<td>--</td>
<td>60.</td>
<td>96.</td>
</tr>
<tr>
<td>293.</td>
<td></td>
<td>9.0</td>
<td>36.</td>
<td>--</td>
<td>4.6</td>
<td>1.0</td>
<td>4.7</td>
<td>--</td>
<td>60.</td>
<td>96.</td>
</tr>
</tbody>
</table>

\[ a) \chi = 1 + (\omega_{\text{H}} + \omega_{\text{C}})^2 \tau_{\text{A}}^2. \]
In the motional narrowing limit, for which $\omega_c\tau_c << 1$, equation (3) reduces to:

$$\frac{1}{T_1} = \frac{1}{T_{1CSA}} + \frac{1}{T_{10}} = \frac{2}{15} \omega_c^2 \Delta \sigma^2 \tau_c + \frac{1}{T_{10}}. \quad (4)$$

In this limiting regime, one may solve explicitly for $\tau_c$ as a function of the measured $T_1$'s at two resonance frequencies. Although not shown, correlation times calculated from the latter equation are close to identical to values obtained without the assumption of motional narrowing at all temperatures. This is not at all surprising since $T_{1CSA}$ depends only upon $\omega_c$ rather than the much larger sum, $\omega_{H} + \omega_c$, which appears in the equation for $^{13}$C dipole-dipole relaxation (equation (1)).

1.2 Molecular Reorientation

The reorientational correlation time of a vector (e.g. CH or CO) in a symmetric top molecule is dependent upon $\theta$, the angle of the vector with respect to the symmetry axis and upon the two diffusion coefficients, $D_{\perp}$ and $D_{\parallel}$, which measure the rates of rotation perpendicular (tumbling) and parallel to the principal axis, respectively:

$$\tau_c(\theta) = \frac{A(\theta)}{6D_{\perp}} + \frac{B(\theta)}{5D_{\perp}D_{\parallel}} + \frac{C(\theta)}{2D_{\perp}D_{\parallel} + 4D_{\parallel}}. \quad (5)$$

In this equation, $A(\theta) = (1/4)(3 \cos^2 \theta - 1)^2$, $B(\theta) = 3 \sin^2 \theta \cos^2 (\theta)$, and

$C(\theta) = (3/4)\sin^4 (\theta)$. 
The CH vector of the phenyl group’s para carbon lies along the symmetry axis \( (\theta = 0^\circ) \), in which case \( B(\theta) = C(\theta) = 0 \) and \( A(\theta) = 1 \). Therefore, the diffusion coefficient characterizing molecular tumbling can be determined directly via the simple relation, \( D_x = \left( 6 \tau_p \right)^{-1} \). Resulting values are displayed in the sixth column of Table 2 and plotted in Figure 4 (\( B_o = 7.05 \) T - open circles; \( B_o = 4.70 \) T - open squares). One sees from the figure that diffusion coefficients calculated at both magnetic fields are generally in excellent agreement with each other, and exhibit Arrhenius behavior, with an activation energy, \( E_a(D_x) = 2.6 \pm 0.1 \) kcal/mol.

As noted in the previous section, if \( 1 + (a + \omega_c)^2 \tau_c^2 \to 1 \), then the system is in the motional narrowing regime, and one may then use the simpler equation (2) to calculate the correlation times. However, as shown in the seventh column of Table 2, the values of this quantity (denoted as \( \chi \) in the table) evaluated using \( \tau_p \) are markedly greater than unity at the lower temperatures, particularly at the higher resonance frequency. To illustrate the errors introduced by incorrectly assuming motional narrowing, we have calculated values of \( \tau_c \) from equation (2) (not shown) and derived diffusion coefficients \( D_x (MN) \) assuming the limiting case. The results are displayed in the table and in Figure 4 (\( B_o = 7.05 \) T - filled circles; \( B_o = 4.70 \) T - filled squares). It is quite clear from the figure that the incorrect assumption of complete motional narrowing leads to calculated diffusion coefficients that are in marked error, by as much as a factor of two. Further, computed values falsely exhibit a dependence upon resonance frequency. One concludes that, prior to using the limiting equation (equation (2)) to determine correlation times, one should either measure the relaxation times at two field strengths.
Figure 4. Temperature dependence of the perpendicular "tumbling" diffusion coefficient, $D_{\perp}$. Complete analysis at $B_{\parallel}=7.05$ T (○); Complete analysis at $B_{\parallel}=4.70$ T (□); Motionally narrowed analysis at $B_{\parallel}=7.05$ T (●); Motionally narrowed analysis at $B_{\parallel}=4.70$ T (■).
to determine if $T_1$ is frequency independent, or compare results using the complete and motionally narrowed equation.

Determination of $D_p$, the diffusion coefficient characterizing rotation of the molecule about the symmetry axis, requires measurement of the correlation time of a vector at a second angle with respect to the axis. The equatorial CO bonds are reported\textsuperscript{29} to lie at an angle, $\theta = 65.6^\circ$. Therefore, $\tau_{\text{CO}}$ was used in equation (5), together with calculated values of $D_x$, to obtain the parallel diffusion coefficients as a function of temperature; the results are presented in Table 2. Since the determination of $\tau_{\text{CO}}$ requires use of the measured $T_1$ at both field strengths, only one value of $D_1$ is obtained at each temperature.

It is seen from the table that $D_1$ varies from somewhat lower than $D_x$ at the lowest measurable temperature to somewhat greater at the highest accessible temperature, and exhibits an activation energy, $E_a = 4.2 \pm 0.7$ kcal/mol. The rather large error estimate arises from the greater imprecision in measurement of $T_1$(CO) resulting from lower sensitivity and from the experimentally limited range in temperature (\~50 K). Because of the large error, the authors hesitate to assign any significance to differences in the two diffusion coefficients characterizing overall molecular reorientation and conclude only that $D_1 \approx D_x$.

1.3 Phenyl Ring Rotation

The phenyl group's meta and ortho CH vectors lie at (equivalent) angles of $60^\circ$ and $120^\circ$ with respect to the symmetry axis. Thus, the dipolar relaxation is dependent upon the molecular tumbling rate, $D_x$, and upon the total rate at which the group
'spins' about the N-C axis. The diffusion coefficient $D_S$, governing the latter motion, is given by the sum of $D_I$ and $R$, the rate of internal rotation relative to the molecular skeleton; $D_S = D_I + R$. It has been shown that the expression governing relaxation in this case is identical to equation (5), with $D_I$ replaced by $D_S$.

The experimental ortho/meta rotational correlation times, $\tau_{OM}$, have been fitted with the modified form of the equation to yield the phenyl group spinning diffusion coefficient as a function of temperature and magnetic field strength; the results are displayed in the penultimate column of Table 2 and plotted in Figure 5 (in the solvent CD$_2$Cl$_2$). As expected, values of $D_S$ obtained at both values of $B_0$ are equal to within experimental error. Significantly, $D_S$ is at all temperatures at least an order of magnitude greater than either $D_\tau$ or $D_I$, indicating that this motion and, thus, the internal rotation, $R (=D_S\cdot D_I)$, is much more rapid than the overall molecular reorientation.

In order to ascertain whether there exists any barrier to internal rotation of the phenyl group, it is informative to compare $D_S$ to the rate of the equivalent rotation of benzene itself (about its C$_2$ axis) dissolved in the same solvent, CD$_2$Cl$_2$. These values are presented in the last column of Table 2 ($D_S$(Benz)) and plotted in Figure 5 (solid line). One observes from both the table and figure that the spinning rates in free benzene are somewhat greater (by 20%-100%) than the values in Ru$_3$(CO)$_6$(µ$_3$-CO)(N-Ph). This result is in contrast to that found earlier in the isolobal benzylidyne complex, Co$_3$(CO)$_6$(µ$_3$-Ph), where $D_S \approx D_S$(Benz) at all temperatures, indicating that there is no barrier to internal rotation. This comparison implies that there is, indeed, a small
Figure 5. Temperature dependence of the "spinning" diffusion coefficient, $D_s$: (A) Experimental data for $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_1-\text{NPh})$ in $\text{CD}_2\text{Cl}_2$ - Complete analysis at $B_0=7.05$ T (○); Complete analysis at $B_0=4.70$ T (□); (B) Free benzene in $\text{CD}_2\text{Cl}_2$. 
barrier to internal rotation in the amido complex studied here. However, the earlier investigation was performed in the solvent CDCl₃. Therefore, we reinvestigated the rotational dynamics of Ru₃(CO)₉(μ₃-CO)(μ₃-NPh) at several temperatures in this solvent, the results are shown in the last three rows of Table 2. Once again, it is found that D₃(Benz)/D₃ > 1. Therefore, it may be concluded that, in contrast to the earlier study, there is a small, but measurable barrier to internal rotation of the phenyl group in the amido-capped tri-ruthenium complex. One may obtain a rough estimate of the barrier via a semi-logarithmic fit of a plot of ln(R) vs. 1000/T (not shown), from which one obtains the result that the barrier height is V₀ ≈ 2.5 ± 0.1 kcal/mol. One must note, though, that the net barrier consists of the sum of contributions from viscous drag, V₀(Visc), and from intramolecular (electronic and/or steric) interactions, V₀(intra). If one takes V₀(Visc) to be equal to the activation energy for T/η, then V₀(Visc) ≈ 2.2 kcal/mol. Therefore, the intramolecular barrier to phenyl group rotation is approximately V₀(intra) ≈ 0.3 kcal/mol.

2. ReCo₅(CO)₁₀(μ₃-CPh)

¹³C spin-lattice relaxation times and nuclear Overhauser enhancements of the ortho, meta and para carbons (at δ = 131.2, 128.6 and 130.4 ppm downfield from TMS, respectively) were measured at a number of temperatures spanning the range from 210 K to 294 K in the solvent CD₂Cl₂. Measurements were performed on a Varian VXR-300 FT-NMR spectrometer operating at 75.4 MHz for ¹³C, and the T₁ values are presented in Table 3. Since the ortho and meta C-H bond vectors lie at 60° and 120° relative to the symmetry axis, their relaxation times should be equal. Hence,
Table 3. $^{13}$C Relaxation Times, Rotational Correlation Times and Diffusion Coefficients in ReCo$_2$(CO)$_{10}(\mu_3$-CPh) in Solvent CD$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$T_{1OM}$ [s]</th>
<th>$T_{1P}$ [s]</th>
<th>$\tau_{1OM}$ [ps]</th>
<th>$\tau_{1P}$ [ps]</th>
<th>$D_\perp$ [ns$^{-1}$]</th>
<th>$D_\parallel$ [ns$^{-1}$]</th>
<th>$D_z$(Benz) [ns$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>210.</td>
<td>0.40</td>
<td>0.3</td>
<td>116.</td>
<td>160.</td>
<td>1.04</td>
<td>2.26</td>
<td>21.</td>
</tr>
<tr>
<td>222.</td>
<td>0.51</td>
<td>0.38</td>
<td>88.</td>
<td>124.</td>
<td>1.35</td>
<td>3.02</td>
<td>28.</td>
</tr>
<tr>
<td>245.</td>
<td>0.97</td>
<td>0.65</td>
<td>46.</td>
<td>69.</td>
<td>2.41</td>
<td>6.27</td>
<td>45.</td>
</tr>
<tr>
<td>268.</td>
<td>1.38</td>
<td>0.96</td>
<td>32.</td>
<td>46.</td>
<td>3.58</td>
<td>8.65</td>
<td>67.</td>
</tr>
<tr>
<td>294.</td>
<td>2.11</td>
<td>1.49</td>
<td>21.</td>
<td>30.</td>
<td>5.61</td>
<td>12.9</td>
<td>96.</td>
</tr>
</tbody>
</table>

$E_a$ [kcal/mol]$^a$

2.5 ± 0.1  2.6 ± 0.1

---

$a$) $E_a$ is obtained from the Arrhenius plot of lnD vs. 1/T.
only the averages of the two measurements are given in the table and used in the
analysis. The relaxation times of the carbonyl carbons were not measured because of
the broad peaks caused by the strong couplings between C-Co and between C-Re.

