

STRUCTURAL, SYNTHETIC AND KINETIC STUDIES OF SOME  
TRANSITION METAL CARBOXYL DIMERS AND TRIMERS

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# ABSTRACT

Carbonyl substitution reactions of some transition metal dimers and trimers were studied.

The kinetics of the thermal and catalysed substitution reactions of  $M_2(CO)_{10-n}(RNC)_n$  ( $M=Mn, Re$ ;  $R=alkyl, aryl$ ;  $n=0-2$ ) by isonitriles were studied and pseudo-first-order kinetics were observed. Results are in agreement with a non-radical mechanism and suggest direct substitution on the dimer is occurring.

Intramolecular and unimolecular isomerisation of the structural isomers of the complex  $Mn_2(CO)_8(Bu^tNC)_2$  was observed at elevated temperatures. Analogous isomerisation for  $Re_2(CO)_8(Bu^tNC)_2$  or  $MnRe(CO)_9(Bu^tNC)$  was not observed. The product of the direct substitution of  $MnRe(CO)_{10}$  and  $Bu^tNC$  was shown by a crystal structure determination to be  $Mn(CO)_5Re(CO)_4(Bu^tNC)$ .

The use of  $PdO$  as a catalyst for the substitution of  $RNC$  on  $[CpRu(CO)_2]_2$  was demonstrated and a series of monosubstituted derivatives,  $Cp_2Ru_2(CO)_3(RNC)$  ( $R=alkyl, aryl$ ) were prepared.

An improved synthesis of the heteronuclear trimer  $Re_2Fe(CO)_{14}$  was developed and the first catalysed substitution reactions by isonitriles on this trimer were performed.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in any other University.



David John Robinson

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# TABLE OF CONTENTS

|                                   | PAGE                                                                                               |
|-----------------------------------|----------------------------------------------------------------------------------------------------|
| ACKNOWLEDGEMENTS                  | ix                                                                                                 |
| LIST OF TABLES                    | ix                                                                                                 |
| LIST OF FIGURES                   | xiii                                                                                               |
| LIST OF ABBREVIATIONS AND SYMBOLS | xiv                                                                                                |
| CHAPTER 1                         | Introduction                                                                                       |
|                                   | 1                                                                                                  |
| CHAPTER 2                         | Aspects of Metal Carbonyl Cluster Chemistry - A Survey of the Literature                           |
|                                   | 5                                                                                                  |
| 2.1                               | Introduction                                                                                       |
|                                   | 5                                                                                                  |
| 2.2                               | Metal Carbonyl Clusters                                                                            |
|                                   | 6                                                                                                  |
| 2.3                               | Kinetic Studies of Substitution Reactions in Transition Metal Carbonyls of Manganese and Rhodium   |
|                                   | 12                                                                                                 |
| 2.4                               | The $M_2(CO)_8$ ( $M = Mn, Re$ ) Substitution Reactions                                            |
|                                   | 19                                                                                                 |
| 2.5                               | Isomerisation and Scrambling in Manganese and Rhodium Carbonyl Complexes                           |
|                                   | 20                                                                                                 |
| CHAPTER 3                         | A Kinetic Study of the Substitution Reactions and Isomerisation of $M_2(CO)_8$ and its Derivatives |
|                                   | 29                                                                                                 |
| 3.1                               | Introduction                                                                                       |
|                                   | 29                                                                                                 |
| 3.2                               | Results                                                                                            |
|                                   | 33                                                                                                 |
| 3.3                               | Discussion                                                                                         |
|                                   | 49                                                                                                 |
| 3.4                               | Experimental                                                                                       |
|                                   | 57                                                                                                 |
| 3.4.1                             | Kinetic Studies                                                                                    |
|                                   | 57                                                                                                 |
| 3.4.2                             | Synthesis of $1,2-M_2(CO)_8(Ru^tNCI)_2$                                                            |
|                                   | 58                                                                                                 |

|                                                                                                            | PAGE |
|------------------------------------------------------------------------------------------------------------|------|
| 3.4.3 synthesis of<br>$1,1-\text{Os}_2(\text{CO})_8(\text{Su}^t\text{NC})_2$                               | 58   |
| 3.4.4 synthesis of<br>$1,2-\text{Os}_2(\text{CO})_8(\text{Su}^t\text{NC})_2$                               | 59   |
| 3.4.5 synthesis of<br>$1,1-\text{Os}_2(\text{CO})_8(\text{Su}^t\text{NC})_2$                               | 60   |
| 3.4.6 isomerisation of<br>$\text{Os}_2(\text{CO})_8(\text{Su}^t\text{NC})_2$<br>( $\text{Su}^t\text{NC}$ ) | 61   |
| CHAPTER 4 Carbonyl substitution reactions<br>of the fixed metal cluster $\text{Os}_2(\text{CO})_{10}$      | 62   |
| 4.1 Introduction                                                                                           | 63   |
| 4.2 Results and Discussion                                                                                 | 68   |
| 4.3 X-ray crystallography of<br>$\text{Os}_2(\text{CO})_{10}(\text{Su}^t\text{NC})$                        | 76   |
| 4.4 Discussion                                                                                             | 76   |
| 4.5 Conclusions                                                                                            | 87   |
| 4.6 Experimental                                                                                           | 89   |
| 4.6.1 synthesis of<br>$\text{Os}_2(\text{CO})_{10}$                                                        | 89   |
| 4.6.2 substitution reactions<br>of $\text{Os}_2(\text{CO})_{10}$                                           | 91   |
| 4.6.3 synthesis of<br>$\text{Os}_2(\text{CO})_8(\text{Su}^t\text{NC})\text{Os}(\text{CO})_3$               | 93   |
| 4.6.4 isomerisation of<br>$\text{Os}_2(\text{CO})_{10}(\text{Su}^t\text{NC})$                              | 98   |
| CHAPTER 5 Substitution reactions of<br>$[\text{Os}(\text{CO})_2]_2$                                        | 91   |
| 5.1 Introduction                                                                                           | 92   |
| 5.2 Results                                                                                                | 96   |

|                                                                        | PAGE |
|------------------------------------------------------------------------|------|
| 5.3 Conclusions                                                        | 98   |
| 5.4 Experimental                                                       | 101  |
| 5.4.1 General                                                          | 101  |
| 5.4.2 Synthesis of<br>$[\text{Co}(\text{H}(\text{C})_2)_2]_2$          | 101  |
| 5.4.3 Synthesis of<br>$\text{Co}_2\text{H}_2(\text{C})_2(\text{HNC})$  | 102  |
| CHAPTER 6 Mixed Metal Trimers $\text{Fe}(\text{C})_2\text{Co}_2$       | 103  |
| 6.1 Introduction                                                       | 103  |
| 6.2 Results and Discussion                                             | 106  |
| 6.3 Conclusions                                                        | 111  |
| 6.4 Experimental                                                       | 112  |
| 6.4.1 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 112  |
| 6.4.2 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2(\text{HNC})_2$ | 112  |
| 6.4.3 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 113  |
| 6.4.4 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 113  |
| 6.4.5 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 114  |
| 6.4.6 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 114  |
| 6.4.7 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2(\text{HNC})$   | 115  |
| 6.4.8 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2$               | 115  |
| 6.4.9 Synthesis of<br>$\text{Fe}(\text{C})_2\text{Co}_2(\text{HNC})$   | 115  |

|                    |                                                                                       | PAGE |
|--------------------|---------------------------------------------------------------------------------------|------|
|                    | 6.4.1.1 Synthesis of $\text{Fe}_2(\text{CO})_9$                                       | 118  |
|                    | 6.4.1.2 Reaction of $\text{Fe}_2(\text{CO})_9$ and $\text{P}(\text{C}_6\text{H}_5)_3$ | 119  |
| CHAPTER 7          | Conclusions                                                                           | 120  |
| Appendix A         | The sources of chemicals used in this study                                           | 126  |
| Appendix B         | General experimental details                                                          | 127  |
| Appendix C         | X-ray Crystal structure data                                                          | 129  |
| Appendix D         | List of publications                                                                  | 130  |
| LIST OF REFERENCES |                                                                                       | 131  |

|           | <u>LIST OF TABLES</u>                                                                                                      | <u>PAGE</u> |
|-----------|----------------------------------------------------------------------------------------------------------------------------|-------------|
| Table 2.1 | Some Examples of Heteronuclear<br>Dimetallic Carbonyl Complexes                                                            | 10          |
| Table 2.2 | Some Examples of Homonuclear Carbonyl<br>Clusters of the 1,0n Triad                                                        | 10          |
| Table 2.3 | Some Examples of Heteronuclear<br>Trimetallic Carbonyl Complexes                                                           | 11          |
| Table 2.4 | Some Examples of Heteronuclear<br>Polymetallic Carbonyl Complexes<br>( $n > 4$ )                                           | 11          |
| Table 2.5 | Thermodynamic Activation Parameters<br>for Carbonyl Substitution Reactions<br>of $M(CO)_5X$ ( $M=Mn, Re$ ; $X=Cl, Br, I$ ) | 14          |
| Table 3.1 | Physical and Spectral Data for the<br>Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$<br>( $M=Mn, Re$ ; $n=1-3$ )                     | 34          |
| Table 3.2 | Infrared Spectral Data for the Complexes<br>$M_2(CO)_{10-n}(Bu^tNC)_n$ ( $M=Mn, Re$ ; $n=1-3$ )                            | 35          |
| Table 3.3 | Physical and Spectral Data for the<br>Complexes $Re(CO)_5-n(Bu^tNC)_nI$ ( $n=0-2$ )                                        | 36          |

|           | <u>LIST OF TABLES</u>                                                                                                       | <u>PAGE</u> |
|-----------|-----------------------------------------------------------------------------------------------------------------------------|-------------|
| Table 2.1 | Some Examples of Heteronuclear<br>Dimetallic Carbonyl Complexes                                                             | 10          |
| Table 2.2 | Some Examples of Homonuclear Carbonyl<br>Clusters of the Iron Triad                                                         | 10          |
| Table 2.3 | Some Examples of Heteronuclear<br>Trimetallic Carbonyl Complexes                                                            | 11          |
| Table 2.4 | Some Examples of Heteronuclear<br>Polymetallic Carbonyl Complexes<br>( $n > 4$ )                                            | 11          |
| Table 2.5 | Thermodynamic Activation Parameters<br>for Carbonyl Substitution Reactions<br>of $M(CO)_5X$ ( $M = Mn, Fe; X = Cl, Br, I$ ) | 14          |
| Table 3.1 | Physical and Spectral Data for the<br>Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$<br>( $M = Mn, Fe; n = 1-3$ )                     | 34          |
| Table 3.2 | Infrared Spectral Data for the Complexes<br>$M_2(CO)_{10-n}(Bu^tNC)_n$ ( $M = Mn, Fe; n = 1-3$ )                            | 35          |
| Table 3.3 | Physical and Spectral Data for the<br>Complexes $Re(CO)_5-n(Bu^tNC)_nI$ ( $n = 0-2$ )                                       | 36          |

PAGE

|           |                                                                                                                    |    |
|-----------|--------------------------------------------------------------------------------------------------------------------|----|
| Table 3.4 | Kinetic Data for the Substitution Reactions on $M_2(CO)_{10}$ ( $M = Mn, Re$ ) by $Bu^tNC$                         | 38 |
| Table 3.5 | Kinetic Data for the Substitution Reactions on $M_2(CO)_9(Bu^tNC)$ by $Bu^tNC$                                     | 40 |
| Table 3.6 | Arrhenius Data for the Reactions:<br>$Mn_2(CO)_9(Bu^tNC) \longrightarrow Mn_2(CO)_8(Bu^tNC)_2$                     | 44 |
| Table 3.7 | Kinetic Data for the Isomerisation of $Mn_2(CO)_8(Bu^tNC)_2$                                                       | 44 |
| Table 3.8 | Arrhenius Data for the Isomerisation of the two Isomers of $Mn_2(CO)_8(Bu^tNC)_2$                                  | 48 |
| Table 3.9 | Kinetic Data for the Reactions of $M_2(CO)_8(Bu^tNC)_2$ ( $M = In, Re$ ) with $Bu^tNC$ using $PdO$ Catalyst        | 48 |
| Table 4.1 | Physical and Spectral Data for the Monosubstituted Metal Dimers<br>$M_2(CO)_9(Bu^tNC)$ ( $M, M' = Mn, Re$ )        | 50 |
| Table 4.2 | Physical and Spectral Data for the Complexes $InRe(CO)_9(R)(NC)$<br>( $R = Bu^t, iPr, Xy, Cy$ )                    | 73 |
| Table 4.3 | Kinetic Data for Monosubstitution of $M(CO)_5$ ( $M = In, Re$ ) with $Bu^tNC$ using $PdO$ Catalyst at $25^\circ C$ | 74 |

|            | PAGE |
|------------|------|
| Table 4.1  | 77   |
| Table 4.2  | 80   |
| Table 4.3  | 81   |
| Table 4.4  | 82   |
| Table 4.5  | 83   |
| Table 4.6  | 84   |
| Table 4.7  | 86   |
| Table 4.8  | 87   |
| Table 4.9  | 88   |
| Table 4.10 | 89   |
| Table 5.1  | 90   |
| Table 5.2  | 100  |
| Table 6.1  | 107  |