The NOE's of these three phenyl carbons were found to be complete ($\eta = \eta_{\text{max}}$
= 2.0) within experimental error, indicating that relaxation results entirely from dipolar
coupling with the attached protons (i.e. $T_1 = T_{1\text{DD}}$).

This cluster is not a perfect symmetric top molecule. Measured from its X-ray
structure, the two semi-axis lengths of its volume ellipsoid in the ReCo$_2$ plane are
very close to each other (b ≈ 5.0 Å and c ≈ 4.7 Å), and are a little shorter than the
unique axis length (a ≈ 5.7 Å). Therefore, this molecule may be treated as a pseudo-
symmetric top. By using the same procedure as we used before in Ru$_3$(CO)$_9$(\text{\textmu}$_3$-
CO)(\text{\textmu}$_\text{NPh}$), the dipolar relaxation times of the para phenyl carbon were used to
calculate the overall tumbling coefficient, $D_\perp$, of the complex. This value, together
with the average relaxation time of ortho and meta phenyl carbons, permits
determination of the total spinal diffusion coefficient, $D_s$, of the phenyl ring. As
discussed before, $D_s$ is composed of contributions from overall parallel reorientation,
$D_p$, of the cluster’s framework and from the internal rotation, $R$, of the phenyl ring
relative to the skeleton. The calculated values of both $D_\perp$ and $D_s$ at different
temperatures are present in Table 3 and plotted in Figure 6. One sees from the figure
that both diffusion coefficients, $D_\perp$ and $D_s$, exhibit Arrhenius behavior with activation
energies, $E_a(D_\perp) = 2.5 \pm 0.1$ kcal/mol and $E_a(D_s) = 2.6 \pm 0.1$ kcal/mol, respectively.
One also finds that $D_s$ is only about two times larger than $D_\perp$. This is different from
a pseudo-symmetric top. By using the same procedure as we used before in Ru$_3$(CO)$_9(\mu_3$-CO)(μ$_3$-NPh), the dipolar relaxation times of the para phenyl carbon were used to calculate the overall tumbling coefficient, D$_t$, of the complex. This value, together with the average relaxation time of ortho and meta phenyl carbons, permits determination of the total spinal diffusion coefficient, D$_s$, of the phenyl ring. As discussed before, D$_s$ is composed of contributions from overall parallel reorientation, D$_\parallel$, of the cluster's framework and from the internal rotation, R, of the phenyl ring relative to the skeleton. The calculated values of both D$_\parallel$ and D$_s$ at different temperatures are present in Table 3 and plotted in Figure 6. One sees from the figure that both diffusion coefficients, D$_\parallel$ and D$_s$, exhibit Arrhenius behavior with activation energies, $E_a(D_\parallel) = 2.5 \pm 0.1$ kcal/mol and $E_a(D_s) = 2.6 \pm 0.1$ kcal/mol, respectively. One also finds that D$_s$ is only about two times larger than D$_\parallel$. This is different from the case in Ru$_3$(CO)$_9(\mu_3$-CO)(μ$_3$-NPh), in which the D$_s$ is about 15 times larger than D$_\parallel$. 

The purpose of this study is to monitor the internal rotation of the phenyl ring in this cluster. It is informative to compare D$_s$ to the rate of the equivalent rotation of benzene itself (about its C$_2$ axis) dissolved in the same solvent, CD$_2$Cl$_2$. One observes that D$_s$ is only about two times larger than D$_\parallel$. This is different from the case in Ru$_3$(CO)$_9(\mu_3$-CO)(μ$_3$-NPh), in which the D$_s$ is about 15 times larger than D$_\parallel$. 

The latter quantity is displayed as D$_s$(Benz) in the last column of Table 3 and plotted in Figure 6. One observes that the rotation of the phenyl group about its C$_2$ axis in this cluster is markedly below the rate observed for free benzene in the same solvent, by approximately
the case in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh), in which the $D_3$ is about 15 times larger than $D_s$.

The purpose of this study is to monitor the internal rotation of the phenyl ring in this cluster. It is informative to compare $D_s$ to the rate of the equivalent rotation of benzene itself (about its C$_2$ axis) dissolved in the same solvent, CD$_2$Cl$_2$. The latter quantity is displayed as $D_s$(Benz) in the last column of Table 3 and plotted in Figure 6. One observes that the rotation of the phenyl group about its C$_2$ axis in this cluster is markedly below the rate observed for free benzene in the same solvent, by approximately one order of magnitude. It is known that phenyl rotation rate in cluster Co$_3$(CO)$_9$(μ$_3$-CPh) is almost the same as the one of free benzene in the same solvent. This comparison implies that the phenyl ring rotation in ReCo$_2$(CO)$_{12}$(μ$_3$-CPh) is substantially restrained by intramolecular interactions.

D. The Nature of the Phenyl Ring Internal Rotation Barrier

The phenyl ring rotation in several tri- or tetra-nuclear metal complexes have been studied in our group. This internal rotation is characterized by the ratio of the rotational diffusion coefficient of benzene itself (about its C$_2$ axis) to the one of the phenyl ring in the complex, $D_s$(Benz)/$D_s$, in the same solvent and at the same temperature. The ratios for several complexes are listed in Table 5. The low limit of the ratio is 1, and the high limit of the ratio is equal to $D_s$(Benz)/$D_I$, where the $D_I$ is the parallel diffusion coefficient of the complex. In the former case, the phenyl ring rotates as rapidly as the equivalent rotation of a free benzene molecule; while in the latter case, the ring is locked to the skeleton by the internal rotation energy barrier and
thus rotates as slowly as the rotation of the skeleton. This energy barrier is caused by the steric and/or electronic interactions between the phenyl ring and the skeleton of the complex.

The concept of a steric effect has its origin in the systematic development of organic chemistry in the mid 1850s, and has been reviewed extensively.\textsuperscript{33,34,35} This arose out of the attempt to rationalize reactivity patterns in terms of chemical structures. The concept of an electronic effect, especially the one of orbital interaction, has its origin in the development of quantum chemistry. In principle, all inter- and intramolecular interactions are described by equations of quantum mechanics, e.g., Schrödinger's equation. However, in practice, the calculations of the quantum equations are not simple and cannot be performed for most large systems even with supercomputers.

Chemists are still using these two concepts for simple but useful explanation and predictions. It is a nontrivial task to separate the steric and electronic effects or to precisely define the two effects. Here, we try to explain the internal rotation barriers through two different approaches: (a) intramolecular approach distances and (b) molecular orbital calculations.

1. Intramolecular Approach Distances

The $T_1$ relaxation of the phenyl ring is caused by the random motion of the ring, which could be small angle rotations (called librations) or complete $360^\circ$ rotations (called flipping). The dynamics simulation for poly($p$-phenyleneterephthalamide) showed that $T_1$ relaxation of meta and ortho protons on the phenyl ring are caused
mainly by the fast small angle random rotation, but not by the slow, complete 360° rotation. It is possible that the complete ring rotation is restrained while the small angle motion is free, and, therefore, the ring rotation observed on the NMR T₁ relaxation time scale (ns to ps) is still free. It is interesting to see over what range the ring can freely rotate in a complex if only determined by the steric interactions.

In general the steric effects can be assessed with empirical parameters such as van der Waals radii, cone angles, solid angles and molecular volumes. The van der Waals radii are the basic ones, and the others are proposed for specific applications.

When the phenyl ring is rotated relative to the metal skeleton, the approach distances of the phenyl group's ortho protons to the carbon and oxygen atoms of the terminal carbonyls will be changed. We measured the closest approach distances at different angles for these complexes with the PC program MOBY. The structures of these clusters are taken directly from the crystal structures (the references are presented in Table 5), except the for Fe₂Co(CO)₁₀(CPh), where it was constructed from the crystal structure of Fe₂W(CO)₆(μ-CO)(η-Cp)(μ₃-PhMe). The symmetry of the crystal structures determined by X-ray experiments are not perfect due both to experimental errors and the slight distortions in the solid state caused by crystal packings. These errors, especially the errors in the angles, can cause large errors in the intramolecular approach distances. Therefore, the experimental data is averaged to preserve the molecular symmetry and to avoid the errors.

When we rotate the phenyl ring to measure the closest approach distances, the
rest of the complex is fixed. Therefore, the gear type movement is not considered here.

Gear movements are observed by exchange NMR in molecules, such as in
9-(3,5-Dimethylbenzyl)triptycene derivatives. These processes happen in the ms to s
time scale, and thus are rigid in the NMR relaxation time scale (ns to ps) measured by
T in the liquid.

The measured closest approach distances in both Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-NPh) and
ReCo$_2$(CO)$_{10}$(μ$_3$-CPh) are presented in Table 4. The angle ϕ is defined to be zero when
the plane of the phenyl ring contains the Re (or one of the Ru) vertice(s). Due to the
six-fold and the two-fold symmetries of the approach distances profile in Ru$_3$(CO)$_6$(μ$_3$-
CO)(μ$_3$-NPh) and ReCo$_2$(CO)$_{10}$(μ$_3$-CPh), respectively, the data is presented for only
one cycle. It is informative to compare these distances with the sum of the van der
Waals radii ($r_\text{H} = 1.2 \, \text{Å}$, $r_\alpha = 1.4 \, \text{Å}$ and $r_c = 1.70 \, \text{Å}$). The steric free rotation region
is defined as a region in which the closest approach distances are always larger than
sum of van der Waals radii, or if they are smaller than the sum of the van der Waals
radii but do not vary much as the angle changes. The range of the region is
represented by the free angle $\phi_{\text{free}}$. For example, in Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-NPh), the
closest approach distance H-O is always larger than 2.6 Å (1.2 + 1.4), and the H-C
distance is always smaller than 2.90 Å (1.2 + 1.70) and only changes by 0.32 Å during
the whole rotation. Therefore, the free rotation angle range $\phi_{\text{free}}$ for this complex is
qualitatively taken as 360°. In ReCo$_2$(CO)$_{10}$(μ$_3$-CPh), both H-C and H-O distances
change a lot, and are larger than the sum of van der Waals radii only in a small angle
range of $\phi$ from 70° to 110°. Therefore, the free rotation range is taken as $\phi_{\text{free}} < 40°$
Table 4. The Closest Approach Distances (Å)

<table>
<thead>
<tr>
<th>A. in Ru$_3$(CO)$_9$($\mu_3$-CO)($\mu_3$-NPh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi^a$</td>
</tr>
<tr>
<td>H-O</td>
</tr>
<tr>
<td>H-C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B. in ReCo$<em>2$(CO)$</em>{10}$($\mu_3$-CPh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi^a$</td>
</tr>
<tr>
<td>H-O</td>
</tr>
<tr>
<td>H-C</td>
</tr>
</tbody>
</table>

| $\phi^b$ | 100$^\circ$ | 110$^\circ$ | 120$^\circ$ | 130$^\circ$ | 140$^\circ$ | 150$^\circ$ | 160$^\circ$ | 170$^\circ$ | 180$^\circ$ |
| H-O     | 3.31     | 3.12     | 2.76     | 2.39     | 2.02     | 1.66     | 1.33     | 1.09     | 0.99     |
| H-C     | 2.99     | 2.82     | 2.68     | 2.37     | 2.05     | 1.76     | 1.51     | 1.33     | 1.27     |

a) Due to the six-fold symmetry of the closest approach distance profile, distances in the range from 60$^\circ$ to 120$^\circ$, etc., replicate those in the displayed range.

b) Due to the two-fold symmetry of the closest approach distance profile, distances in the range from 180$^\circ$ to 360$^\circ$ replicate those in the displayed range.
Table 5. The Free Angle $\phi_{\text{free}}$ in Complexes

<table>
<thead>
<tr>
<th>Complexes*</th>
<th>$\phi_{\text{free}}$</th>
<th>$\text{D}_5[\text{Benz}]/\text{D}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$</td>
<td>360.0</td>
<td>1.4 ~ 2.6b</td>
</tr>
<tr>
<td>$\text{Co}_3(\text{CO})_6(\mu_3-\text{CPh})$</td>
<td>360.0</td>
<td>1.04</td>
</tr>
<tr>
<td>$\text{FeCo}_2(\text{CO})_6(\mu_3-\text{PPh})$</td>
<td>360.0</td>
<td>1.55</td>
</tr>
<tr>
<td>$\text{Co}_3(\text{CO})_5(\mu_2-\text{CO})_2(\mu_3-\text{CPh})$</td>
<td>&lt; 20.0</td>
<td>7.0 ~ 8.6s</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{Co}(\text{CO})_6(\mu_2-\text{CO})(\mu_1-\text{CPh})$</td>
<td>~ 30.0</td>
<td>R = 0.10</td>
</tr>
<tr>
<td>$\text{Co}_4(\text{CO})_6(\mu_2-\text{CO})_2(\mu_3-\text{PPh})$</td>
<td>&lt; 20.0</td>
<td>14. ~ 19.4</td>
</tr>
<tr>
<td>$\text{ReCo}_2(\text{CO})_1(\mu_3-\text{CPh})$</td>
<td>&lt; 40.6</td>
<td>7.4 ~ 9.3b</td>
</tr>
</tbody>
</table>

a) The reference for the X-ray data is marked on each complex.

b) Measured in this work.
for ReCo₂(CO)₁₀(μ₃-CPh). The $\phi_{\text{free}}$ for other complexes measured in the same way are present in Table 5. One can find that the ratio Dₛ/Dₛ₅(Benz) is closely related to the value $\phi_{\text{free}}$. If $\phi_{\text{free}}$ is small, the ring rotation is restrained; if $\phi_{\text{free}}$ is large, the ring rotates like a free benzene molecule. This suggests that the ring rotations in these complexes can be explained by the steric interactions.

2. Molecular Orbital Calculations

The fragment orbital of M₃L₉ complex was first constructed in 1979 to show the orbital interaction between the M₃L₉ skeleton and the capped ligand, such as -CH, -CCH₂, -S, -CO and -PtL₂. This kind of interaction was also used to explain the bent structure of [Co₃(CO)₉CCO]⁺ and the phenyl ring internal rotation in complexes M₃L₉(CPh) in 1986. The explanation for phenyl ring rotation is dependent on the degeneracy of the two 2e orbitals of the M₃L₉ skeleton, and assumed that there are multiple bond components in the bonding between the phenyl ring and the metal skeleton.

To further investigate the nature of the internal rotation barrier, we have utilized the Fenske-Hall (FH) and extended Hückel (EH) approximate quantum mechanical techniques to determine the potential energy surface characterizing rotation of the phenyl group relative to the tri-ruthenium skeleton in Ru₃(CO)₅(μ₃-CO)(μ₃-NPh). The relative energies are plotted as a function of the dihedral angle, $\phi$, in Figure 7 (FH - open circles, EH - open squares). As defined before, this angle is taken to be zero when the plane of the benzene ring contains one of the Ru vertices. It is found that both methods predict a maximum in energy at $\phi = 30^\circ$, with minima at $0^\circ$ and $60^\circ$. 
Figure 7. Energy and C-H distance dependence upon phenyl group dihedral angle, $\Phi$: (A) Fenske-Hall energy (O); (B) Extended Hückel Energy (□); (C) Distance between the ortho proton and the equatorial carbonyl carbon, $R_{\text{CH}}$ (■ - ordinate scale on right axis).
One notes, though, that the barrier predicted with the FH method, 5.2 kcal/mol, is substantially larger than both the value calculated by the EH procedure, 1.4 kcal/mol, and the experimental result.

Also plotted in Figure 7 is the closest approach distance of the phenyl group's ortho proton to the carbon atom of the equatorial carbonyls (solid squares - ordinate scale on right axis). This distance is less than the sum of the van der Waals radii, and, further, exhibits a minimum around 30°, coincident with the maximum energy barrier calculated by both methods. This result implies that the barrier is primarily steric in nature. To test this conclusion, both the FH and EH energy surfaces were recalculated with arbitrarily increased angle of the equatorial carbonyl relative to the principal axis (increasing the H-C approach distance). Indeed, the calculated energy barriers diminished to near zero, verifying that the barrier to internal rotation in \( \text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-\text{NPh}) \) is due to intramolecular steric interactions.

We also calculated the potential energy surface of phenyl rotation in \( \text{ReCo}_2(\text{CO})_{10}(\mu_3-\text{CPh}) \) with both EH and FH methods. When \( \phi \) is far away from 90°, the calculated energies are too high due to the too close approach distances between the phenyl group's ortho protons and the upward CO at the \( \text{Re}(\text{CO})_4 \) moiety. Only the energies at angles close to 90° are plotted in Figure 8. For comparison, the closest approach distances of C-H and O-H are also plotted in Figure 8. Both energies have minima at \( \phi = 90° \) position, which are coincident with the maxima of the closest approach distances. The closest approach distances in this complex are mainly determined by the upward CO at the \( \text{Re}(\text{CO})_4 \) moiety. To see the dependence of the
Figure 8. Energy and distance dependence upon phenyl group dihedral angle, $\Phi$: (A) Fenske-Hall energy (O), (B) Extended Hückel Energy (□); (C) Distance between the ortho proton and the equatorial carbonyl carbon, $R_{CH}$ ($\times$ - ordinate scale on right axis); (D) Distance between the ortho proton and the equatorial carbonyl oxygen, $R_{OH}$ (+).
energy barrier on the approach distances, both the FH and EH energy surfaces were recalculated with arbitrarily increased angle and dihedral angle of the terminal carbonyl relative to the principal axis (increasing the H-C approach distance). Again, the calculated barriers diminished to near zero.

A 14 kcal/mol energy barrier was calculated for the phenyl ring rotation in Fe₂Co(CO)₉(μ-CO)(CPh) complex with the extended Hückel method by Evans. The geometry was based on the crystal structure of Fe₂W(CO)₈(μ-CO)(η-Cp)(μ₃-PhMe). The existence of the barrier is in agreement with the low-temperature NMR results, and the barrier is assigned to be due to the orbital interaction. We repeated the EH calculation for this complex and calculated the energy barrier at about 20 kcal/mol, which is larger than the 14 kcal/mol energy in Evans paper. This energy difference is caused by the geometry differences in the estimated structures. As we did above, it was found that the calculated energy barriers diminished to near zero when the approach distances are increased, implying that the barrier in this complex is also mainly due to the intramolecular steric interactions.

E. Summary and Conclusions

The phenyl ring rotation in two complexes, Ru₃(CO)₉(μ₁-CO)(μ₁-NPh) and ReCo₂(CO)₁₁(μ₃-CPh), has been monitored by NMR relaxation. It was found that the rotation is relatively free in the first complex, but is restrained in the second one.

We measured the closest approach distances of the phenyl group's ortho protons to the carbon and oxygen atoms of the terminal carbonyl in the two clusters, according to their crystal structures. It is found that the phenyl ring rotation is
relatively free of steric interactions in \( \text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_2-\text{NPh}) \), but is restrained by steric interactions, mainly from the upward terminal \( \text{CO} \) at the \( \text{Re}(\text{CO})_4 \) moiety, in \( \text{ReCo}_2(\text{CO})_{10}(\mu_3-\text{CPh}) \). We also measured the closest approach distances for several other clusters, and found that the ring rotations in these clusters are consistent with the steric interactions.

We also calculated the phenyl ring internal rotation energy barriers in the two complexes by both the EH and FH methods. It was found that the barrier in \( \text{ReCo}_2(\text{CO})_{10}(\mu_3-\text{CPh}) \) is much higher than the one in \( \text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_2-\text{NPh}) \). However, both barriers are diminished to near zero with arbitrarily increased angle of the terminal carbonyl relative to the principal axis (increasing the H-C approach distance). This implies that the barrier is mainly due to the steric interactions.

We prefer to use steric interaction to explain and predict the phenyl ring rotation in the tri- and tetra-nuclear metal clusters. Normally, the straight upward \( \text{CO} \) will cause large steric interactions with the phenyl ring and restrain the ring rotation. The straight upward \( \text{CO} \) often exists at the \( \text{M}(\text{CO})_4 \) moiety (e.g., the straight upward \( \text{CO} \) at the \( \text{Re}(\text{CO})_4 \) moiety in \( \text{ReCo}_2(\text{CO})_{10}(\mu_3-\text{CPh}) \)), and at the moiety with bi-bridging \( \text{CO} \) (e.g., the one at the \( \text{Co}(\text{CO})_2(\mu_2-\text{CO}) \) moiety in \( \text{Co}_4(\text{CO})_9(\mu_2-\text{CO})_2(\mu_3-\text{PPh}) \) and the one at the \( \text{Fe}(\text{CO})_5(\mu-\text{CO}) \) moiety in \( \text{Fe}_2\text{Co}(\text{CO})_9(\mu_2-\text{CO})(\mu_3-\text{CPh}) \)). The equatorial \( \text{CO} \) at a \( \text{M}(\text{CO})_3 \) moiety normally does not cause enough steric interactions with the phenyl ring to restrain the ring rotation.
CHAPTER REFERENCES


21. The authors wish to thank Dr. Michael B. Hall for supplying us with the FENHALL program.


23. The authors wish to thank Dr. Carlo Mealli for supplying us with the CACAO program.


46. Ryan, R. C. *Ph. D. Disseration*, University of Wisconsin, Madsion, WI, 1976
CHAPTER III

NMR Study of Ligand Exchange Dynamics
in Transition Metal Complexes

A. Introduction

The fluxional behavior of ancillary CO groups about polynuclear metal clusters has been extensively studied over the last two decades by variable-temperature $^{13}$C NMR spectroscopy. Such studies have provided valuable insight into the relationship between the observed solid-state structure (X-ray) and the solution structure adopted by a given cluster, and have also provided information about thermally accessible excited-state structures, which in turn may have relevance to the intermediates involved in catalytic conversions at heterogeneous surfaces. The complete scrambling of terminal carbonyls about a cluster polyhedron generally proceeds via a series of terminal-to-bridge CO exchange sequences, of which the one-for-one, two-center and merry-go-round exchange processes represent the best known mechanisms.