|                                                                                                                                           | <u>PAGE</u> |
|-------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| Table C1    Isotropic Temperature Factors for<br>Methyl Group Protons                                                                     | 131         |
| Table C2    Anisotropic Temperature Factors for<br>Molecule 1                                                                             | 132         |
| Table C3    Anisotropic Temperature Factors for<br>Molecule 2                                                                             | 133         |
| Table C4    Observed and Calculated Structure<br>Factors for $\text{InSe}(\text{D}_{2d})_{12}(\text{Sb}^{\text{I}}\text{Sb}^{\text{II}})$ | 134         |

|            | <u>LIST OF FIGURES</u>                                                                                                                                                                                                                      | <u>PAGE</u> |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| Figure 3.1 | Structural isomers of the complex<br>$\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$                                                                                                                                                     | 32          |
| Figure 3.2 | Typical infrared spectra recorded<br>during the reactions of<br>$\text{In}_2(\text{CO})_9(\text{Bu}^t\text{NC})$ and $\text{Bu}^t\text{NC}$ in the<br>presence of $\text{PbO}$                                                              | 41          |
| Figure 3.3 | Isomerization equilibria for<br>$\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$                                                                                                                                                          | 43          |
| Figure 3.4 | Typical infrared spectra recorded<br>during the isomerization of<br>1,1- $\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ to an equilibrium<br>mixture of the structural isomers of<br>$\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | 45          |
| Figure 3.5 | Thermodynamic data for the isomeriza-<br>tion of $\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$                                                                                                                                         | 46          |
| Figure 4.1 | Molecular structure of<br>$\text{In}(\text{CO})_5\text{In}(\text{CO})_4(\text{PF}_6)$                                                                                                                                                       | 65          |
| Figure 4.2 | Crystal structure of $\text{In}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$                                                                                                                                                                    | 79          |
| Figure 4.3 | Unit Cell Molecular Packing Diagram<br>for $\text{In}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$                                                                                                                                              | 131         |

LIST OF ABBREVIATIONS AND SYMBOLS

|                    |                                                        |
|--------------------|--------------------------------------------------------|
| M                  | central (usually metal) atom in a compound             |
| L                  | ligand                                                 |
| R                  | alkyl or aryl group                                    |
| Me                 | methyl, $\text{CH}_3$                                  |
| Et                 | ethyl, $\text{C}_2\text{H}_5$                          |
| Pr                 | propyl, $\text{C}_3\text{H}_7$                         |
| Bu                 | butyl, $\text{C}_4\text{H}_9$                          |
| Ph                 | phenyl, $\text{C}_6\text{H}_5$                         |
| Cy                 | cyclohexyl, $\text{C}_6\text{H}_{11}$                  |
| Xy                 | xylyl, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$          |
| o-phe              | ortho-phenanthroline                                   |
| 1,4                | 1,4-diazabutadiene                                     |
| Cp                 | cyclopentadienyl, $\text{C}_5\text{H}_5^-$             |
| Me <sub>5</sub> Cp | pentamethylcyclopentadienyl, $\text{C}_5\text{Me}_5^-$ |
| THF                | tetrahydrofuran                                        |
| TLC                | thin layer chromatography                              |
| IR                 | infrared                                               |
| UV                 | ultra-violet                                           |
| NMR                | nuclear magnetic resonance                             |
| MS                 | mass spectrometry                                      |
| mp                 | melting point                                          |
| n, l, t            | normal, iso, tertiary                                  |
| o, m, p            | ortho, meta, para                                      |
| N.C.S.L.           | National Chemical Research Laboratory                  |
| N.P.R.L.           | National Physical Research Laboratory                  |
| C.S.I.R.           | Council for Scientific and Industrial Research         |

## 7. INTRODUCTION

Over the last 5 years work in these laboratories has involved the study of catalysed substitution reactions of transition metal carbonyl complexes. This study was undertaken to elucidate the usefulness of a variety of catalysts in specific aspects of synthetic organometallic chemistry as well as to compare mechanistic results for both catalysed and uncatalysed carbonyl substitution reactions.

In this chapter a brief outline of the areas that were studied in the course of this work will be given. To place this work in context a survey of the literature was undertaken and is presented in Chapter 2. More detailed assessments of the literature as they relate to specific aspects of this work are given at the beginning of Chapters 3, 4, 5 and 6.

Catalysts have been used previously to bring about substitution on the mononuclear dimer  $\text{W}_2(\text{CO})_{10}$  with isocyanides. However, no attempt had previously been made to obtain quantitative data for the rates of these catalysed reactions or to relate such information to an interpretation of the mechanism of the carbonyl substitution reaction. It was therefore decided that the first part of this dissertation (Chapter 1) would involve the generation of kinetic data and the calculation of rate constants for the catalysed and





literature methods and catalysts were used to prepare a series of monosubstituted complexes,  $\text{Mn}(\text{C}_5\text{H}_4\text{R})_2$ . The crystal structure of the monosubstituted complex  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$  was determined to confirm the site of substitution. The other structure  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$  was synthesized indirectly and the possible interconversion of these two isomers was studied at elevated temperatures. New complexes of the type  $\text{Mn}(\text{C}_5\text{H}_4\text{R})_2$  for several alkyl and aryl groups were synthesized and fully characterized.

The possibility of the reaction of the catalyzed carbonyl substitution reaction in synthetic organometallic chemistry was examined and new systems for this type of reaction were considered (Scheme 1 and 2). Catalysts were found useful for the carbonyl substitution reactions of  $[\text{Cp}^*\text{Mn}(\text{CO})_2]$  with nitriles. A series of monosubstituted dimeric or the formula  $\text{Cp}^*\text{Mn}(\text{CO})_2\text{R}$  were prepared. The requirements for such substitution reactions in the catalytic cycle involving the site of substitution were studied.

In the course of the study of the reaction of  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$  and  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$  with  $\text{C}_6\text{H}_5\text{CN}$  it was found that the reaction proceeded via a  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$  intermediate and the reaction was catalyzed by  $\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)_2$ .

the latter product is unstable in most organic solvents. The first substitution reactions of  $\text{Co}_2\text{Fe}(\text{CO})_{14}$  by isocyanide were performed using a catalyst and attempts were also made to prepare indirectly substituted derivatives of this trimer.

Some of the results of this work which have been reported or are to be reported in the literature in the near future and a list of such references is given in Appendix I.

## 2. ASPECTS OF METAL CARBONYL CLUSTER CHEMISTRY - A SURVEY OF THE LITERATURE

---

### 2.1 Introduction

The ultimate aim of a complete understanding of the processes occurring at metal surfaces during catalysis may be indirectly realized when certain reactions of simple model systems are understood. Only in the last 10 years has the use of molecular metal clusters as models for metal surfaces in either chemisorption or catalytic processes been considered.<sup>1-5</sup> Such model systems are important because their reactions are related to the steps in a catalytic sequence such as ligand substitution, ligand migration etc. The suggestion is that the factors responsible for chemical (and catalytic) reactivity of metal surfaces can be related to those factors responsible for the reactivity of smaller metal aggregates. Thus as one progresses from the study of monometallic complexes through metal dimers to oligomers and larger clusters the trend in chemical reactivity should give information about the chemistry of larger arrays or metal atoms (i.e. surfaces). This stepwise approach was proposed by Mortimer and co-workers<sup>4</sup> and other research groups and provides incentive for the study of metal cluster complexes as a vehicle for understanding surface phenomena.

Only recently have meaningful comparisons of the reactions of metal surfaces and of transition metal complexes been made.<sup>7</sup> There is considerable disagreement about the actual participation of clusters as catalysts in many processes, with the question of whether the metal cluster maintains its integrity during a catalytic reaction or if the active particles are the products of cluster breakdown remaining unanswered in some cases. Further, the study of cluster complexes in their own right must not be overlooked as a knowledge of the chemical nature of these molecules is vital.

The area of cluster chemistry, using the broad definition of clusters as consisting of two or more atoms in a bonding interaction,<sup>8</sup> is vast and no attempt will be made to assess the various directions that this chemistry has taken over the years. Instead the background information relating to some specific issues of cluster chemistry as they relate to this work will be outlined in this chapter.

## 2.2 Metal Carbonyl Clusters

One approach to an understanding of the chemistry of metal surfaces is via a study of metal species (mono- and multinuclear) in low oxidation states and such species commonly involve carbonyl ligands. The metal to carbonyl synergic bonding mode<sup>9</sup> allows for the reduction of a

charge build up on the metal atom and an increased stability of the low oxidation state metal complex results.

The chemistry of mononuclear transition metal carbonyls has been extensively studied<sup>10</sup> since the discovery of nickel tetracarbonyl in 1890<sup>11</sup> and iron pentacarbonyl one year later.<sup>12,13</sup> Much more recent are studies of binuclear carbonyl complexes which are the simplest transition metal carbonyl clusters. These binuclear carbonyl clusters<sup>\*</sup> can be subdivided in two ways 1) those containing a homonuclear metal-metal bond either with or without bridging carbonyl ligands or 2) those with a heteronuclear metal-metal bond again either with or without bridging carbonyl ligands.

Clusters of these types were studied in this work and more details of the complexes used will be presented where relevant. Examples of these clusters include

1)  $M_2(CO)_8$  ( $M = \text{Co, Ni, Fe}$ )<sup>14,15</sup>  $Co_2(CO)_8$ <sup>16-18</sup> and  $Fe_2(CO)_9$ <sup>19-21</sup> or 2)  $MnRe(CO)_9$  etc. (Table I.1).

\* For the purpose of this study di- or multimetallic complexes not containing a metal-metal bond have not been considered.

\*\*  $Co_2(CO)_8$  exists in three isomeric structures in solution.

The development of the chemistry and synthesis of transition metal carbonyl clusters is well illustrated by the history of the homonuclear clusters in the iron triad of elements  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Co}_2(\text{CO})_8$ , and  $\text{Ni}_2(\text{CO})_8$  known as early as 1905<sup>19</sup> but  $\text{Fe}_3(\text{CO})_{12}$  has only recently been reported.<sup>21</sup>  $\text{Fe}_2(\text{CO})_9$  was the first metal carbonyl to be the subject of a full X-ray crystal structure investigation<sup>20</sup> and is a very useful source of the unstable species  $\text{Fe}(\text{CO})_4$  which is a building block for high nuclearity carbonyl clusters of iron. Examples of the known homonuclear carbonyl clusters of the iron triad are listed in Table 2.2. Methods of synthesis vary in their ease and selectivity and some examples are 1) photolysis of  $\text{Fe}(\text{CO})_5$  to give  $\text{Fe}_2(\text{CO})_9$ ,<sup>22</sup> 2) thermal decomposition of  $\text{Fe}_3(\text{CO})_{12}$  to give  $\text{Fe}_2(\text{CO})_9$ ,<sup>23</sup> 3) carbonylation of  $\text{FeCl}_2$  to give  $\text{Fe}_2(\text{CO})_9$ ,<sup>24</sup> and 4) pyrolysis of  $\text{Fe}_3(\text{CO})_{12}$  to give mainly  $\text{Fe}_2(\text{CO})_9$ .<sup>25</sup> There have been many reviews on the subject of metal carbonyl clusters and examples pertinent to this study include reviews on tetranuclear carbonyl clusters<sup>26</sup> and high nuclearity metal carbonyl clusters.<sup>27</sup>

Finally the development of the area of heteronuclear cluster chemistry and in particular heteronuclear carbonyl clusters should be mentioned. Heteronuclear transition metal carbonyl clusters are being investigated not only

as models to increase our understanding of the processes which occur at metal catalyst surfaces <sup>2,4,6,28</sup> but also as catalysts in their own right. The variety of heteronuclear dimetallic, heteronuclear trimetallic and higher nuclearity heteronuclear carbonyl clusters is illustrated by the examples listed in Tables 2.1, 2.3, 2.4 respectively. The first heteronuclear metal carbonyl cluster to be prepared is thought to be  $[\text{AgCo(CO)}_4]_4$ .<sup>29</sup> Since then synthetic strategies have been developed such that the logical approach to building polymetallic complexes, adding one metal group at a time to the cluster, is now feasible. An approach using the isolobal analogy of metal fragments to classical organic chemistry fragments has been made by Hoffmann.<sup>30</sup> The methods that are thus available include 1) ligand substitution by a metal anion, 2) addition reactions of two metallic species, 3) condensation reactions and 4) metal exchange reactions.