Our group's research has focused on the NMR behavior of a wide variety of organometallic compounds, especially with regard to bonding considerations between a metal center(s) and different ancillary ligands, as deduced by NMR spin-lattice ($T_1$) measurements and quadrupole coupling constants (QCC's). For example, exploration of the dynamics of internal rotation of capping benzylidyne and phenylphosphinidene ligands in tri- and tetranuclear clusters has yielded useful information concerning the
nature of the internal rotational energy barrier. Recently, we examined the rotation rates of the phenyl ligand in the amido-capped cluster Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-NPh) due to its isolobal relationship to the phenylphosphinidene fragment, and we observed that all of the carbonyl groups undergo rapid exchange at room temperature. Accordingly, we next conducted a more in-depth investigation into the exchange pathways operative for the carbonyl groups in Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-NPh) and Ru$_3$(CO)$_8$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh). The molecular structures of these clusters are shown in Figure 9.

The study of rotational barriers in compounds is also a topic of interest to chemists, as conformational stability is important in terms of understanding both chemical bonding and stereospecific reactivity. The hindered rotation about the M-P bond of a triphenylphosphine ligand in organometallic compounds of the form [(η$_5$-C$_5$R$_5$)M(CO)(PPh$_3$)X] has been studied recently. We also investigated here the dynamic processes of the triphenylphosphine ligand in Ru$_3$(CO)$_8$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh). Our investigations utilize a combination of exchange and relaxation NMR experiments.

B. Experimental

1. Synthesis

All the clusters were synthesized in Professor Michael G. Richmond's laboratory. Ru$_3$(CO)$_{12}$ was synthesized from RuCl$_3$·nH$_2$O using the high-pressure carbonylation procedure of Bruce. Nitrosobenzene and $^{13}$CO were purchased from Aldrich Chemical Co. and Isotec, respectively, and used as received. The amido
Figure 9. Structures of the clusters, \( \text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh}) \) (a), \( \text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3-\text{CO})(\mu_3-\text{NPh}) \) (b), and \( \text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3-\text{CO})(\mu_3-\text{NPh}) \) viewed along the P-Ru bond (c).
cluster Ru$_3$(CO)$_6$($\mu_1$-CO)(µ$_3$-NPh) (cluster 1) was prepared by using the thermolysis conditions reported by Gladfelter.\textsuperscript{7} $^{13}$CO enriched Ru$_3$(CO)$_6$($\mu_1$-CO)(µ$_3$-NPh) (ca. 15% enriched) was prepared from $^{13}$CO enriched Ru$_3$(CO)$_6$. The substitution of CO in the cluster Ru$_3$(CO)$_6$($\mu_1$-CO)(µ$_3$-NPh) by an equimolar amount of PPh$_3$ was examined in CH$_2$Cl$_2$ at room temperature using the oxidative-decarbonylation reagent Me$_3$NO.\textsuperscript{9} Under these conditions the major product is mono-substituted Ru$_3$(CO)$_6$(PPh$_3$)(µ$_1$-CO)(µ$_3$-NPh) (cluster 2).

2. NMR Experiments

All solvents and NMR tube preparations were carried out by using inert-atmosphere techniques. All $^{13}$C NMR spectra were obtained on a Varian VXR-300 FT-NMR spectrometer operating at 75.4 MHz. The concentrations of the $^{13}$C enriched samples of both cluster 1 and 2 were about 0.1 M, and the concentrations of non-enriched samples of both clusters were about 0.2 M. Temperature was regulated by cooled gas flow and measured from the control panel after calibration with a methanol NMR thermometer.\textsuperscript{9} The $^{13}$C spin-lattice relaxation times for the phenyl carbons of cluster 2 were measured by using the standard IRFT pulse sequence.

Variable temperature $^{13}$C NMR spectra were recorded on natural abundance samples of cluster 1 and 2 at various temperatures between 210 K and 281 K. The spectra of the carbonyl region of cluster 1 and the spectra of the phenyl region of cluster 2 were digitized at intervals of 0.2 Hz and the bandshapes were fitted using the DNMR5 program adapted for use on a Solbourne 902/e computer with a Unix operating system.
$^{13}$C 2D-EXSY$^{10,11}$ spectra were obtained on $^{13}$C enriched samples of both clusters 1 and 2 using the standard pulse sequence, $[t_0-\pi/2-t_1-\pi/2-t_m-\pi/2-t_2]_n$. Spectra were acquired in either the absolute value or pure absorption modes.

Absolute value mode spectra were obtained for cluster 1 at 240 K with various mixing times, $t_m$, ranging from 0.01 to 0.6 s. The initial delay time, $t_0$, was 5 s. The spectral width in both the $F_1$ and $F_2$ dimensions was 6300 Hz. $F_2$ contained 1024 words, and $F_1$ was 64 words, zero-filled to 1024 points. The number of scans, $n$, per experiment ranged from 16 to 64; a four term phase cycle was employed$^{10,12}$.

Pure absorption mode spectra were obtained for both clusters 1 and 2 at different mixing times, with an initial delay of approximately $2T_1$ to $5T_1$. The same number of words in each dimension were used as in the absolute intensity measurements. The spectral width was varied to cover the region where interesting peaks appear and to get the resonable spectral resolution. The number of scans per run ranged from 32 to 48, using a sixteen term phase cycle.$^{10,13}$

In both modes, the spectra were symmetrized prior to analysis. Spectral intensities were obtained using the "box integration" routine on the spectrometer, with several different box widths.

C. Results

1. Carbonyl Exchanges in Ru$_3$(CO)$_3$(μ$_3$-CO)(μ$_3$-NPh)

1.1 Bandshape Analysis

At low temperature (210 K), the carbonyl region of the $^{13}$C NMR spectrum of cluster 1 (see structure in Figure 9) contains three peaks which appear (downfield from
TMS) at 192.3 ppm (equatorial, e), 194.4 ppm (axial, a) and 260.0 ppm (triply bridged, b), in the expected 6:3:1 intensity ratio. Upon increasing the temperature all three resonances broaden, and the equatorial-axial chemical shift difference diminishes with peak coalescence at $T=270 \pm 2$ K. Above this temperature, the intensity of the bridging carbonyl peak is too low to be discerned from the level of the background. The rate constant at the coalescence temperature can be estimated using eq. (6.5) of ref. 14, which assumes exchange between two unequally populated sites. The chemical shift difference between the equatorial and axial peaks at coalescence in the absence of exchange was obtained by extrapolation from low temperatures. At the coalescence temperature, the equatorial/axial exchange rate constant estimated in this way is approximately $k_{ea} = 136$ s$^{-1}$, in excellent agreement with the result obtained from complete bandshape analysis (vide infra).

In a multi-site exchanging system, the absorption mode intensity, $I(v)$, is a function of a number of kinetic and NMR parameters, $I(v) = f(v, C, \delta v, J_{a}, T_{2}, P, k)$. In this expression, $C$ is a scaling constant, $\delta v$ are the relative chemical shifts, $J_{a}$ are the scalar coupling constants, $P$ represents the populations of each site, $T_{2}$ are the spin-spin relaxation times and $k$ are the exchange rate constants. One may neglect the scalar coupling constants in both the natural abundance and 15% enriched $^{13}$C samples. The three rate constants required to characterize this system are $k_{ea}$, $k_{eb}$ and $k_{ab}$, representing equatorial/axial, equatorial/bridging and axial/bridging carbonyl exchange, respectively.

We have used the DNMR5 analysis program to fit the carbonyl region
bandshapes as a function of temperature. A typical simulated and an experimental spectrum at 250 K are presented in Figure 10. The chemical shifts of the equatorial and axial peaks were constrained to values obtained by linear extrapolation from low temperatures, where there is no exchange; the chemical shift of the bridging CO as well as the scaling constant, the relaxation times and the three rate constants were varied to obtain the closest fit to experiment.

The resultant rate constants with their associated errors are presented in Table 6 and Figure 11. The two exchange rates involving the triply-bridging carbonyl were not obtained at the highest temperature, because this resonance was too broad to be measurable. Activation free energies (at the coalescence temperature), $\Delta G^\ddagger$, enthalpies, $\Delta H^\ddagger$, and entropies, $\Delta S^\ddagger$, are given at the bottom of the table; the latter two quantities were obtained from a plot of ln($k/T$) vs. 1000/T. As noted earlier, the equatorial/axial rate constant at the coalescence temperature (270 K) is quite close to the value obtained using the simple two site exchange formula.

It can be observed from Table 6 that $k_{ea}$ is much greater than either $k_{eb}$ or $k_{ab}$, indicating that the most efficient exchange pathway is that linking the equatorial and axial carbonyls. More significantly, it was found that $k_{ab}$ appears to be zero at all temperatures within experimental error, implying, somewhat surprisingly, that there is no direct exchange between the axial CO’s and the triply bridging CO, even though they are adjacent in the molecule.
Figure 10. The experimental (bottom) and simulated (top) $^{13}$C NMR bandshapes of $\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{NPh})$ in the carbonyl region at 250 K.
Table 6. Temperature Dependence of Carbonyl Exchange

Rate Constants in Ru₃(CO)₉(μ₃-CO)(μ₁-NPh)ₖ.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>kₑₑ</th>
<th>kₑᵇ</th>
<th>kₑᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>281.</td>
<td>224. ± 3.</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>270.</td>
<td>140. ± 2</td>
<td>33. ± 2</td>
<td>0.01 ± 3.</td>
</tr>
<tr>
<td>257.</td>
<td>51. ± 2</td>
<td>9.2 ± 0.7</td>
<td>0.01 ± 3.</td>
</tr>
<tr>
<td>250.</td>
<td>23. ± 3</td>
<td>3.5 ± 0.1</td>
<td>0 ± 3</td>
</tr>
<tr>
<td>236.</td>
<td>8.3 ± 0.1</td>
<td>1.6 ± 4</td>
<td>0.008 ± 5</td>
</tr>
<tr>
<td>223.</td>
<td>1.8 ± 0.1</td>
<td>0.3 ± 0.01</td>
<td>0.3 ± 7</td>
</tr>
</tbody>
</table>

ΔGₖ (kJ/mol) | 54.9 ± 0.03 | 58.1 ± 0.14 |
ΔHₖ (kJ/mol) | 41.7 ± 1.4 | 45.4 ± 3.4 |
ΔSₖ (J/mol-K) | -50 ± 6 | -49 ± 14 |

a) Rate constants in units of s⁻¹.
b) The activation free energy is calculated at the coalescence temperature (270 K).
Figure 11. Temperature dependence of the equatorial/axial, $k_{ea}$ (●) and equatorial/bridging, $k_{eb}$ (■) rate constants of $\text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-\text{NPh})$. 
1.2. 2D-EXSY Spectra Analysis

The Axial/Bridging Exchange Rate Constant

The above implication that there is no exchange pathway between the axial and bridging carbonyls is quite interesting, but may not be taken as definitive since both rate constants involving the latter CO are quite small. Hence the result that $k_{ab} \approx 0$ may represent an anomaly in the fitting process.

It has been shown in many systems that 2D-EXSY spectra can be used to furnish unambiguous data on NMR rate constants. We have performed two series of experiments using this technique to investigate the carbonyl exchange pathways in cluster 1.

In the first series, we have measured the relative intensities (in the absolute value mode) of the axial/bridging to equatorial/bridging cross peaks. It may be shown that the ratio of the two cross peaks involving the bridging carbonyls will approach

$$\frac{I_{ab}}{I_{eb}} = \frac{(p_{a}k_{ab})/(p_{b}k_{eb})}{\frac{1}{2}k_{ab}/k_{eb}} = \frac{I_{a}}{2k_{ab}/k_{eb}}$$

at short mixing times, and the asymptotic long $t_{m}$ limit of this ratio is independent of the relative rate constants and is given by

$$\frac{I_{a}}{I_{b}} = \frac{p_{a}/p_{b}}{\frac{1}{2}}.$$

The intensity ratio, $I_{ab}/I_{eb}$, as a function of $t_{m}$ is displayed in Table 7. One observes that at long mixing times, this ratio approaches the expected limiting value of 0.5 and, more significantly, that it diminishes to zero, within experimental error, at the shortest value of $t_{m}$. Thus, one is led to conclude, once again, that $k_{ab} \approx 0$.

Quantitative Determination of Rate Constants

Absolute value mode spectra cannot be used to obtain numerical values of the
Table 7. Mixing Time Dependence of the Intensity Ratio.

$I_{ab}/I_{eh}$ in Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-NPh) at 240 K.

<table>
<thead>
<tr>
<th>$t_m$ [s]</th>
<th>$I_{ab}/I_{eh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>0.10</td>
<td>0.3</td>
</tr>
<tr>
<td>0.20</td>
<td>0.45</td>
</tr>
<tr>
<td>0.60</td>
<td>0.50</td>
</tr>
</tbody>
</table>
exchange rates since the equatorial/axial cross peak overlaps with the two diagonal peaks. We have repeated the 2D-EXSY experiments in the pure absorption mode for two values of the mixing time, \( t_m = 0.05 \) s and 0.10 s. These times were chosen to be long enough to observe all cross peaks, but far from the asymptotic limit, in which the intensities are insensitive to the rate constants. The 2D-EXSY spectrum at 240 K for \( t_m = 0.10 \) s is displayed in Figure 12. One notes that the spectrum exhibits all cross peaks, including one between the axial and bridging carbonyls. However, it has been pointed out that the presence of a cross peak does not necessarily imply a direct exchange pathway between two sites, but may be due, instead, to indirect exchange involving two or more paths involving the two sites.\(^{18,19}\)

The matrix of 2D-EXSY intensities, \( I \), is given by

\[
I = \exp(Lt_m) P
\]  

where \( L \) is a matrix containing the exchange rate constants \( (k_e) \) and relaxation rates \( (T_1, T_2) \), \( t_m \) is the mixing time and \( P \) is a matrix containing the relative site populations (see chapter I). The procedure of direct matrix transformations was performed by a program written in FORTRAN. The intensities and resulting rate constants are presented in Table 8. Errors in the rate constant were estimated by estimating the error in each intensity, varying the intensities within the error limits, and then taking the \( \text{rms} \) sum of squared error in the rate constants.

It is satisfying to note that rate constants calculated at the two mixing times are in good agreement with each other, as well as in reasonable agreement with values obtained using bandshape analysis. As before, \( k_{ab} = 0 \), within experimental error.
Figure 12. Carbonyl region $^{13}\text{C}$ 2D-EXSY spectrum of $\text{Ru}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_1-\text{NPh})$ at 240 K and $t_m = 0.10$ S.
Table 8. 2D-EXSY Intensities and Rate Constants in Ru$_4$(CO)$_{12}$($\mu_3$-CO)$_4$(μ-$\mu$-NPh) at 240 K.

<table>
<thead>
<tr>
<th>$t_m$ (s)</th>
<th>a</th>
<th>b</th>
<th>e</th>
<th>j</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>100</td>
<td>-</td>
<td>e</td>
<td>7.4 ± 1.3</td>
</tr>
<tr>
<td>0.1</td>
<td>300</td>
<td>39.3</td>
<td>474</td>
<td>0.60 ± 0.08</td>
</tr>
</tbody>
</table>

$k_{ea}$ [s$^{-1}$] = 8.2 ± 2.1
$k_{eb}$ [s$^{-1}$] = 0.05 ± 0.1
$k_{eb}$ [s$^{-1}$] = -0.03 ± 0.1
2 Carbonyl Exchanges in Ru₃(CO)₆(PPh₃)(μ₂-CO)(μ₂-NPh)

The crystal structure of cluster 2 has been reported.²⁰ The bulky PPh₃ ligand adopts one of the less sterically hindered axial positions of the cluster. The equatorial carbonyls are thus classified as e₁, e₂ and e₃ groups. At low temperature (180 K), the carbonyl region of the $^{13}$C NMR spectrum of cluster 2 contains five peaks which appear (downfield from TMS) at 193.4 ppm (equatorial, e₁/e₂), 193.8 ppm (equatorial, e₂/e₁), 195.2 ppm (axial, a), 198.8 ppm (doublet, $J=13$ Hz, equatorial, e₃), and 267.7 ppm (triply bridging, b), in the expected 2:2:2:2:1 intensity ratio. This is consistent with the crystal structure. Upon increasing the temperature all peaks broaden, and the first two peak's (at 193.4 ppm and 193.8 ppm) chemical shift difference diminishes with peak coalescence at about 260 K. The peak at 198.8 ppm always remains a doublet, even above room temperature. The peak assignments are based on peak assignments of cluster 1, and the well known fact²¹ that a substituted PPh₃ ligand will cause the chemical shift of the other carbonyls to shift downfield. The only ambiguity is the relative assignments of carbonyls e₁ and e₂. The $^{31}$P{$^1$H} spectrum has only a single resonance at about δ 44 ppm (downfield from H₃PO₄) in the temperature range between 180 K and 300 K, which strongly suggests that only one isomer exists in solution.

The $^{13}$C 2D-EXSY experiments in the pure absorption mode were performed in the carbonyl region with temperatures ranging from 211 K to 295 K. An important qualitative feature is evident; the intensities of cross peaks between bridging carbonyl and the terminal carbonyls are much weaker than the ones among the terminal
carbonyls, confirming that the exchange among the bridging and terminal carbonyls is much slower than the exchange among the terminal carbonyls. It is difficult to observe the exchange cross peaks between the terminal and bridging carbonyls at low temperature. The $^{13}$C chemical shift of the carbonyls span a range of 75 ppm, while the chemical shift difference between $e_1$ and $e_2$ at 180 K is only 0.4 ppm. To measure accurate rate constants among the terminal carbonyls, we thus narrowed our 2D-EXSY spectra to include only terminal carbonyls, which was 900 Hz in spectrum width and had 64 words in the $F_1$ dimension. This is sufficient to resolve the $e_1/e_2$ peaks. A typical 2D-EXSY spectrum of these is showed in Figure 13. With different mixing times in the temperature range from 211 K to 252 K, the intensities of the cross peaks among the $e_1$, $e_2$, and $a$ peaks are from 0.1 to 1 times the intensities of the diagonal peaks, but the intensities of cross peaks between the $e_3$ and others are below the noise background. This confirms that the exchanges between the $e_3$ and other terminal carbonyls, i.e. the ones between different metal centers, are much slower than the exchanges among the $e_1$, $e_2$, and $a$ groups. The exchange rate constants among the $e_1$, $e_2$, and $a$ groups with their associated error are presented in Table 9 and Figure 14. They are equal to each other within experimental error. The estimated enthalpy, $\Delta H^\ddagger$, and entropy, $\Delta S^\ddagger$, from the Eyring plot of the rate constants are given at the bottom of the table.

The 2D-EXSY spectra for the whole carbonyl region were recorded from 240 K to 295 K. The spectrum width was 7000 Hz, and the $F_1$ dimension contained 128 words. The spectra can barely resolve the $e_1$ and $e_2$ peaks at 240 K and 250 K, and
Figure 13. Terminal carbonyl region $^{13}$C 2D-EXSY spectrum of Ru$_3$(CO)$_6$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh) at 240 K and $t_m = 0.10$ S.
Table 9: The Terminal Carbonyl Exchange Rate Constants (1/s)

in \( \text{Ru}_3(\mu_2^-\text{NPh})(\text{CO})_6(\mu_3^-\text{CO})(\text{PPh}_3) \)

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( k_{\text{el-#}} ) &amp; ( k_{\text{el-s}} )</th>
<th>( k_{\text{el-b}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>252.</td>
<td>--</td>
<td>9.5 ± 0.1</td>
</tr>
<tr>
<td>252.</td>
<td>--</td>
<td>9.7 ± 1.</td>
</tr>
<tr>
<td>252</td>
<td>7.13 ± 2.</td>
<td>7.13 ± 2.</td>
</tr>
<tr>
<td>240.</td>
<td>2.06 ± 0.4</td>
<td>2.06 ± 0.4</td>
</tr>
<tr>
<td>240.</td>
<td>1.58 ± 0.7</td>
<td>1.58 ± 0.7</td>
</tr>
<tr>
<td>240.</td>
<td>2.35 ± 0.1</td>
<td>2.15 ± 0.1</td>
</tr>
<tr>
<td>240.</td>
<td>1.85 ± 0.4</td>
<td>1.85 ± 0.4</td>
</tr>
<tr>
<td>226.</td>
<td>0.55 ± 0.1</td>
<td>0.55 ± 0.1</td>
</tr>
<tr>
<td>211.</td>
<td>0.098 ± 0.02</td>
<td>0.102 ± 0.02</td>
</tr>
</tbody>
</table>

\( \Delta G^\ddagger \) (kJ/mol) \( 58. \)

\( \Delta H^\ddagger \) (kJ/mol) \( 45. \pm 2. \)

\( \Delta S^\ddagger \) (J/mol-K) \( -48. \pm 10. \)

a) \( \Delta G^\ddagger \) at 270 K calculated with \( \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \).
\text{Figure 14. Temperature dependence of the equatorial/axial, } k_{e1a}(D), k_{e1a}(O) \text{ and } k_{e2a}(\Lambda), \text{ rate constants of } \text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_3-\text{NPh}).
can not resolve them at higher temperature. There are 5 peaks when e1 and e2 are resolved. The rate constants at 252 K and 240 K are presented in Table 10. This shows that the exchange rate constant between the bridging and axial carbonyls, $k_{a,b}$, is zero within experimental error. It is interesting to note the difference between rate constants $k_{e1,b}$ and $k_{e2,b}$. Because the two peaks, e1 and e2, were not well separated, we are reluctant to say that $k_{e1,b}$ is zero within experimental error. A high field NMR instrument would give better resolution and signal-to-noise ratio, and thus a more definite conclusion. Here we treat e1 and e2 as one peak and give only the overall exchange rate $k_{e1,e2:b}$. When the temperature is higher than 260 K, the three peaks, e1, e2 and a, are not well separated. Thus, the whole spectrum has only three well separated peaks: (e1+e2+a), e3 and b, and will give three rate constants: $k_{e1,e2,a,e3}$, $k_{e1,e2,a,b}$ and $k_{e3,b}$. The $k_{e1,e2,a,e3}$ is zero within experimental error. The $k_{e1,e2,a,b}$ is scaled with the population factors 3/2 to yield the value of $k_{e1,e2,b}$, because we already know that $k_{a,b}$ is zero (or small compared to $k_{e1,e2,b}$) from the lower temperature data. The data obtained in this way is also presented in Table 10 and Figure 15. One can see that $k_{e3,b}$ is larger than $k_{e1,e2,b}$.