TABLE 2.1      Some Examples of Heteronuclear Bimetallic Carbonyl Complexes

|                 |                                 |                 |
|-----------------|---------------------------------|-----------------|
| $M_2M'(CO)_9$   | ( $M=Cr, Mo, W$ ; $M'=Mn, Re$ ) | (31-37)         |
| $MnFe(CO)_9$    |                                 | (32)            |
| $Co_2(CO)_8$    | ( $M=Mn, Tc, Re$ )              | (38-47)         |
| $Mn_2(CO)_{10}$ | ( $M=Tc, Re$ )                  | (37, 39, 48-54) |

TABLE 2.2      Some Examples of Heteronuclear Metal Carbonyl Clusters of the Iron Triad

|                      |                    |                 |
|----------------------|--------------------|-----------------|
| $M_2(CO)_8$          | ( $M=Fe, Ru, Os$ ) | (19, 30, 76-77) |
| $M_3(CO)_{12}$       | ( $M=Fe, Ru, Os$ ) | (78-83)         |
| $Os_5(CO)_{16}$      |                    | (22, 84)        |
| $Os_5(CO)_{15}^{2-}$ |                    | (22, 85)        |
| $Os_2(CO)_{22}$      |                    | (22)            |
| $Os_2(CO)_{23}^{2-}$ |                    | (22)            |

TABLE 2.3      Some Examples of Heteronuclear  
Trimetallic Carbonyl Complexes

|                   |                                  |                 |
|-------------------|----------------------------------|-----------------|
| $M_2M'(CO)_{14}$  | ( $M=Mn, Re$ ; $M'=Fe, Co, Os$ ) | (89, 59, 86-92) |
| $MnReFe(CO)_{14}$ |                                  | (91, 59, 86)    |
| $Mn_2Pt(CO)_{12}$ |                                  | (93)            |
| $Fe_2(CO)_{12}^-$ | ( $M=Mn, Fe, Re$ )               | (32, 91, 94-96) |
| $Os_2(CO)_{12}^-$ | ( $M=Mn, Re$ )                   | (97)            |
| $Mn_2Au(CO)_{10}$ |                                  | (98)            |

TABLE 2.4      Some Examples of Heteronuclear  
Polymeric Carbonyl Clusters ( $n \geq 4$ )

|                      |                           |            |
|----------------------|---------------------------|------------|
| $Co_nRh_m(CO)_{12}$  | ( $n=1, 2, 3$ ; $m=4-n$ ) | (99-102)   |
| $Ru_3Re(CO)_{16}$    |                           | (77)       |
| $Fe_4(CO)_{14}^{2-}$ | ( $M=Os, Pt$ )            | (103, 104) |
| $Rh_5(CO)_{15}^-$    | ( $M=Ni, Fe$ )            | (105, 106) |

2.3 Kinetic Studies of Substitution Reactions in  
Transition Metal Carbonyls of Manganese and  
Rhenium

One of the more important reactions of transition metal carbonyls is ligand substitution which may occur by one or more competing pathways. These pathways involve associative, dissociative or interchange mechanisms,<sup>10, 107-113</sup> and these mechanisms may be easily distinguished when the stoichiometry of the reaction intermediate is considered; 1) associative mechanisms involve an intermediate with an increased coordination number, 2) dissociative mechanisms proceed via an intermediate with a reduced coordination number and 3) the interchange mechanism has no determinable intermediate. The interchange mechanism may be further subdivided into an Ia or Id pathway that involve either strong or weak bonding of the metal to the entering and leaving groups in the transition state. A more detailed general account of the mechanisms of the substitution reactions of metal carbonyls has been given by Darensbourg.<sup>114</sup>

Kinetic studies have a major role to play in establishing the mechanisms of reactions of transition metal carbonyls such as ligand substitution. Yet relatively little effort has been expended in this type

of study when compared to the effort expended on the synthetic and structural aspects of metal carbonyl complexes. For instance only recently has any kinetic work on transition metal carbonyls, other than on mono- or dinuclear complexes been reported.<sup>115-120</sup>

To place the kinetic work of this dissertation in perspective a literature survey of kinetic studies of manganese and rhenium carbonyl complexes has been undertaken and the results described below.

Kinetics of the substitution reactions of the complexes  $M(CO)_5X$  ( $M = Mn, Re$ ;  $X = Cl, Br, I$ ) represent one of the few areas of metal carbonyl chemistry that has been comprehensively studied. The values for the enthalpy and entropy of activation for carbonyl substitution reactions on the complexes  $M(CO)_5X$  from a series of studies are given in Table 2.5 and the results show the manganese-carbonyl bond strength to be less than the rhenium-carbonyl bond strength. It was also observed that the rate of  $CO$  substitution varied with the halide  $X$  such that the rate of substitution increased in the order  $I < Br < Cl$ .<sup>121,126</sup> When carbonyl exchange reactions were studied using labelled carbon monoxide ( $^{14}C$ ) it was seen that the equatorial carbonyls exchanged more rapidly than the axial carbonyl ligands.<sup>125,127</sup>

TABLE 2.5

Thermodynamic Activation Parameters  
for Carbonyl Substitution Reactions  
of  $M(CO)_5X$  ( $M = Mn, Fe$ ;  $X = Cl, Br, I$ )<sup>a</sup>

| COMPLEX      | $\Delta H^\ddagger$ (kJ mol <sup>-1</sup> ) | $\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> ) |
|--------------|---------------------------------------------|-----------------------------------------------------------|
| $Mn(CO)_5Cl$ | 116 <sup>b</sup>                            | 66 <sup>b</sup>                                           |
| $Fe(CO)_5Cl$ | 114 (124 <sup>c</sup> )                     | 26 (73 <sup>c</sup> )                                     |
| $Mn(CO)_5Br$ | 118                                         | 64                                                        |
| $Fe(CO)_5Br$ | 123 (124 <sup>c</sup> )                     | 41 (45 <sup>c</sup> )                                     |
| $Mn(CO)_5I$  | 116 <sup>d</sup>                            | 46 <sup>d</sup>                                           |
| $Fe(CO)_5I$  | 133 (113 <sup>c</sup> )                     | 54 (9 <sup>c</sup> )                                      |

<sup>a</sup> Ref. 121 unless otherwise stated.

<sup>b</sup> Ref. 122

<sup>c</sup> Ref. 123

<sup>d</sup> Ref. 124

\* Data in ref. 121 is for monosubstitution of  
 $M(CO)_5X$  by  $PhH$

The carbonyl substitution reactions of  $\text{Re}(\text{CO})_5\text{Br}$  and its derivatives  $\text{Re}(\text{CO})_4\text{LBr}$  ( $\text{L}=\text{PPh}_3, \text{NC}_2\text{H}_5, \text{P}(\text{OPh})_3$ ) were the subject of a series of papers by Brown and co-workers.<sup>128-130</sup>

The studies led to the recognition of the phenomenon called cis-labilization which has become increasingly important in the design and rationalization of the pathways of organometallic substitution reactions. (See later)

The carbonyl substitution reaction of  $\text{Mn}(\text{CO})_5\text{NO}$  with phosphines, phosphites and arsines was shown to occur by an associative mechanism,<sup>131</sup> which involved changes in the bonding mode of the NO ligand. The NO ligand changes from a 3 electron donor to a 1 electron donor and in so doing creates a vacant site on the metal i.e. a 16 electron species, thus allowing an associative mechanism to occur. The reaction of  $\text{MeMn}(\text{CO})_5$  with a variety of ligands was seen to occur by methyl migration giving the acetyl product<sup>132,133</sup> and a first-order rate dependence on both reactant concentrations was observed.<sup>133</sup> The reactions of acylmanganese pentacarbonyl  $\text{RCOMn}(\text{CO})_5$  with  $\text{PPh}_3$  or  $\text{I}^-$  were seen to exhibit a first-order dependence on metal carbonyl<sup>134,135</sup> whereas the cleavage of the manganese-acyl bond by base was seen to be a two step mechanism involving attack of acyl carbon atom and dissociation of  $[\text{Mn}(\text{CO})_5]^-$ .<sup>136</sup>

The rate of the carbonyl exchange reaction with labelled CO was found to be much more rapid for  $\text{HMn(CO)}_5$  than for  $\text{In}_2(\text{CO})_{11}$  and the rate determining step was thought to be carbonyl dissociation.<sup>137</sup> The carbonyl substitution reactions of the hydrides  $\text{HM(CO)}_5$  ( $\text{M}=\text{Mn, Re}$ ) by phosphine have been studied and the rhenium complex shown to be far more inert to substitution than the manganese complex.<sup>138, 139</sup> The kinetics of some substitution reactions of radical species have been studied; for example the replacement of L by L' in  $\text{Mn(CO)}_4\text{L}$  where L, L' = phosphine or phosphite.<sup>140</sup> Recent studies have shown that carbonyl substitution in radicals such as  $\text{Re(CO)}_5$  is extremely rapid and occurs by an associative mechanism.<sup>141, 142</sup>

The carbonyl substitution reactions of  $\text{CpM(CO)}_2$  ( $\text{M}=\text{Mn, Fe, Re}$ ) were seen to be much slower than the analogous reaction with  $\text{CpM(CO)}_2$  ( $\text{M}=\text{Co, Rh, Ir}$ ) which was shown to proceed by a  $\text{S}_\text{N}2$  mechanism.<sup>137, 143</sup> The carbonyl substitution reaction of  $\text{CpMn(CO)}_3$  using U.V. irradiation proceeded via a mechanism in which ligand dissociation was the rate determining step.<sup>144</sup> A recent study of the kinetics of the substitution reaction of  $(\eta\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_2\text{L}$  (L = substituted pyridine) showed the second-order rate constant to be dependent upon both the electronic and steric effects of the pyridine ligand L and the incoming ligand (i.e. phosphine). Thus an associative  $\text{S}_\text{N}2$  mechanism

is thought to be the pathway of these substitution reactions,<sup>145</sup> in which the cyclopentadienyl ligand changes in its bonding mode to accommodate the increased number of ligands at the metal. The carbonyl exchange reaction was much more rapid for  $(\text{Cp}^*\text{Ir}(\text{CO})_2)_2$  than for  $(\text{Cp}^*\text{Ir}(\text{CO})_3)_2$ .<sup>146</sup>

Other mononuclear metal carbonyls whose substitution reactions have been studied for example the hexacarbonyls  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ )<sup>147-150</sup> will only be mentioned where pertinent.

As will be discussed later (section 2.4) kinetic studies have played a major role in the study of the substitution reactions of the dicarbonyls  $\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ )<sup>151,152</sup> and phosphines and phosphites.<sup>153,154</sup> A study of the substitution reactions of  $\text{M}_2(\text{CO})_{10}$  by phosphines and phosphites<sup>155</sup> led to a rate equation of the type

$$k_{\text{obs}} = (k_1 + k_2) \left[ \text{P} \right] + \left[ \text{M}_2(\text{CO})_{10} \right]$$

a rate law which had been demonstrated in substitution reactions of other metal carbonyls.<sup>156,157,158</sup> Scrambling reactions between  $\text{M}_2(\text{CO})_{10}$  and  $\text{M}_2(\text{CO})_{10}$  have been observed at high temperatures<sup>159</sup> but a more recent

suggests the reaction occurs by two possible pathways<sup>154</sup> which gives a complex rate equation of the type:

$$\text{Rate} = k_2 \left[ \text{Mn}_2(\text{CO})_{10} \right] \left[ \text{Fe}_2(\text{CO})_{9} \right]$$

$$k_2 = p / \left[ 1 + qn(\text{CO}) \right]$$

where  $p$  is partial pressure of  $\text{CO}$  and  $q$  is an expression in rate constants. Both pathways involve aggregation to form intermediates that are tetranuclear clusters and only differ on whether carbonyl dissociation occurs before or after aggregation takes place. A study of the reaction of iodine with  $\text{Mn}_2(\text{CO})_{10}$ <sup>155</sup> or  $\text{Fe}_2(\text{CO})_9$ <sup>156</sup> led to a very complex rate equation and the mechanism remains poorly understood.

The reaction of  $[\text{Fe}(\text{CO})_4]_2$  (isolated with  $\text{Ph}_3\text{C}$  or pyridine obeys a 2nd order rate equation with the rate depending on the basicity of the incoming ligand and only cis -  $[\text{Fe}(\text{CO})_4]_2\text{X}$  was formed in the reactions.<sup>157</sup> The analogous reaction between  $[\text{Mn}(\text{CO})_5\text{X}]_2$  and  $\text{L}$  ( $\text{L}$  = pyridine, 2 - picoline, 2-chloropyridine) gave a two term rate equation thought to reflect competing associative and dissociative reaction pathways.<sup>158</sup>

There have been a limited number of studies on transition metal carbonyl clusters (with a nuclearity of 3 or more) which are pertinent to this study. The substitution kinetics of the tetranuclear carbonyl clusters of cobalt and iridium i.e.  $\text{Co}_4(\text{CO})_9(\mu\text{-CO})_3$ <sup>115,116</sup> and  $\text{Ir}_4(\text{CO})_{12}$ <sup>117-120</sup> and their derivatives provide information which may be important for the interpretation of the  $\text{M}_2(\text{CO})_{10}$  ( $\text{M}=\text{Ir, Re}$ ) substitution kinetics and will be mentioned where applicable in this work.

#### 2.4 The $\text{M}_2(\text{CO})_{10}$ ( $\text{M}=\text{Ir, Re}$ ) Substitution Reactions

The problems of data interpretation that arise when a specific reaction is studied in detail are well illustrated in the literature by the substitution reactions of  $\text{M}_2(\text{CO})_{10}$  ( $\text{M}=\text{Ir, Re}$ ) with phosphines (e.g.  $\text{PPh}_3$ ). Interest in this reaction was initiated by the observation that initial substitution of  $\text{M}_2(\text{CO})_{10}$  by phosphines or phosphites affected the rate of subsequent substitution reactions<sup>121,126,129,130</sup> and that these ligands directed the second substitution exclusively onto the second metal centre.

Complexes of the type  $\text{M}_2(\text{CO})_{10}$  ( $\text{M}=\text{Ir, Re}$ ) have been shown to have metal-metal bonds that are significantly longer than the sum of the "normal" covalent radii of the metals and the equatorial metal carbonyl bonds (normal to the metal-metal bond) are bent towards the centre of

the molecule.<sup>14,15,161,162</sup> The increased metal-metal bond length suggests a low bond order and although estimates of the energy required to break the metal-metal bonds have varied,<sup>58,148,163,164</sup> the values that have been accepted  $\pm 154 \text{ kJmol}^{-1}$  (In-Mn) and  $\pm 188 \text{ kJmol}^{-1}$  (Re-Re) suggest that bond fission may be a fairly facile process. Indeed when these complexes are irradiated at or near the frequency of the  $\sigma \rightarrow \sigma^*$  transition of the metal-metal bond<sup>37,48-50,185</sup> in halogenated organic solvents or in hydrocarbons in the presence of free ligands e.g. phosphine, either mononuclear complexes<sup>166</sup> or substituted dimers are formed.<sup>40,167</sup>

It has been generally accepted, until recently,<sup>100</sup> that the major pathway for the photochemical substitution reaction on  $\text{X}_2(\text{CO})_4$ , (X=In, Re) involves a radical mechanism in which the first step is homolytic fission of the metal-metal bond.<sup>11,14,16,113,114</sup> A recent publication<sup>186</sup> suggests that even the photochemical substitution reaction follows two pathways of approximately equal importance, one involving initial metal-metal bond scission and the other pathway involving initial CO dissociation, probably followed by metal-metal bond fission. There has been a great deal more disagreement

about the thermal ligand substitution reaction of  $M_2(CO)_{10}$ . The two mechanisms most widely supported involve either carbonyl dissociation from the dimer (Scheme 2.1) or a radical mechanism in which CO dissociation occurs after fission of the metal-metal bond (Scheme 2.2). The disagreement could not be resolved by establishing a rate expression for the reaction as both mechanisms predict first-order dependence in metal dimer concentration and zero-order dependence in incoming ligand concentration.

Poë and co-workers have reported less than first-order kinetic behaviour in the thermal decomposition of  $Mn_2(CO)_{10}$  when the reaction occurs in the presence of oxygen<sup>51,53</sup> and for the decomposition of  $Mn_2(CO)_8(P(OPh)_3)_2$  and  $Re_2(CO)_8(PPh_3)_2$  in the presence of free ligand or oxygen.<sup>58,59,162</sup> No inhibition of the decomposition of  $Mn_2(CO)_{10}$  is observed when carbon monoxide is added to the oxygen/nitrogen atmosphere. Thus it was concluded that the decomposition goes by a radical process in which carbonyl dissociation is not a rate determining step. These observations about the decomposition mechanism

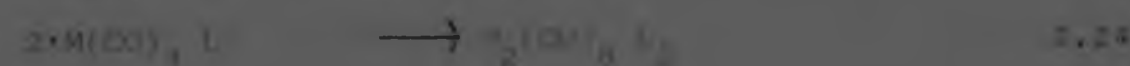
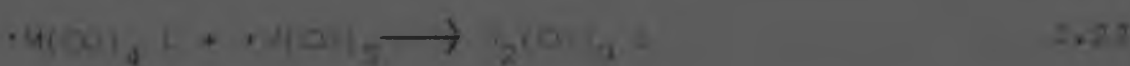
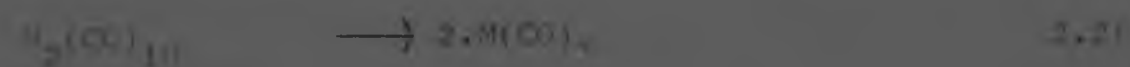
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\* An interchange mechanism Ia is not ruled out by the observed independence of reaction rate upon incoming ligand concentration.

SCHEME 2.1



SCHEME 2.2



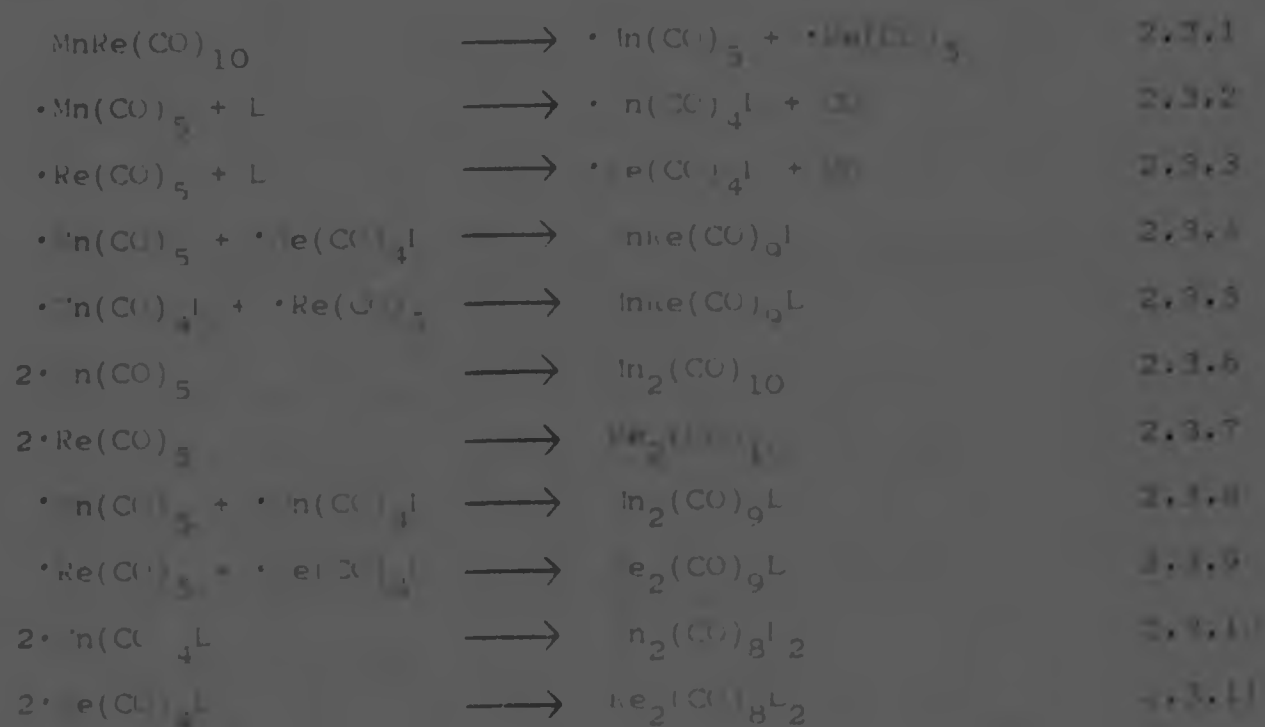
are only relevant to the substitution reaction if both the carbonyl substitution and the decomposition processes occur by a common mechanism. The similarity of their reaction rates over a wide range of temperatures suggested this to be true. Poe suggested further that the radical decomposition mechanism was precedent for radical involvement in other reactions, in particular the thermal substitution reaction of transition metal carbonyls.<sup>170</sup> Atwood and others, however, maintained that these reactions (decomposition and substitution) were occurring by different mechanisms<sup>171</sup> and so direct comparisons were not meaningful.

One of the strongest arguments in favour of Poe's mechanism was the observation of the synthesis of the bis-phosphine substituted products very early in the reaction of  $\text{In}_2(\text{CO})_{10}$  with  $\text{PPh}_3$ <sup>155</sup> or  $\text{MnRe}(\text{CO})_{10}$  with  $\text{Ph}_3\text{P}$ .<sup>51</sup> Such observations are more readily rationalized by Scheme 2.2 than Scheme 2.1. Others have claimed that the disubstituted product only appears at a later stage of the reaction,<sup>52</sup> and that the reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{PPh}_3$  is totally suppressed in the presence of a carbon monoxide atmosphere.

If the mixed metal dimer  $\text{MnRe}(\text{CO})_{10}$  is considered, at no point in its substitution reactions<sup>51,52</sup> or its thermal decomposition under oxygen<sup>53</sup> are any homonuclear dimetallic species observed. To explain these observations in terms of a radical mechanism (Scheme 2.3) requires some unreasonable postulates to be made. For instance recombination of radicals to give homonuclear dimers (reaction steps 2.3.6-11) must occur to a negligible extent relative to those steps which reform a mixed metal dimer (steps 2.3.4, 5). Independent evidence is available to show that the radicals  $\cdot\text{M}(\text{CO})_5$  recombine at or near diffusion controlled rates<sup>172,173</sup> yet negligible amounts of the mixed metal dimer  $\text{MnRe}(\text{CO})_{10}$  are formed on heating a solution of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$ .<sup>152,174</sup>

Thus the data strongly suggest that a radical mechanism is not an important pathway in the thermal ligand substitution reaction. Conclusive evidence to support this has recently been obtained in studies by Muetterties and co-workers, employing isotopically labelled complexes. When either a mixture of  $^{185}\text{Re}_2(\text{CO})_{10}$  and  $^{187}\text{Re}_2(\text{CO})_{10}$ <sup>174</sup> or  $\text{Mn}_2(^{12}\text{CO})_{10}$  and  $\text{Mn}_2(^{13}\text{CO})_{10}$ <sup>175</sup> was reacted with triphenylphosphine (thermal reaction), negligible amounts of products that would result from metal-metal bond cleavage and reformation were observed.

## Scheme 2.3



Thus in the thermal ligand substitution reactions of  $M_2(CO)_6$  ( $M = \text{In, Re}$ ) a radical process can be ruled out but care must be taken in generalizing these results to other complexes, metals or even ligands.

## 2.5 Isomerisation and Scrambling in Manganese and Rhenium Carbonyl Complexes

The most conclusive method of determining structures especially in chiral molecules is X-ray crystallography but this gives the structure in the crystalline state and may not indicate structural isomerisation or ligand scrambling that can occur when in solution.

One of the first observations of such an isomerisation in a manganese complex was the intermolecular isomerisation of  $Mn(CO)_5L_2X$  ( $L, L' = \text{phosphine}$ ,  $X = \text{halide}$ ) which was thought to occur via ligand (L) dissociation.<sup>176</sup> The fac-complex is the kinetic product as expected from cis-labilizing considerations and when heated it isomerizes to the more thermodynamically stable mer-complex.

Carbon - 13 nuclear magnetic resonance developed in the early 1970's into a powerful tool for structure elucidation of organometallic complexes<sup>177</sup> such as transition metal carbonyl complexes. Due to the quadrupole moment of manganese ( $^{55}\text{Mn}$ ,  $I = 5/2$ ) the  $^{13}\text{C}$  NMR signals tend to be broad and unresolved<sup>178-182</sup> but may be

sharpened in some cases by isotopic enrichment<sup>179</sup> or by thermal decoupling at lower temperatures.<sup>180</sup> The sharp signals for equatorial and axial carbonyl carbon atoms in  $\text{PhCH}_2\text{Mn}(\text{CO})_5$  ( $-87^\circ\text{C}$ ),  $\text{Re}_2(\text{CO})_{10}$  ( $-60^\circ\text{C}$ ) and  $\text{Re}(\text{CO})_5\text{Br}$  ( $30^\circ\text{C}$ )<sup>181</sup> shows no scrambling of ligands is occurring at these temperatures. The  $^{13}\text{C}$  NMR spectrum of  $\text{Mn}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$ <sup>179, 180</sup> gave only a single broad signal at room temperature and it was uncertain if intramolecular ligand exchange was occurring or if the broadening was just a result of  $^{55}\text{Mn}$ - $^{13}\text{C}$  spin-spin coupling. When  $^{17}\text{O}$  NMR spectra of these two complexes were obtained,<sup>181</sup> two ligands for each complex were observed in a 1:4 ratio and assigned to axial and equatorial carbonyl oxygen atoms in each case. Thus under these conditions ( $28^\circ\text{C}$ ) no ligand scrambling is occurring in  $\text{Mn}(\text{CO})_5$  or  $\text{Mn}_2(\text{CO})_{10}$ . Similarly the  $^{17}\text{O}$  NMR spectra at ambient temperatures of  $\text{Mn}_2(\text{CO})_9(\text{Ph}_3\text{P})$ <sup>184</sup> and  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ <sup>185</sup> implied ligand scrambling was not significant.