3. PPh₃ rotation in Ru₃(CO)₄(PPh₃)(μ₁-CO)(μ₁-NPh)

There are four phenyl rings (one from the μ₁-NPh ligand and three from the PPh₃ ligand) in cluster 2. The phenyl ring region (between 110 ppm and 170 ppm) of the $^{13}$C{'H} NMR spectrum of this cluster contains twelve singlet- and doublet-peaks at low temperature (180 K). The spectra at different temperatures are shown in Figure 16. As one can see, upon increasing the temperature all except four of the peaks
Table 10: The Exchange Rate Constants (1/s) Between the Terminal and Bridging Carbonyl in $\text{Ru}_3(\mu_3-N\text{Ph})(\text{CO})_6(\mu_3-\text{CO})(\text{PPh}_3)_4$

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$k_{e1,b}$</th>
<th>$k_{e2,b}$</th>
<th>$k_{eb}$</th>
<th>$k_{e1,e2-b}$</th>
<th>$k_{e3,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>--</td>
<td>--</td>
<td>2.3 ± 0.4</td>
<td>10.7 ± 2.</td>
<td></td>
</tr>
<tr>
<td>279</td>
<td>--</td>
<td>--</td>
<td>0.97 ± 0.2</td>
<td>4.9 ± 1.</td>
<td></td>
</tr>
<tr>
<td>267</td>
<td>--</td>
<td>--</td>
<td>0.52 ± 0.07</td>
<td>1.64 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>--</td>
<td>--</td>
<td>0.003 ± 0.03</td>
<td>0.11 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>--</td>
<td>--</td>
<td>-0.08 ± 0.08</td>
<td>0.06 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>0.03 ± 0.08</td>
<td>0.20 ± 0.06</td>
<td>-0.04 ± 0.06</td>
<td>0.09 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.01 ± 0.07</td>
<td>0.06 ± 0.05</td>
<td>0.008 ± 0.04</td>
<td>0.062 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.006 ± 0.05</td>
<td>0.035 ± 0.03</td>
<td>-0.001 ± 0.03</td>
<td>0.022 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta G^\ddagger$ (kJ/mol) -- -- 68. 64.

$\Delta H^\ddagger$ (kJ/mol) -- -- 45. ± 5. 44. ± 4.

$\Delta S^\ddagger$ (J/mol-K) -- -- -84. ± 19. -76. ± 14.

a) $\Delta G^\ddagger$ at 270 K calculated with $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. 
Figure 15. Temperature dependence of the equatorial/bridging, $k_{e1,e2,3}(\circ)$ and $k_{e3,4}(\theta)$ rate constants of $Ru_3(CO)_4(PPh_3)(\mu_3-CO)(\mu_3-NPh)$. 
Figure 16. The variable-temperature $^{13}$C($^1$H) NMR spectrum of Ru$_3$(CO)$_4$(PPh$_3$)(µ$_1$-CO)(µ$_1$-NPh).
broaden and merge. The dynamic processes that cause the peak broadening belong to the PPh$_3$ ligand. Therefore, the four peaks which are not broadened belong to the phenyl ring of the capped μ$_3$-NPh group and are assigned as the ipso (δ = 166.1 ppm, not shown in Figure 16), ortho (δ = 128.9 ppm), meta (δ = 126.0 ppm) and para (δ = 123.8 ppm) carbons of the ring, according to the NMR peak assignment in Ru$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-NPh).

To assign the rest of the peaks and to map the exchange pathways, a 2D-EXSY spectrum for this region at 218 K was recorded, and is shown in Figure 17. Direct exchanges between three sets of paired-peaks, O'-O", P'-P" and M'-M", were observed, and the three rate constants are equal to each other within experimental error (see Table 11). The errors in the rate constants are calculated by assuming that there are 10% errors in the measured peak intensities. The intensity ratios of each paired-peak, which are 2 : 1, are in agreement with the crystal structure (Figure 9) in which the three phenyl rings are in two different environments with a population ratio of 2 : 1. Therefore, the dynamic process that causes the exchange is the rotation about the Ru-P bond, which interchanges the three phenyl rings. The peaks, O', O", P', P", M' and M", are assigned as the ortho, para and meta carbons of the rings, respectively. The same exchange is expected between the I'-I" paired-peak, but no cross peaks between them are observed. This is because that there is no effective $^1$H NOE enhancement for the ipso carbons, and the peaks are too weak. The doublets are caused by the P-C couplings. The complete peak assignments and the P-C coupling constants are presented in Table 12.
Figure 17. Phenyl region $^{13}$C 2D-EXSY spectrum of Ru$_3$(CO)$_6$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh) at 218 K and $t_m = 0.10$ S.
Table 11. 2D-EXSY Intensities and Rate Constants for PPh₃ Rotation in Ru₃(CO)₆(PPh₃)(μ₃-CO)(μ₃-NPh) at 218 K With tᵣ = 0.1 s.

A. Intensity

<table>
<thead>
<tr>
<th></th>
<th>O'</th>
<th>O''</th>
<th>P'</th>
<th>P''</th>
<th>M</th>
<th>M''</th>
</tr>
</thead>
<tbody>
<tr>
<td>O'</td>
<td>10.0</td>
<td>2.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O''</td>
<td>--</td>
<td>3.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>P'</td>
<td>--</td>
<td>--</td>
<td>4.93</td>
<td>1.42</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>P''</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.35ₐ</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>M'</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>10.0</td>
<td>2.75</td>
</tr>
<tr>
<td>M''</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.75</td>
</tr>
</tbody>
</table>

B. Rate Constant

<table>
<thead>
<tr>
<th>kₒ (1/s)</th>
<th>O&quot;O'</th>
<th>P&quot;P'</th>
<th>M&quot;M'</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7 ± 0.9</td>
<td>7.4 ± 0.5ₐ</td>
<td>6.8 ± 0.9</td>
<td></td>
</tr>
</tbody>
</table>

a) This peak is merged with the one of the ipso carbon peak, and the intensity is not correct.

b) This rate is calculated from I_p/p/I*p*p, according to the formula on page 500 of ref. 10.
Table 12. $^{13}$C NMR Data (Phenyl Region) for Ru$_3$(CO)$_4$(PPh$_3$)(μ$_3$-CO)(μ$_3$-NPh).

<table>
<thead>
<tr>
<th>Carbon Label$^a$</th>
<th>Chemical Shift (ppm)$^b$</th>
<th>$J_{P,C}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ipso I</td>
<td>166.1</td>
<td></td>
</tr>
<tr>
<td>ortho O</td>
<td>128.9</td>
<td></td>
</tr>
<tr>
<td>meta M</td>
<td>126.0</td>
<td>3.2$^c$</td>
</tr>
<tr>
<td>para P</td>
<td>123.8</td>
<td></td>
</tr>
<tr>
<td>PPh$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ipso I'</td>
<td>130.0, 129.3</td>
<td>47.7</td>
</tr>
<tr>
<td>ortho O'</td>
<td>134.4, 134.1</td>
<td>11.4</td>
</tr>
<tr>
<td>meta M'</td>
<td>128.3, 128.2</td>
<td>10.5</td>
</tr>
<tr>
<td>para P'</td>
<td>130.9</td>
<td>0.</td>
</tr>
<tr>
<td>ipso I''</td>
<td>136.7, 136.0</td>
<td>49.5</td>
</tr>
<tr>
<td>ortho O''</td>
<td>131.9, 131.7</td>
<td>10.2</td>
</tr>
<tr>
<td>meta M''</td>
<td>128.9, 128.8</td>
<td>10.1</td>
</tr>
<tr>
<td>para P''</td>
<td>130.3</td>
<td>0.</td>
</tr>
</tbody>
</table>

a) See Figure 9.

b) At 180 K, in CD$_2$Cl$_2$, downfield from TMS.

c) This peak is always a doublet in the temperature range from 180 K to 300 K.
The variable temperature $^{13}$C spectra were analyzed with the DNMR5 program\textsuperscript{16} to obtain the rotation rate constant. Because the paired-peaks P'-P" and M'-M" are mixed with other peaks, only paired-peak O'-O" was used for this analysis. A typical simulated and an experimental spectrum at 213 K are presented in Figure 18. The resultant rate constants with their associated error are presented in Table 13 and Figure 19. Activation enthalpy, $\Delta H^\ddagger$, and entropy, $\Delta S^\ddagger$, calculated from a plot of $\ln(k/T)$ vs. 1000/T, are also displayed at the bottom of the table.

In the crystal structure, the two ortho carbons, as well as the two meta carbons, of each of the phenyl rings have different environments. However, there is no observed split for these peaks at temperatures down to 180 K. This strongly suggests that the rotation of phenyl rings about the P-C\textsubscript{ipso} bond is still rapid on the exchange NMR time scale (from ms to s). As we know, the relaxation NMR time scale (from ps to ns for this complex) is much shorter, and a NMR relaxation study will supply more information on the dynamic behavior of the PPH\textsubscript{3} ligand. Therefore, we further measured the $T_1$ relaxation times of the phenyl carbons at different temperatures, and the measured values are presented in Table 14. The phenyl $^{13}$C relaxation is entirely from dipolar coupling with the attached protons (i.e. $T_1 = T_{1\text{DD}}$).\textsuperscript{4} The dipolar relaxation time ($T_{1\text{DD}}$) of a $^{13}$C nucleus with one attached proton may be expressed in terms of the rotational correlation time ($\tau_c$) of the C-H bond vector as\textsuperscript{22}

$$\frac{1}{T_{1\text{DD}}} = \frac{\gamma_C^2 \gamma_H^2 h^2}{40\pi^2 R_{\text{CH}}^6} \left[ \frac{\tau_c}{1 + (\omega_B - \omega_C)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_B + \omega_C)^2 \tau_c^2} \right].$$

(2)
Figure 18. The experimental (bottom) and calculated (top) $^{13}$C{H} NMR bandshapes for the phenyl ortho carbons of the PPh$_3$ ligand in Ru$_3$(CO)$_4$(PPh$_3$)(µ$_1$-CO)(µ$_3$-NPh) at 213 K.
Table 13. The Rotation Rate of PPh₃ Ligand in Ru₃(CO)₆(PPh₃)(μ³-CO)(μ³-NPh).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{rot}$ (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>218.</td>
<td>7.0⁵</td>
</tr>
<tr>
<td>218.</td>
<td>9.3</td>
</tr>
<tr>
<td>230.</td>
<td>18.3</td>
</tr>
<tr>
<td>253.</td>
<td>37.8</td>
</tr>
<tr>
<td>268.</td>
<td>700.</td>
</tr>
<tr>
<td>293.</td>
<td>3100.</td>
</tr>
</tbody>
</table>

\[
\Delta H^\ddagger \text{ (kJ/mol)} \quad 40. \pm 4. \\
\Delta S^\ddagger \text{ (J/mol-K)} \quad -43. \pm 14. \\
\Delta G^\ddagger \text{ (kJ/mol) at 300 K} \quad 53. \pm 8.
\]

a) The rotation rate $k_{rot} = k_{O^\bullet-O^\bullet} = 2 k_{C^\bullet-O^\bullet}$.

b) From 2D-EXSY data.
Figure 19. Temperature dependence of the rotation rate of the PPh₃ ligand about the P-Ru bond in \( \text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_3-\text{NPh}) \).
Table 14. $^1$C Relaxation Times (Phenyl Region) and Diffusion Coefficients in Ru$_3$(CO)$_8$(PPh$_3$)(µ$_3$-CO)(µ$_3$-NPh).