Using  $^1\text{H}$  NMR spectroscopy the isomerisation of  $\text{Mn}_2(\text{CO})_7(\text{MeNC})_3$  has been observed, the two signals clearly resolved at  $30^\circ\text{C}$  are seen to coalesce on heating until at  $100^\circ\text{C}$  only one singlet is seen.<sup>186</sup> The best known

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\* The low temperature  $^1\text{H}$  NMR spectra of  $\text{Mn}_2(\text{CO})_7(\text{MeNC})_3$  consists of two singlets with intensities in a 1:2 ratio. This corresponds to one manganese atom having a single isonitrile bonded to it and the other manganese atom having two isonitriles bonded to it.

system in which ligand isomerisation is important is that of  $[\text{CoFe}(\text{CO})_3]_2$  and its derivatives for which the Cotton-Adams mechanism<sup>187</sup> is widely accepted. A similar mechanism is proposed for the isomerisation of  $\text{Mn}_2(\text{CO})_7(\text{P}(\text{t}^-\text{Bu})\text{NC})_3$  in which two ligands reversibly and simultaneously take up bridging positions and return to equatorial positions on either metal atom.<sup>188</sup> Finally  $\text{Co}_2\text{In}_2(\text{CO})_2(\text{NO})_2$  exists as two isomers in solution<sup>189</sup> and the  $^1\text{H}$  NMR data available has been interpreted in terms of the Cotton-Adams mechanism.<sup>187</sup>

### 3. A KINETIC STUDY OF THE SUBSTITUTION REACTIONS AND ISOMERISATION OF $M_2(CO)_{10}$ AND ITS DERIVATIVES

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#### 3.1 Introduction

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The synthesis of compounds  $M_2(CO)_{10-n}(CNR)_n$  ( $M = Re, Ir$ ) has been documented since the early 1960's and synthetic strategies were recently reviewed by Yamamoto<sup>189</sup> and Singleton and Oosthuizen.<sup>190</sup> The more successful of the methods of approach are listed below.

The direct substitution of isonitrile on  $M_2(CO)_{10}$  has been performed thermally,<sup>191</sup> using trimethylamine - N - oxide,<sup>192,193</sup> photochemically,<sup>188,191,194</sup> and by catalytic means.<sup>192-200</sup> Other indirect methods have been utilized to give a variety of isonitrile compounds.<sup>198,199</sup> Generally the upper limit to direct substitution has been  $n = 4$  with only equatorial positions being substituted. However, a series of complexes  $M_2(CO)_8(CNR)_4$  ( $M = Re, Ir$ ) have been prepared indirectly from  $M(CO)_5^-$  and  $M(CNR)_4^+$  ( $M = halide$ ).<sup>201</sup> Substitution into the axial position has been achieved when phosphines rather than isonitriles are used, e.g.  $ax-M_2(CO)_8(PPh_3)_2$ ,<sup>195,196,198,199</sup>  $ax-Re_2(CO)_8(PPh_3)_2$ ,<sup>196,198,201-203</sup>  $ax-M_2(CO)_8(PPh_3)_2$ ,<sup>195,204,205</sup> and  $di-ax-Re_2(CO)_8(PPh_3)_2$ .<sup>201-203</sup>

Although  $M_2(CO)_{10-n}(CNR)_n$  ( $n=1-4$ ) complexes are

known, <sup>186, 191, 192-197, 200</sup> no kinetic data for the reaction of  $M_2(CO)_4$ , or its derivatives with RNC is available. Further, no kinetic evidence for the mechanisms of any of the transition metal catalysed carbonyl substitution reactions <sup>193-197</sup> has been reported. A limited number of kinetic studies have, however, been undertaken on these types of dimers containing a metal-metal bond. <sup>52, 206</sup> An extensive kinetic study of the reactions of  $M_2(CO)_4$  ( $M = n, Re$  and  $R = Ph$ ) was reported and led to some controversy about the mechanism <sup>151, 155, 206, 207</sup> which was only recently resolved by isotopic labelling studies. <sup>174, 175</sup> (see Section 2.4)

The strong evidence now available suggests that the substitution of CO on  $M_2(CO)_4$  and  $n_2(CO)_4L$  by  $L'$  ( $L, L' = Ph, CH_3, C_6H_5, iBu, nBu, iPr, nPr$ ) occurs via a dissociative process <sup>151</sup> with  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  being 133-160 kJmol<sup>-1</sup> and 55-97 JK<sup>-1</sup>mol<sup>-1</sup> respectively. A similar study on  $Re_2(CO)_4$  <sup>52, 151</sup> reactions with  $L$  ( $L = Ph, CH_3, C_6H_5, nBu$ ) showed that the first substitution occurred mainly on the rhenium atom with  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  being 138-166 kJmol<sup>-1</sup> and 67-86 JK<sup>-1</sup>mol<sup>-1</sup> respectively. Such reactions have been shown to be first-order in metal carbonyl <sup>181</sup> although the order in the incoming ligand is uncertain. <sup>52</sup>

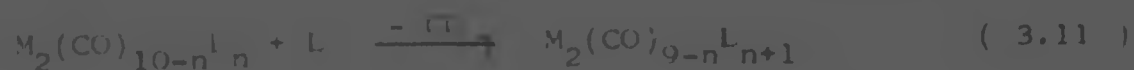
A mixture of the dimers  $M_2(CO)_4$  ( $M = n, Re$ ) scramble at elevated temperatures by a pathway involving homolytic

fission of the metal-metal bond.<sup>154</sup> There is presently only one report of movement of a non-carbonyl ligand across a Mn-In bond.<sup>155</sup> The rearrangement of  $\text{In}_2(\text{CO})_7(\text{CNMe})_3$  was shown to be unimolecular and intramolecular and occurred rapidly at 100°C. Observing the coalescence of the proton magnetic resonance signals due to the methyl isonitrile ligands allowed the activation parameters for the isomerisation process to be calculated and the values are

$$\Delta H^\ddagger = 54.2 (4.2) \text{ kJmol}^{-1}, \quad \Delta S^\ddagger = -74.0 \text{ JK}^{-1}\text{mol}^{-1}$$

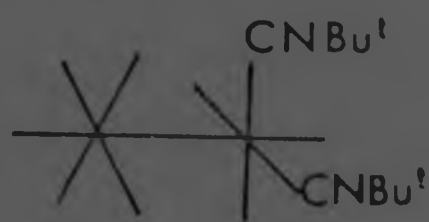
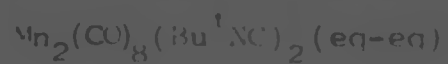
and  $\Delta G^\ddagger = 76.4 (6.1) \text{ kJmol}^{-1}.$

A kinetic investigation of the reactions of  $\text{M}_2(\text{CO})_{10-n}\text{L}_n$  ( $\text{M}=\text{In, Re}; n=0-2$ ) with L ( $\text{L}=\text{Bu}^t\text{NC}$ ) (3.11) was thus undertaken with the hope of further clarifying the reaction mechanism (3.11) and to obtain kinetic data for a comparison of the catalysed and uncatalysed reactions.

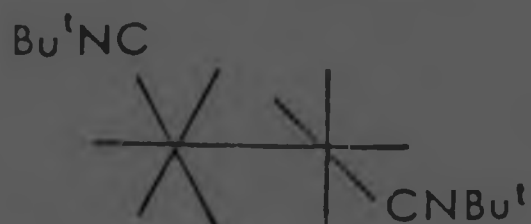


There are two structural isomers of the complex  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  (eq-eq) (Fig.3.1) and the isolation of the pure isomers and their possible interconversion was also investigated.

Figure 3.1      structural Isomers of the Complex



1,1- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$



1,2- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

### 3.2 Results

The spectral and physical data for the substituted homonuclear dimers  $M_2(CO)_{10-n}(Bu^tNC)_n$  ( $M=In, Re$ ;  $n=1-3$ ) is given in Tables 2.1 and 3.2 and similar data for the complexes  $Re(CO)_{10-n}(Bu^tNC)_n$  ( $n=0-2$ ) is presented in Table 3.3. The reactions were followed by infrared spectrophotometry using the intensities of peaks in the absorbance mode as a measure of the extent of the reaction. Data were recorded at various temperatures and reactant concentrations, although a large excess of isonitrile was always maintained to allow the use of pseudo-first-order kinetics.

The substitution of  $Mn_2(CO)_{10}$  by  $Bu^tNC$  (3.21) was only observed at a reasonable rate ( $t_{1/2} < 2$  hours) when temperatures in excess of  $70^\circ C$  were used. The second substitution (3.22) at these temperatures occurs at a comparable rate but it was generally possible to follow the first substitution to over three half-lives before significant deviations from the first-order kinetics was observed. It was assumed that these reactions were zero-order in incoming ligand concentration and first-order in metal dimer concentration, and this was confirmed later.

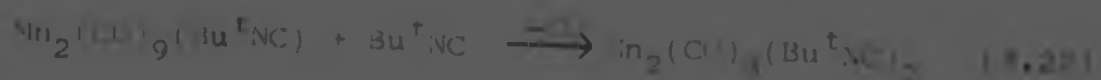
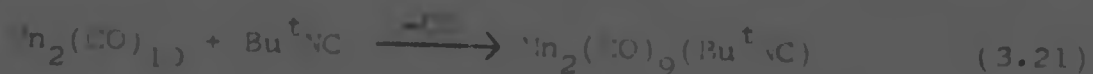


Table 3.1 Physical and Spectral Data for the Complexes

| Complex                                                                | $\text{Mol}^a$ | Colour | $\epsilon_{\text{M}}^b$ |
|------------------------------------------------------------------------|----------------|--------|-------------------------|
| $\text{Mn}_2(\text{O})_4(\text{Hn}^+\text{SCl})_2$                     | 91 - 92        | Yellow | 0.77                    |
| $\text{1,1-bis}(\text{Mn}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2$     | 99 - 102       | Yellow | 0.95                    |
| $\text{1,2-bis}(\text{Mn}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2$     | 78 - 80        | Yellow | 0.91                    |
| $\text{1,1,2-bis}(\text{Mn}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2^c$ | 109 - 111      | Yellow | 1.06, 1.00 <sup>d</sup> |
| $\text{Fe}_2(\text{O})_4(\text{Hn}^+\text{SCl})_2$                     | 104 - 106      | White  | 0.75                    |
| $\text{1,1-bis}(\text{Fe}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2$     | 101 - 105      | White  | 0.93                    |
| $\text{1,2-bis}(\text{Fe}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2$     | 95 - 98        | White  | 0.87                    |
| $\text{1,1,2-bis}(\text{Fe}_2(\text{O})_4)(\text{Hn}^+\text{SCl})_2^e$ | 151 - 152      | White  | 1.02, 0.90 <sup>d</sup> |

<sup>a</sup> Uncorrected ( $^{25}^\circ\text{C}$ ). <sup>b</sup> Run in  $\text{C}_6\text{H}_6$  relative to  $\text{TiO}_2$  (6) <sup>c</sup> Ref. 198.<sup>d</sup> Ratio 1:2. <sup>e</sup> Ref. 197.

Table 3.2

Infrared Spectral Data for the Compounds

 $\nu_{\text{max}}(\text{cm}^{-1})_{\text{film}}$  ( $\nu = \text{cm}^{-1}$ ,  $\text{ref} = 1-3$ )

| Compound                                                                     | $\nu_{\text{max}}$        | Infrared Spectra ( $\text{cm}^{-1}$ ) <sup>a</sup>             | $\nu_{\text{max}}$ |
|------------------------------------------------------------------------------|---------------------------|----------------------------------------------------------------|--------------------|
| $\text{CH}_2(\text{CH}_2)_4(\text{CO}_2\text{Me})$                           | 2170(s)                   | 2952(s), 2917(s), 1996(vs), 1968(m), 1950(s)                   |                    |
| 1,1-bis- $\text{CH}_2(\text{CH}_2)_6(\text{CO}_2\text{Me})_2$                | 2160(s), 2136(m)          | 2955(s), 1993(vs), 1977(s), 1964(m), 1952(m), 1934(s)          |                    |
| 1,2-bis- $\text{CH}_2(\text{CH}_2)_6(\text{CO}_2\text{Me})_2$                | 2142(s)                   | 2949(s), 1990(s), 1977(vs), 1947(s), 1939(m)                   |                    |
| 1,1,2-bis- $\text{CH}_2(\text{CH}_2)_7(\text{CO}_2\text{Me})_2$ <sup>b</sup> | 2130, 2130, 2070          | 2916, 1986, 1957, 1920                                         |                    |
| $\text{CH}_2(\text{CH}_2)_6(\text{CO}_2\text{Me})$                           | 2175(s)                   | 2907(s), 2946(s), 2015(s), 1995(vs), 1970(s), 1971(s), 1953(s) |                    |
| 1,1-bis- $\text{CH}_2(\text{CH}_2)_8(\text{CO}_2\text{Me})_2$                | 2180(m), 2157(s)          | 2903(s), 2972(s), 1987(s), 1952(s), 1935(s)                    |                    |
| 1,2-bis- $\text{CH}_2(\text{CH}_2)_8(\text{CO}_2\text{Me})_2$                | 2155(m)                   | 2900(s), 2943(s), 1979(vs), 1955(s)                            |                    |
| 1,1,2-bis- $\text{CH}_2(\text{CH}_2)_9(\text{CO}_2\text{Me})_2$ <sup>c</sup> | 2154(s), 2134(s), 2114(s) | 2900(s), 2987(vs), 1967(s), 1924(m), 1925(s)                   |                    |

<sup>a</sup> Run in hexane.<sup>b</sup> Ref. 195.<sup>c</sup> Ref. 197.

Table 1.3 Physical and spectral data for the complexes

| $\text{Co}(\text{CO})_2\text{P}(\eta^5\text{-C}_5\text{H}_5)(\text{Bu}^t\text{C}_6\text{H}_4)_2$ (mol-%) |        |
|----------------------------------------------------------------------------------------------------------|--------|
| Compound                                                                                                 | Colour |
| $\text{Co}(\text{CO})_2\text{P}(\eta^5\text{-C}_5\text{H}_5)(\text{Bu}^t\text{C}_6\text{H}_4)_2$         | White  |
| $\text{Co}(\text{CO})_2\text{P}(\eta^5\text{-C}_5\text{H}_5)(\text{Bu}^t\text{C}_6\text{H}_4)_2$         | Red    |
| $\text{Co}(\text{CO})_2\text{P}(\eta^5\text{-C}_5\text{H}_5)(\text{Bu}^t\text{C}_6\text{H}_4)_2$         | Red    |

<sup>a</sup> recorded in  $\text{C}_6\text{H}_6$ . <sup>b</sup> Spectroscopic multiplicity (for  $1,2,4,6\text{-C}_6\text{H}_4$ )  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{Co}$ .

An inert atmosphere was used throughout these experiments. When the system was insufficiently purged an "induction" period (initial period during which no reaction occurred) was observed and much decomposition occurred.<sup>53,20P</sup> The rate constant calculated for this reaction (3.21) was found to be  $3.7 \times 10^{-3} \text{ s}^{-1}$  (73°C) (Table 3.4) which is considerably greater than those calculated for the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with phosphines<sup>151,155</sup> (see Discussion).

The catalysed reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Bu}^t\text{NC}$  (3.23) occurs rapidly at much lower temperatures. The reaction was followed at room temperature (18°C) and at temperatures up to 26°C, the upper temperature being limited by the speed at which monitoring could be performed. A constant amount of catalyst was used and the same stirring rate was used for all reactions. The catalysed reactions were assumed to follow the same kinetics as the uncatalysed reactions. This was investigated and indeed the rate constant appears to be independent of isonitrile concentration (Table 3.4) and does follow first-order kinetics to at least 3 half-lives before deviating significantly from a linear plot. The



rate constant for the catalysed reaction was estimated to

TABLE 3.4 Kinetic Data for the Substitution Reactions  
 of  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  with  $\text{C}_2\text{H}_5\text{I}$  by  $\text{Sn}^{2+}\text{Cl}_2$

| Reaction          | $T(^{\circ}\text{C})$ | Catalyst <sup>a</sup> | $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ <sup>b</sup> | $\text{C}_2\text{H}_5\text{I}$ <sup>b</sup> | $k$ <sup>c</sup> | $t_{1/2}$ <sup>d</sup> |
|-------------------|-----------------------|-----------------------|----------------------------------------------------------|---------------------------------------------|------------------|------------------------|
| 3.21              | 75                    | —                     | 0.0002                                                   | 0.001                                       | 3.723            | 11.7(3.5)              |
| 3.22              | 15                    | —                     | 0.0002                                                   | 0.001                                       | 6.205            | 3.2(3.7)               |
| 3.23              | 26                    | —                     | 0.0002                                                   | 0.001                                       | 25.793           | 2.2(1.9)               |
| 3.24              | 18                    | —                     | 0.0002                                                   | 0.001                                       | 6.621            | 13.9(4)                |
| 3.25              | 35                    | —                     | 0.0002                                                   | 0.001                                       | 7.000            | 18.7(4.6)              |
| 3.26              | 25                    | —                     | 0.0002                                                   | 0.001                                       | 21.998           | 3.4(4.3)               |
| 3.27 <sup>e</sup> | 10                    | —                     | 0.0002                                                   | 0.001                                       | —                | —                      |

<sup>a</sup>  $\text{Sn}^{2+}$  is  $10^{-3}$  M.

<sup>b</sup> Initial concentrations in M.

<sup>c</sup> Second-order rate constant in  $\text{M}^{-1}\text{s}^{-1}$ .

<sup>d</sup> Half-life for reaction in min; number of half-lives

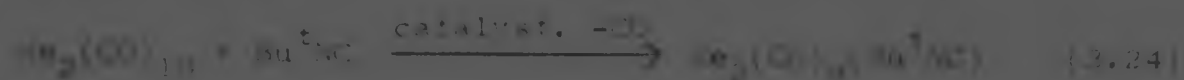
the reaction was followed is in parentheses.

<sup>e</sup> For  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  instead of  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ .

<sup>f</sup> Reaction observed after 6 hours.

be greater than that for the uncatalysed reaction by a factor of approximately 40 at 72°C with a catalyst to dimer ratio of 1:20 (by mass, or 1:7 by moles).

Attempts at substitution on  $\text{Co}_2(\text{CO})_8$  by  $\text{Bu}^t\text{NC}$  without catalyst were not successful (110°C, 8 hours). The catalysed reaction (3.24) did however, occur at much lower temperatures and the reaction rate was found to be dependent on the choice of catalyst, see Table 3.4. Using  $\text{Co}$  catalyst the reaction occurred at almost the same rate as the equivalent catalysed reaction with  $\text{Ni}_2(\text{CO})_8$  (3.23).



The second substitution (3.23) was shown by reactant concentration variation to be independent of isocyanide concentration (when in large excess), see Table 3.5. Figure 3-8 shows examples from a typical set of spectra, in this case corresponding to the reaction of  $\text{Ni}_2(\text{CO})_8(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  in the presence of a catalyst ( $\text{Co}$ ) at 70°C. The rate constant for this reaction was calculated for several temperatures over a 25°C range (Table 3.6) and an Arrhenius plot yielded the activation parameters  $\Delta H^\ddagger = 29.26 \text{ (0.48) kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 154.2 \text{ (2.3) J K}^{-1} \text{ mol}^{-1}$  and  $\Delta G^\ddagger = 26.1 \text{ (0.5) kJ mol}^{-1}$ .

TABLE 3.5      Kinetic Data for the Substitution Reactions  
on  $M_2(CO)_9(Bu^tNC)$  by  $Bu^tNC$

| Reaction          | T(°C) | Catalyst <sup>a</sup> | $M_2(CO)_9$ <sup>b</sup> | $Bu^tNC$ <sup>b</sup> | k <sup>c</sup>  | $t_{1/2}$ <sup>d</sup> |
|-------------------|-------|-----------------------|--------------------------|-----------------------|-----------------|------------------------|
| 3.22              | 52    | -                     | 1.0030                   | 17.73                 | 1.272           | 51.0(7)                |
| 3.22              | 52    | -                     | 1.0030                   | 35.48                 | 1.223           | 26.6(5.1)              |
| 3.22              | 52    | -                     | 2.1000                   | 17.73                 | 1.209           | 54.0(4)                |
| 3.22              | 65    | -                     | 0.7205                   | 19.74                 | 3.382           | 17.3(5)                |
| 3.22              | 77    | -                     | 1.3350                   | 20.19                 | 8.060           | 7.1(6)                 |
| 3.25              | 18    | PdO                   | 1.0900                   | 13.25                 | 4.651           | 7.5(8)                 |
| 3.25              | 23    | PdO                   | 0.4131                   | 27.71                 | 6.324           | 6.6(10)                |
| 3.25              | 25    | PdO                   | 0.9641                   | 21.21                 | 6.726           | 8.1(6)                 |
| 3.22 <sup>e</sup> | 110   | -                     | 0.4210                   | 23.41                 | nr <sup>f</sup> | -                      |
| 3.26              | 25    | dO                    | 0.7645                   | 13.79                 | 3.260           | 25.7(4)                |

<sup>a</sup> Using PdO or no catalyst.

<sup>b</sup> Initial concentrations in mol l<sup>-1</sup> (x10<sup>2</sup>).

<sup>c</sup> Pseudo-first-order rate constant in s<sup>-1</sup> (x10<sup>4</sup>).

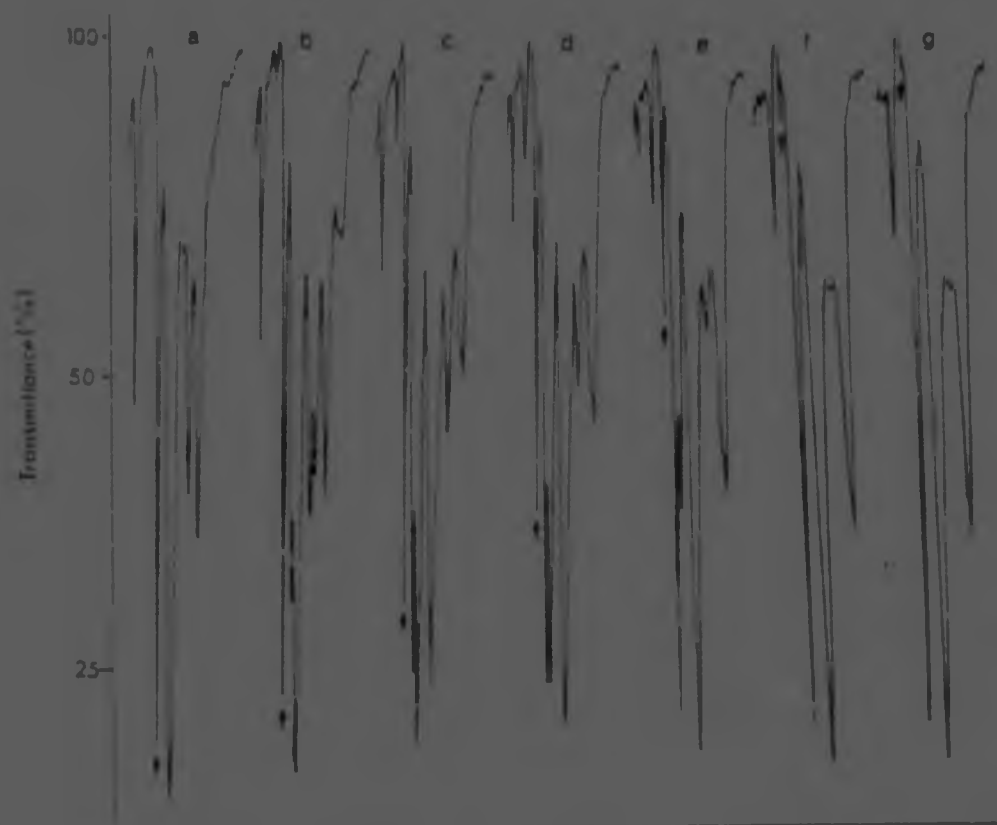
<sup>d</sup> Half-life for reaction (min.) and number of half-lives the reaction was followed for in parentheses.

<sup>e</sup> for  $Fe_2(CO)_9(Bu^tNC)$  instead of  $M_2(CO)_9(Bu^tNC)$ .

<sup>f</sup> No reaction observed after 4 hours.

Figure 3.2

Typical Infrared Spectra Recorded During  
the Reaction of  $\text{Mn}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$  and  
 $\text{Bu}^t\text{NC}$  in the presence of  $\text{PdO}$ \*



\* Infrared spectra recorded between  $2100$  and  $1900\text{cm}^{-1}$  for the reaction of  $\text{Mn}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  in the presence of  $\text{PdO}$  at  $25^\circ\text{C}$  recorded at various times  
a) start, b) 8 mins, c) 16 mins, d) 21 mins  
e) 29 mins, f) 41 mins, g) 50 mins. The change in intensity of certain absorbance bands (e.g. that indicated by the arrow) could be used to measure the extent of the reaction.

A variable temperature study of the catalysed (PdO) second substitution on  $\text{Ir}_2(\text{CO})_{10}$  by  $\text{Bu}^t\text{NC}$  (3.25) over a  $7^\circ\text{C}$  range in temperature gave a similar Arrhenius plot and the activation parameters so obtained are  $\Delta H^\ddagger = 39.2$  (0.4)  $\text{kJmol}^{-1}$ ,  $\Delta S^\ddagger = 90.0$  (1.3)  $\text{JK}^{-1}\text{mol}^{-1}$  and  $\Delta G^\ddagger = 12.2$  (0.3)  $\text{kJmol}^{-1}$ .



The second substitution on  $\text{Re}_2(\text{CO})_{10}$  by  $\text{Bu}^t\text{NC}$  could not be followed without a catalyst although prolonged heating of a solution of  $\text{Re}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$  and excess  $\text{Bu}^t\text{NC}$  was attempted ( $110^\circ\text{C}$ , 6 hours). The catalysed reactions (3.26) proceeds rapidly at low temperatures although it is still considerably slower than the catalysed reactions of  $\text{Ir}_2(\text{CO})_9(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  (3.25).