A. Relaxation Times (s)

<table>
<thead>
<tr>
<th>T [K]</th>
<th>T$_{10}$ NPh</th>
<th>T$_{1M}$</th>
<th>T$_{1P}$</th>
<th>T$_{10'}$</th>
<th>T$_{1M'}$</th>
<th>T$_{1P'}$</th>
<th>T$_{1P'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180.</td>
<td>0.295</td>
<td>0.295</td>
<td>0.115</td>
<td>0.140</td>
<td>0.148</td>
<td>0.151</td>
<td>0.150</td>
</tr>
<tr>
<td>193.</td>
<td>0.428</td>
<td>0.438</td>
<td>0.121</td>
<td>0.169</td>
<td>0.213</td>
<td>0.174</td>
<td>0.170</td>
</tr>
<tr>
<td>205.</td>
<td>0.609</td>
<td>0.616</td>
<td>0.139</td>
<td>0.218</td>
<td>0.272</td>
<td>0.253</td>
<td>0.246</td>
</tr>
<tr>
<td>293.</td>
<td>3.26</td>
<td>3.67</td>
<td>0.712</td>
<td>1.16</td>
<td>1.16</td>
<td>1.22</td>
<td>1.22</td>
</tr>
</tbody>
</table>

B. Diffusion Coefficients (1/ns)

<table>
<thead>
<tr>
<th>T [K]</th>
<th>NPh</th>
<th>D$_P$</th>
<th>D$_S$</th>
<th>PPh$_3$</th>
<th>D$_P$</th>
<th>D$_S$</th>
<th>D$_S$</th>
<th>free Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D$_S$(Benz)</td>
</tr>
<tr>
<td>180.</td>
<td>0.138</td>
<td>4.05</td>
<td>0.152</td>
<td>0.145</td>
<td>0.77</td>
<td>0.88</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>193.</td>
<td>0.178</td>
<td>6.58</td>
<td>0.324</td>
<td>0.330</td>
<td>0.78</td>
<td>1.12</td>
<td>13.</td>
<td></td>
</tr>
<tr>
<td>205.</td>
<td>0.289</td>
<td>9.18</td>
<td>0.567</td>
<td>0.441</td>
<td>1.18</td>
<td>1.92</td>
<td>19.</td>
<td></td>
</tr>
<tr>
<td>293.</td>
<td>2.65</td>
<td>46.0</td>
<td>3.08</td>
<td>3.08</td>
<td>7.06</td>
<td>7.85</td>
<td>96.</td>
<td></td>
</tr>
</tbody>
</table>
In this equation, $\gamma_c$ and $\gamma_H$ are the magnetogyric ratios of the $^{13}$C and $^1$H nuclei, $\omega_c$ and $\omega_H$ are their resonance frequencies, $R_{CH}$ is the C-H bond length (1.08 Å) and $h$ is Planck's constant. Correlation times for each carbon, calculated by a fit via non-linear regression of the experimental data with equation (2), are displayed in Table 14.

Cluster 2, with the bulky PPh$_3$ ligand, is an asymmetric molecule. The relation between the correlation times and the diffusion coefficients for an asymmetric molecule is complicated. To simplify the calculation, we can simply approximate it as a pseudo-sphere, and thus the tumbling of the molecular skeleton is characterized by one overall diffusion coefficient $D_t$. This assumption is justified later. The C-H vector of the phenyl group's para carbon lies along the axis of the ring rotation. Therefore, the dipolar relaxation of the para carbon is only dependent on the tumbling diffusion of the skeleton, and the tumbling diffusion coefficient $D_t$ can be calculated from the correlation time of the para carbons through the simple relation, $D_t = 1/(6\tau_c)$. The diffusion coefficients, $D_p$, $D_p$, and $D_{ipso}$, calculated in this way from the correlation times of the three different kinds of para carbons, are presented in Table 14 and plotted in Figure 20. One can see that they are close to each other at each temperature of the temperature range from 180 K to 293 K. The three kinds of para carbons are on sites at different positions of the molecule. The fact that the diffusion coefficients are close to each other implies that it is reasonable to treat the molecule as a pseudo-sphere.

The dipolar relaxation of the phenyl group's meta and ortho carbons are dependent not only upon the molecular tumbling rate, $D_t$, but also upon the total rate at which the group 'spins' about the P-C$_{ipso}$ (or N-C$_{ipso}$) axis. The diffusion coefficient,
Figure 20. Temperature dependence of the phenyl rotational diffusion constants in 
\( \text{Ru}_3(\text{CO})_6(\text{PPh}_3)(\mu_3-\text{CO})(\mu_1-\text{NPh}) \): (A) \( D_s \) of free benzene, solid line; (B) \( D_s \) of the \( \mu_3-\text{NPh} \) group (■); (C) and (D) \( D_5 \) and \( D_s \) of the \( \text{PPh}_3 \) ligand (▲ and ●); (E) and (F) \( D_{\rho} \) and \( D_{\rho} \) of the \( \text{PPh}_3 \) ligand (Δ and ○); (G) \( D_{\rho} \) of the \( \mu_1-\text{NPh} \) group (□).
D₅, governing the latter motion is given by the sum of Dₜ and R, the rate of internal rotation relative to the molecular skeleton, D₅ = Dₜ + R. It has been shown that the correlation time in this case can be expressed as:

\[ \tau_c(\theta) = \frac{A(\theta)}{6D_t} + \frac{B(\theta)}{5D_t + D_5} + \frac{C(\theta)}{2D_t + 4D_5}. \]  

(3)

In this equation, θ is the angle of the vector with respect to the symmetry axis, A(θ) = (1/4)(3 cos2θ-1)², B(θ) = 3 sin²(θ)cos⁴(θ), and C(θ) = (3/4)sin⁴(θ). The experimental ortho / meta rotational correlation times have been fitted with equation (3) to yield the spinning diffusion coefficients for different phenyl groups at different temperatures. Resulting values are displayed in Table 14 and plotted in Figure 20.

In order to estimate the rotation rate of the phenyl ring, it is informative to compare our results for D₅ with the rates of rotation of the free benzene molecule about its C₃ axis, D₅(Benz). The values of D₅(Benz) in CD₂Cl₂²⁴ are displayed in the last column of Table 14 and plotted in Figure 20. If the ring rotation is free, the D₅ value will be close or equal to D₅(Benz), like the ring rotation in Co₃(CO)₉(μ₃-Ph).³ If the ring rotation is substantially restrained, the D₅ value will be much lower than D₅(Benz) and close or equal to the skeleton tumbling diffusion coefficient, Dₜ. The value difference between the D₅(Benz) and Dₜ is the dynamic range in which the phenyl ring rotation can be observed with a T₁ relaxation method. One can easily see from the Table 14 and Figure 20 that the D₅ values for the capped NPh group are close to the D₅(Benz) values while the D₅ and Dₜ values for the PPh₃ ligand are much
smaller than the $D_3(Benz)$ values and are close to $D_1$ values. Therefore, it was found that the phenyl ring rotation about N-C bond in the NPh group is relatively free, while the rotation about the P-C$_{ipso}$ bond in PPh$_3$ ligand is substantially restrained on the NMR relaxation time scale.

D. Discussion and Conclusions

1. The Exchange Mechanism Among the Terminal Carbonyls

It was observed that there is exchange among the terminal carbonyls in both cluster 1 and 2, which are the fastest carbonyl exchange process in each cluster. The information about terminal carbonyl exchange from cluster 1 is limited, because the symmetry in the cluster makes all the equatorial carbonyls equivalent. The substituted PPh$_3$ ligand in cluster 2 breaks down the symmetry, and the equatorial carbonyls are classified as e1, e2 and e3 groups. The fact that there is no direct exchange between the carbonyls at the Ru(CO)$_3$ moieties and the ones at the Ru(CO)$_2$(PPh$_3$) moiety supports that the exchange of axial/equatorial carbonyl groups occurs through an intra-rather than an inter-nuclear process. The fact that the exchange rates among the carbonyls e1, e2 and a at the Ru(CO)$_3$ moieties are equal to each other suggests that the internuclear exchange process is a tripodal rotation.

Therefore, we propose that the exchange of the axial/equatorial CO groups at each ruthenium Ru(CO)$_3$ moiety occurs via a tripodal rotation mechanism, as depicted in Scheme 1. In this mechanism, the scrambling at the Ru(CO)$_3$ moieties proceeds in a completely intranuclear fashion. This scheme is in agreement with the many examples of axial-equatorial CO exchange in a wide variety of polynuclear compounds.$^{25}$
2. The Exchange Mechanism Between the Terminal and Triply-Bridging Carbonyls

The exchange process between the terminal and the triply-bridging carbonyls is a more interesting process. It was observed that there is direct exchange between the equatorial and triply-bridging carbonyls, but no direct exchange between the axial and triply-bridging carbonyls. And it is known that the axial and equatorial carbonyls are exchanged faster. These facts imply that the exchange is through a coincident process, but not a random process.

We proposed two possible mechanisms for this exchange process. The first one is shown in Scheme 2. Here the concerted motion of the $\mu_3$-CO ligand to a $\mu_2$-CO ligand at a single Ru-Ru edge is accompanied by the conversion of one terminal CO group at a Ru(CO)$_3$ center to a $\mu_2$-CO edge-bridging moiety. Related face-edge conversions involving CO ligands make this process attractive. This intermediate may then collapse with reformation of the $\mu_3$-CO, which derives from the old equatorial CO
(labeled e) group, and concomitant generation of the required terminal CO group. The net result of these two transformations is the pairwise equilibration of an equatorial and triply-bridging CO group, which is mandated by the NMR data.

Scheme 2
This mechanism is similar to the SN2 reaction in organic chemistry, which has two features: (a) the attacking group attacks from the opposite side of the leaving group, and (b) the bond formation and the bond breaking happen at the same time. The first feature, the attack from the opposite side of the leaving group, prevents the involvement of the axial carbonyl, and the second feature guarantees that there is no direct exchange between the axial and triply-bridging carbonyls, even through the axial carbonyl is exchanged more quickly with equatorial carbonyls.