The low temperature catalysed reaction of  $\text{Ir}_2(\text{CO})_9(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  (3.25) gave a product with an infrared spectrum different from that previously reported for  $\text{Ir}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ .<sup>195</sup> All peaks in the spectrum of the product from the low temperature reaction were common to the spectrum previously reported. Upon heating the product from the low temperature reaction to temperatures

greater than 50°C the spectra changed to that previously reported. The first (low temperature) product was assigned the structure of 1,2- $\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  (see later) and the heating clearly induced an isomerisation to the equilibrium mixture of the disubstituted products (Fig. 3.3).

Figure 3.3 Isomerisation Equilibrium for  
 $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

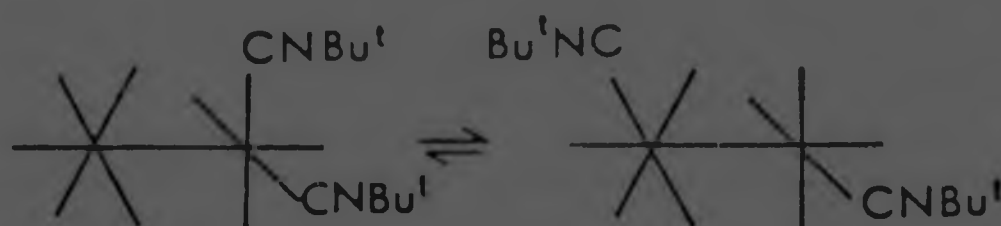


Figure 1,2-disubstituted product could be obtained by work up of the low temperature catalysed synthesis and pure 1,1-disubstituted product was obtained as orange crystals from a refrigerated hexane solution of a mixture of the isomers. The assignment of the structures of the two isomers was made possible by a mass spectral study and a crystal structure determination of the complex 1,1- $\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ .

Kinetic data for the isomerisation were collected over a temperature range of greater than 30°C and is presented in Table 3.7. Typical spectra collected during an isomerisation are presented in Fig. 3.4; they form a part of the complete set of spectra for the isomerisation of

TABLE 3.6

Arrhenius Data for the Reaction:



| Reaction | (°C) | $k^a$ | $1/T(\text{K}^{-1})$ | $\ln k$ |
|----------|------|-------|----------------------|---------|
| 3.22     | 52   | 1.235 | 3.0755               | -6.6967 |
| 3.22     | 65   | 3.382 | 2.9573               | -5.6893 |
| 3.22     | 77   | 8.060 | 2.8559               | -4.8205 |
| 3.25     | 18   | 4.651 | 3.4347               | -5.3707 |
| 3.25     | 23   | 6.324 | 3.3767               | -5.0634 |
| 3.25     | 25   | 6.726 | 3.354                | -5.0118 |

<sup>a</sup> pseudo-first-order rate constants in  $\text{s}^{-1} \times 10^3$ .

TABLE 3.7

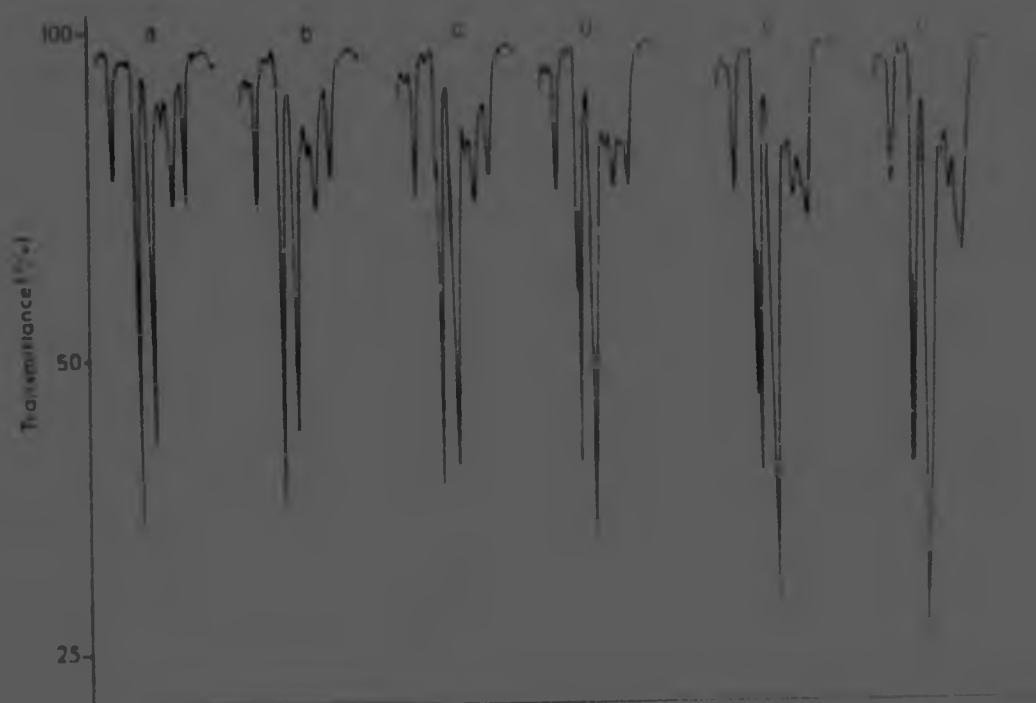
Kinetic Data for the Isomerisation of



| $T(^{\circ}\text{C})$ | $\text{In}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | $k_A^b$ | $k_B^b$ | $K_{eq}^c$ |
|-----------------------|----------------------------------------------------|---------|---------|------------|
| 52                    | 0.3157                                             | 0.6191  | 0.0410  | 0.058      |
| 62 <sup>d</sup>       | 0.2321                                             | 0.5856  | 0.0783  | 0.067      |
| 71                    | 0.2074                                             | 3.2280  | 4.1740  | 0.775      |
| 73                    | 0.4023                                             | 4.7110  | 5.2705  | 0.799      |
| 84                    | 0.5171                                             | 9.0640  | 11.5660 | 0.850      |

<sup>a</sup> Concentration in  $\text{mol l}^{-1} \times 10^3$ .<sup>b</sup> rate constant  $\text{s}^{-1} \times 10^3$ ,  $K_{eq} = k_A/k_B$ .<sup>c</sup>  $\text{Bu}^t\text{NC}$  present in concentration  $0.225 \text{ mol l}^{-1}$ .

Figure 3.4 Typical Infrared Spectra Recorded During the Isomerisation of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  to an Equilibrium Mixture of the Structural Isomers of  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

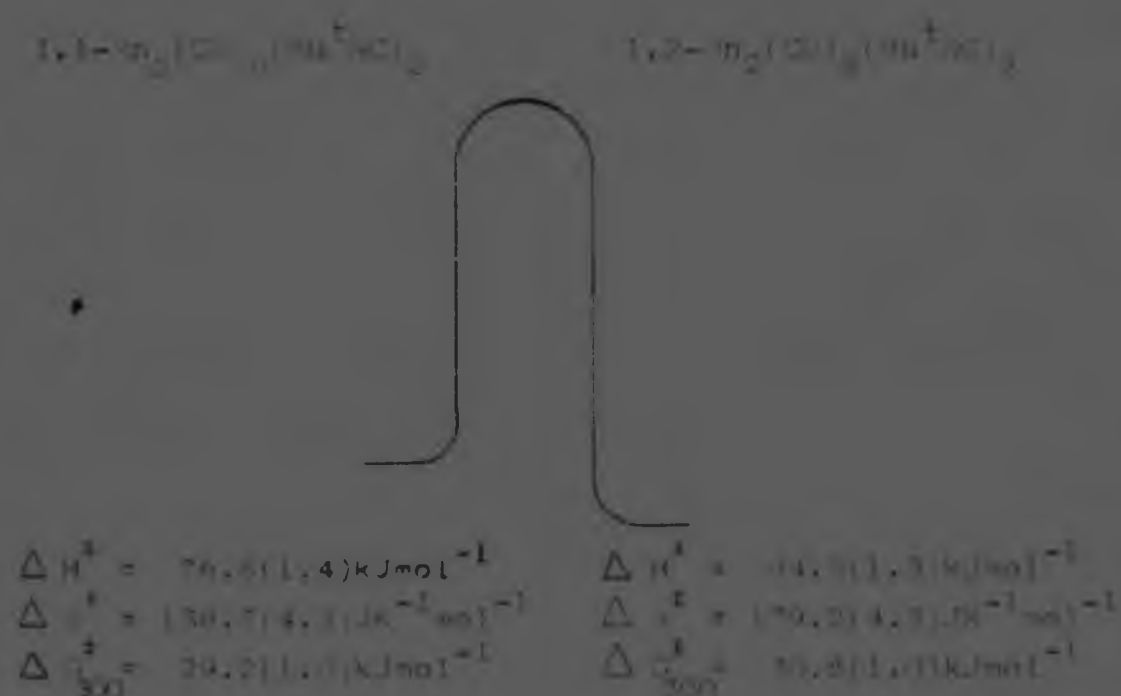


\* Infrared spectra between  $2100$  and  $1900\text{cm}^{-1}$  for the structural isomerisation of  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  at  $52^\circ\text{C}$  recorded at various times

- a) start, b) 12 mins, c) 31 mins, d) 60 mins  
e) 95 mins, f) 130 mins.

1,1-dimethyl-2,2-dichloroethane to the equilibrium mixture at 52°C. No inhibition of the isomerisation was observed when in the presence of a large excess of isonitrile. The rate of isomerisation was not affected by a change in the concentration of the dimer. From the data in Table 3.8 Arrhenius plots yielded the thermodynamic data presented in Fig. 3.5.

Figure 3.5 Thermodynamic data for the isomerisation of  $\text{Me}_2(\text{CO})_2$  in  $\text{CH}_3\text{NC}$



The sample  $\text{Me}_2(\text{CO})_2$  produced by the catalysed reaction of  $\text{Me}_2(\text{CO})_2$  and  $\text{CH}_3\text{NC}$ , had an infrared spectrum which suggested the presence of only the 1,2-isomer. Heating of the sample did not cause any isomerisation to occur as detected by infrared and NMR spectroscopy. The

other isomer, 1,1-Re<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub>, was synthesised indirectly from NaRe(CO)<sub>5</sub> and Re(CO)<sub>5</sub>(Bu<sup>t</sup>NC)<sub>2</sub> and also did not isomerise to the 1,2-isomer on prolonged heating at 110°C. The physical and spectral data for both the isomers of the complex M<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub> (M = Ir, Re) are presented in Tables 3.1 and 3.2.

The reaction of Ir<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub> with Bu<sup>t</sup>NC (3.27) was only observed at elevated temperatures in the presence of a catalyst. When a mixture of the two isomers of Ir<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub> was used the 1,1-isomer was seen to react at a greater rate than the 1,2-isomer (by a factor of approximately 2.5). Similarly Re<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub> and Bu<sup>t</sup>NC reacted (3.28) in the presence of Pd at elevated temperature, and the 1,1-isomer reacted more rapidly than the 1,2-isomer. The kinetic data for these reactions is presented in Table 3.0.

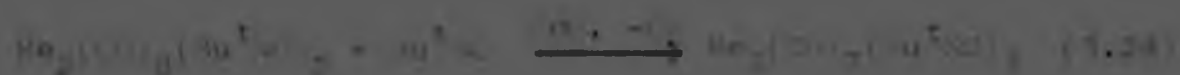
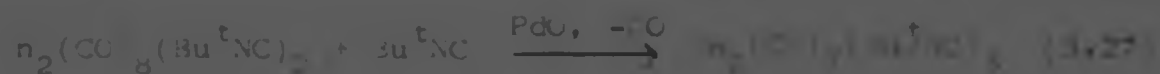


TABLE 3.8 Arrhenius Data for the Isomerisation of  
the Two Isomers of  $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

| $T(^{\circ}\text{C})$ | $k_A^a$ | $k_B^a$ | $T^{-1b}$ | $\ln k_A$ | $\ln k_B$ |
|-----------------------|---------|---------|-----------|-----------|-----------|
| 52                    | 0.6124  | 2.9107  | 3.076     | -9.717    | -9.305    |
| 71                    | 3.2280  | 4.1741  | 2.906     | -8.038    | -7.781    |
| 73                    | 4.2111  | 5.2705  | 2.889     | -7.773    | -7.548    |
| 84                    | 9.0041  | 11.5661 | 2.810     | -6.921    | -6.762    |

<sup>a</sup> Rate constants in  $\text{s}^{-1} \times 10^3$ .

<sup>b</sup>  $\text{K}^{-1} (\times 10^3)$ .