The second mechanism we proposed is very similar to the first one. This mechanism, as shown in Scheme 3, has an intermediate involving three edge-bridging CO ligands. Here migration of the \( \mu_3 \)-CO to an edge-bridging position is accompanied by the concerted movement of a pair of equatorial carbonyl groups to edge-bridging positions, rather than a single one. The resulting intermediate, with its three \( \mu_3 \)-CO ligands, is akin to the intermediate responsible for the in-plane “merry-go-round” process, a term originally coined by Muetterties. However, given the presence of the unique Ru(CO)\(_3\) site in this intermediate, we do not favor the existence of an in-plane scrambling of the \( \mu_3 \)-CO groups via a “merry-go-round” sequence.

Both cluster 1 and 2 represent classical examples of a cluster that cannot be adequately described by using an electron-precise formalism. The presence of the \( \mu_3 \)-CO ligand negates any possible two-center, two-electron bonding argument in these two clusters. However, the bonding in these clusters is easily described by using the electron topology developed by Wade and Mingos. Here either cluster 1 or 2 may be regarded as a four-vertex nido cluster that possesses six skeletal electron pairs (SEP).
The proposed intermediates in Schemes 2 and 3 may also be regarded as nido clusters based on their six SEP count. One major structural difference between these two schemes lies in an accurate electron-precise description of the intermediate edge-bridged cluster in Scheme 2, where the 2e-donor bond from the capping amido group to the unique Ru(CO)₂ center is explicitly shown. Here each bond may be considered as electron precise, and for this reason we favor this scheme for the exchange of the μ₁-CO and equatorial CO groups. Another kinetic difference between these two schemes is that the mechanism in Scheme 2 involves less bonding formation than the
mechanism in Scheme 3. From the consideration of entropy change, we also favor Scheme 2.

It was also observed in cluster 2 that the equatorial carbonyls at the Ru(CO)$_2$(PPh$_3$)$_2$ moiety exchange with the triply-bridging carbonyl faster than the one at the Ru(CO)$_3$ moiety. It is difficult to use this difference to distinguish between the mechanisms in Scheme 2 and 3.

3. The Effects of the Substituted PPh$_3$ Ligand

It is interesting to see the effects of the substituted PPh$_3$ ligand on the reaction rates. Comparing the $\Delta G^\circ$ values at 270 K listed in Table 6 and 9, one finds that the $\Delta G^\circ$ for the tripodal rotation in cluster 2 is about 3 kJ/mol higher than the corresponding one in cluster 1, and the $\Delta G^\circ$ for the equatorial/bridging exchange in cluster 2 are about 10 and 6 kJ/mol higher than the corresponding ones in cluster 1. All the exchange processes in cluster 2 are slower than the ones in cluster 1. This can be explained by the crowding caused by the bulky PPh$_3$ ligand in cluster 2.

Another interesting effect is that the exchange rate $k_{e3\rightarrow b}$ is larger than $k_{e1,e2\rightarrow b}$. It is informative to see how these two exchange processes happen. To exchange with the triply-bridging carbonyl, the equatorial carbonyl must attack on the other Ru nuclear and form a bi-bridging intermediate. As shown in Scheme 4, the two intermediates for the two exchange processes are different. The Ru(CO)(µ$_2$-CO)$_2$(PPh$_3$) moiety in intermediate 2B, which induces the exchange of e3 and b, has a symmetric structure and has the PPh$_3$ ligand in the symmetric axial position. However, the Ru(CO)$_2$(µ$_2$-CO)(PPh$_3$) moiety in intermediate 2B, which induces the exchange of e1/e2 and b, has
an asymmetric structure. This asymmetry will push the PPh₃ ligand away from the perfect axial position and cause more steric interaction. Because the PPh₃ in intermediate 2B is less crowded than in intermediate 2A, $k_{e_3,b}$ is larger than $k_{e_1,e_2,b}$. 

Scheme 4

![Scheme 4 Diagram]
It is known that phosphine substitution increases the internuclear carbonyl exchange rates in Os$_3$(CO)$_{11}$(PEt$_3$)$_3$, Os$_3$(CO)$_{12}$+[P(OMe)$_3$]$_3$, and in Os$_3$Pt(µ-H)(CO)$_6$(Pt-PCy$_3$)(Os-PR$_3$)$_3$, which have non-bridging ground-state structures and exchange through bridging intermediates. Substitution also decreases the carbonyl exchange rates in Fe$_3$(CO)$_{12}$+[P(OR)$_3$]$_3$, which has a bridging ground-state structure and exchanges through a non-bridging intermediate. These effects suggest that phosphorus-donor ligands stabilize structures with bridging carbonyls. Randy explained these effects in Os$_3$ clusters as the electronic effect, i.e., the phosphorus-donor ligand causes an increase in the electronic density at the osmium atom and causes expansion of the filled 5d orbitals. This in turn could result in better overlap with π* orbitals of the carbonyls on the adjacent osmium atom, and thereby lower the activation energy for formation of the intermediate with bridging carbonyls. Note that these effects can also be explained as a steric effect: the bulky phosphorus ligand causes more steric repulsion and thus creates a preference for the bridging carbonyl structure.

The electronic and steric effects of phosphorus ligands in organometallic complexes have been reviewed. The concepts of electronic and steric effects have been used based only on loose definitions. A definition of steric interaction based on the topological properties of molecular electron density has been proposed recently, but it is not satisfactory. More work on the effects of substituted ligands on the exchange rates needs to be done to understand the steric and electronic effects of phosphorus ligands in Ru$_3$(CO)$_{8-x}$L$_x$(µ$_3$-CO)(µ$_3$-NPh).
4. The Rotation of the PPh₃ Ligand

The PPh₃ ligand in cluster 2 possesses two kinds of rotations, namely, the rotation about the Ru-P bond and the rotation about the P-C_ipso bond. The rotation about the Ru-P bond was observed by $^{13}$C exchange NMR in the temperature range of 218 K to 293 K with $\Delta G^\circ = 53$ kJ/mol at 300 K. However, the rotation about the P-C_ipso bond is rapid on the exchange NMR time scale down to 218 K. Further studied by $^{13}$C T₁ relaxation experiments, it was found that the rotation about the P-C_ipso is not free but is restrained on the NMR relaxation time scale (ns).

As has been well documented, the three phenyl rings of triphenylphosphine prefer, for steric reasons, to adopt a chiral propeller-like conformation with either a clockwise or anticlockwise screw configuration. Molecular modelling studies showed that the complete rotation about the P-C_ipso is restrained by the steric interactions between the ortho protons of the three phenyl rings. This kind of interaction accounts for the non-free rotation observed by relaxation NMR experiments. Even though the complete rotation about the P-C_ipso bond is restrained, each ring can still rotate freely in a small angle region. The range of the free rotation region measured by the PC program MOBY based on the crystal structure is about 40°. This kind of fast, small angle rotation makes the ring spin diffusion coefficients, $D_s$, in the PPh₃ ligand is little larger than the skeleton tumbling diffusion coefficient, $D_t$.

Low-temperature exchange NMR studies failed to observe arrest of the rotation about the P-C_ipso bond down to 218 K. This suggests that the complete rotation of the
rings still happen. The complete rotations must occur through a gear type movement.

To avoid the strong steric interactions between the ortho protons, the complete rotation of one ring requires a cooperative sequence of motions of the other two rings.

Rotation about the Ru-P bond is a considerably higher energy process with \( \Delta G^1 = 53 \text{ kJ/mol} \) at 300 K. It is commonly believed that this energy barrier is caused by the steric interactions between the bulky PPh\(_3\) ligand with its surroundings.

E. Summary

The carbonyl exchange in two complexes, Ru\(_3\)(CO)\(_9\)(\(\mu_3\)-CO)(\(\mu_3\)-NPh) and Ru\(_3\)(CO)\(_8\)(PPh\(_3\))(\(\mu_3\)-CO)(\(\mu_3\)-NPh), has been studied by exchange NMR experiments. Two processes have been established. The lower energy process is the exchange among the terminal carbonyls, which is a tripodal rotation process. The higher energy process results in the exchange between the equatorial and the bridging carbonyls, but not between the axial and the bridging carbonyls. Either of two mechanisms, both involving the concerted formation of edge-bridging \(\mu_3\)-CO moieties, can explain the observed equatorial/bridging exchange pathway. A substituted PPh\(_3\) ligand decreases carbonyl exchange rates in all pathways, and makes the exchange rates between the bridging and different equatorial carbonyls unequal. The steric effect can be used to explain these effects.

The dynamics of the PPh\(_3\) ligand in Ru\(_3\)(CO)\(_9\)(PPh\(_3\))(\(\mu_3\)-CO)(\(\mu_3\)-NPh) has also been studied by both relaxation and exchange NMR experiments. The ligand rotation about the Ru-P bond was observed by exchange NMR experiments. The phenyl ring rotation about the P-C\(_{ipso}\) bond was found to be fast on the exchange NMR time scale,
but to be restrained on the NMR relaxation time scale. The mechanism of the complete rotation of the phenyl ring about the P-C<sub>≡</sub> bond is a concerted rotation of all three phenyls.
CHAPTER REFERENCES


15. Ref. 14; Chaps. 2, 6.

16. Kleier, D. A.; Binsch, G. Program No. QCPE 365, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405

17. Ref. 14; Chap. 7.


Commun. 1975, 452. (b) Ewing, P.; Farrugia, L. J.; Rycroft, D. S.
Organometallics 1988, 7, 859. (c) Cotton, F. A.; Hanson, B. E. Inorg.
Chem. 1985, 284, 379. (e) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir,
D. L.; Lahuerta, P. Inorg. Chem. 1975, 14, 511. (g) Li, L.; D'Agostino,
(h) Aime, S.; Dastru, W.; Gobetto, R.; Arce, A. J. Organometallics
1994, 13, 3737.

26. (a) Lawson, R. J.; Shapley, J. R. Inorg. Chem. 1978, 17, 772. (b) Roberts, D.
A.; Harley, A. D.; Geoffroy, G. L. Organometallics 1982, 1, 1050. (c)
Geiger, W. E.; Rheingold, A. L. Inorg. Chem. 1994, 33, 5615 and
references therein.

27. Mingos, D. M. P.; Wales, D. J. "Introduction to Cluster Chemistry," Prentice


1982, 104, 405.
BIBLIOGRAPHY


Heatley, F. Progress in NMR Spectroscopy, 1978, 13, 47.

Heatley, F. Annual Reports on NMR Spectroscopy, 1986, 17, 179.


Kleier, D. A.; Binsch, G. Program No. QCPE 365, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.

Kleier, D. A.; Binsch, G. Program No. QCPE 365, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.


Mann, B. E. Ibid. 1977, 11, 95.


Orrell, K. G.; Sik, V. Annual Reports on NMR spectroscopy. 1993, 27, 103.


Schaefer, Top. C-13 NMR Spectros., 1974, 1, 150.


Shen, H.; Senter, R. A.; Bott, S. G.; Richmond, M. G., *Organometallics*, (Submitted).


Tanabe, K. *Chem. Phys.*, 1979, 38, 125.


Yuan, P. Raman and NMR Investigation of Molecular Reorientation and Internal Rotation in Liquids, 1991, Ph.D. Dissertation, Univ. of North Texas, Denton, TX.