TABLE 3.9 Kinetic Data for the Reactions of  
 $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  ( $\text{M} = \text{n.i.e.}$ ) with  $\text{Bu}^t\text{NC}$   
using  $\text{M}^0$  Catalyst

| Complex                                                | $T(^{\circ}\text{C})$ | dimer <sup>a</sup> | $\text{Bu}^t\text{NC}^a$ | $k^b$ |
|--------------------------------------------------------|-----------------------|--------------------|--------------------------|-------|
| 1,1- $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | 73                    | 0.2186             | 17.71                    | 3.58  |
| 1,2- $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | 73                    | 0.2577             | 17.73                    | 1.43  |
| 1,1- $\text{e}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | 80                    | 0.3211             | 28.67                    | 4.15  |
| 1,2- $\text{e}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ | 82                    | 0.3576             | 33.25                    | 2.97  |

<sup>a</sup> Initial concentrations in  $\text{mol l}^{-1} (\times 10^3)$ .

<sup>b</sup> pseudo-first-order rate constant in  $\text{s}^{-1} \times 10^3$ .

TABLE 3.8 Arrhenius Data for the Isomerisation of the Two Isomers of  $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$

| $T(^{\circ}\text{C})$ | $k_1^a$ | $k_2^a$ | $t \times 10^3$ | $\ln \eta_1$ | $\ln k_2$ |
|-----------------------|---------|---------|-----------------|--------------|-----------|
| 52                    | 0.0024  | 0.0037  | 1.076           | -0.747       | -7.305    |
| 71                    | 3.2260  | 4.174   | 2.000           | -1.120       | -7.781    |
| 73                    | 4.2411  | 5.2705  | 2.089           | -1.771       | -7.548    |
| 84                    | 9.0043  | 11.5000 | 2.000           | -0.720       | -5.762    |

<sup>a</sup> Rate constants in  $\text{s}^{-1} (\times 10^3)$ .

<sup>b</sup>  $t \times 10^3 (\text{s})$ .

TABLE 3.9 Kinetic Data for the Reactions of  $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$  (Isomerised with  $\text{Au}^{\text{I}}\text{SCl}$  as Ion-Pair Catalyst)

| Complex                                                     | $T(^{\circ}\text{C})$ | Order <sup>a</sup> | $\ln^+ \text{Au}^{\text{I}}\text{SCl}$ | $k^b$ |
|-------------------------------------------------------------|-----------------------|--------------------|----------------------------------------|-------|
| 1,1- $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$ | 49                    | 0.2100             | 17.77                                  | 8.58  |
| 1,2- $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$ | 73                    | 0.3777             | 17.73                                  | 1.43  |
| 1,1- $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$ | 81                    | 0.5130             | 18.07                                  | 4.17  |
| 1,2- $\pi_2(\text{CO})_2(\text{Au}^{\text{I}}\text{SCl})_2$ | 81                    | 0.6776             | 18.05                                  | 3.97  |

<sup>a</sup> Initial concentrations in mol  $(\text{dm}^3)^{-1}$ .

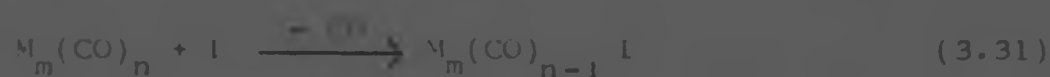
<sup>b</sup> pseudo-first-order rate constant in  $\text{s}^{-1} (\times 10^3)$ .

### 3.3 Discussion

The results obtained suggest that the reaction (3.31) involves carbonyl ligand dissociation as the rate determining step. This is evidenced by the correlation of the data with first order dependence in metal dimer concentration and the apparent lack of ligand concentration dependence on the reaction rate (Tables 3.4 and 3.5). The data are thus not inconsistent with the general rate law observed in other systems (2,151,153,210)

$$k_{\text{obs}} = \frac{k_1}{k_1 + k_2 [L]} \left[ M_m(\text{CO})_n \right] \\ (k_2 < k_1).$$

e.g. reaction 3.31, in which a small ligand



dependence was observed. The limited data do not preclude some ligand dependence and further studies with other isonitriles will be needed to complete this study.

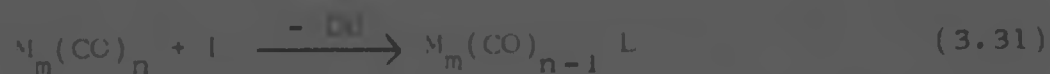
A surprising feature of the reaction between  $Mn_2(\text{CO})_{10}$  and isonitrile is that the observed rate constant ( $k_{\text{obs}}$ ) is larger than that for the reaction with phosphines (151) or even labelled CO (175) ( $3.7 \times 10^{-3} \text{ s}^{-1}$  at  $73^\circ\text{C}$  for  $\text{Bu}^t\text{NC}$ ,  $2.6 \times 10^{-4} \text{ s}^{-1}$  for  $\text{PPh}_3$  at  $120^\circ\text{C}$ ). Since the

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reaction with  $\text{Rh}_3$  and  $^{13}\text{CO}$  is assumed to occur via a dissociative mechanism (and there is comprehensive data to support this), this would imply that the reaction with isonitrile must be different i.e. the  $k_2[\text{L}]$  term is non-zero. However, the data at least suggest the reaction occurs predominantly via a dissociative mechanism.

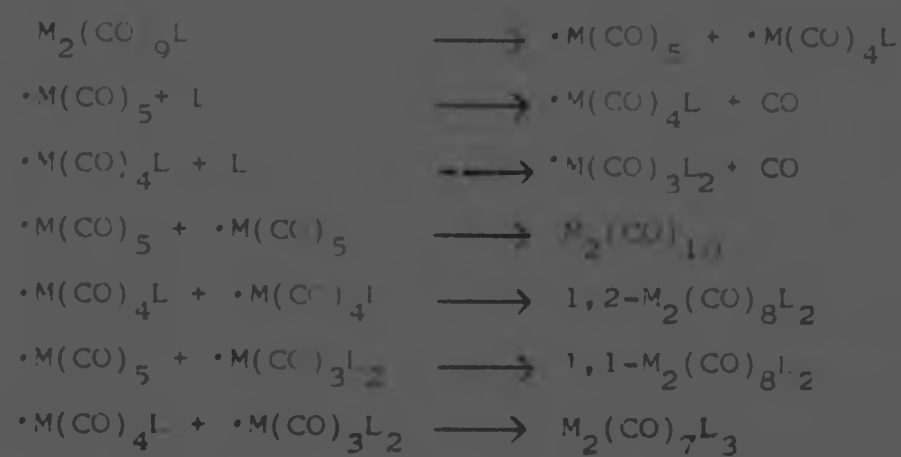
There has been much controversy over the mechanism of these substitution reactions although all types of associative processes have been ruled out.<sup>52</sup> Extensive kinetic studies by Poe and others<sup>51,155,156,159,163,169,208,211</sup> led to a proposed mechanism involving homolytic cleavage of the metal-metal bond as the first step in the substitution reactions of the homonuclear dimers  $\text{M}_2(\text{CO})_4$  and their derivatives<sup>159,170,212</sup> (see earlier). Poe's mechanism (Scheme 2.3) would be expected to give a mixture of di, mono and unsubstituted dimers from a reaction of  $\text{M}_2(\text{CO})_4$  and  $\text{RNC}$  in 1 to 1 proportions but it was observed that no detectable amounts of disubstituted product appeared in under 3 half-lives of the reaction of dimer with excess isonitrile. When the reaction of  $\text{In}_2(\text{CO})_9(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  was followed no  $\text{In}_2(\text{CO})_9$  was detected during the reaction. Further, Poe's mechanism (Scheme 2.1) would lead to a mixture of radicals  $\cdot\text{In}(\text{CO})_3$  and  $\cdot\text{In}(\text{CO})_4(\text{Bu}^t\text{NC})$  and from Brown's work (cis-labilization<sup>128-130</sup>) the substitution on  $\cdot\text{InCO}_4(\text{Bu}^t\text{NC})$  would be

expected to occur more rapidly than that on  $\cdot\text{Mn}(\text{CO})_5$ . Thus the major initial product (before isomerisation) would be expected to be the 1,1-disubstituted dimer. This is not seen in this work or reported work with phosphines. No trisubstituted products were observed either when phosphines or isonitriles were used and thus none of the results agree with those predicted by Poë's mechanism unless further postulates are made about the positions of equilibria or the relative rates of recombination of different radicals. Indeed a recent communication by Poë *et al*<sup>141</sup> showed that reactions upon the radical species  $\cdot\text{Re}(\text{CO})_5$  proceed by an associative pathway, the CO dissociation being negligible.

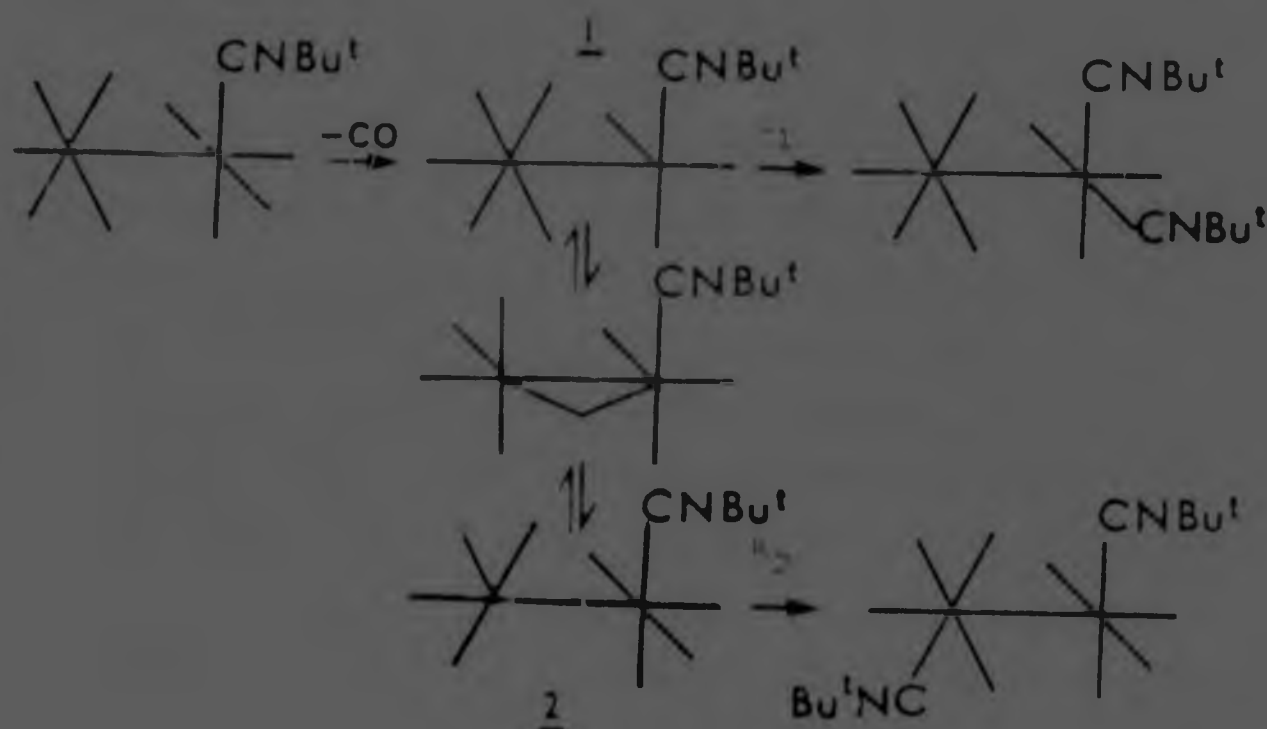
An alternative mechanism suggested initially by Bascio and Hawersik<sup>140</sup> and later by Atwood and co-workers<sup>171,208</sup> involves carbonyl dissociations from the dimer as the first and rate determining step in the substitution reactions (see earlier). This explains the kinetic data for the substitution on  $\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Ni, Fe}$ ). However, when  $\text{M}_2 = \text{Re}$  (see later) or the second substitution of CO by I is considered this mechanism also fails to satisfactorily explain the available results. Work by Brown *et al*<sup>142</sup> has shown *cis*-labilization to be important in substitution reactions of many metal carbonyls and so  $\text{M}_2(\text{CO})_{10}(\text{R}^t\text{NC})$



Scheme 1.1



Scheme 3.2



the rate of reaction of the  
 $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  to  $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$   
 at the same temperature was found to be  $5.1 \times 10^{-5} \text{ s}^{-1}$ .  
 The photochemical reaction of the  
 to give the 1,1 isomer followed  
 the reaction of  $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  to  $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  was not  
 achieved even on prolonged heating with or without catalyst  
 present. Thus substitution to give the 1,1 isomer followed  
 a reaction which was ruled out as a possible pathway.

If one considers the substitution reactions of the  
 monomeric complexes  $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  they are first  
 order in metal carbonyl concentration.<sup>121,123,128,213</sup>  
 In the carbonyl substitution reactions by phosphines or  
 $\text{C}_6\text{H}_5$  the rate determining step appears to be carbonyl  
 dissociation.<sup>125,124,217</sup> and the carbonyl *cis*-to-bromine  
 dissociate more rapidly than the *trans*-carbonyl.<sup>217</sup>  
 The reactions of the substituted carbonyl bromides  
 $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  have also been studied, and the  
 substituted carbonyl bromides for substituted carbonyl bromides,  
 the ligands  $(\text{C}_6\text{H}_5)_3\text{P}$ ,  $(\text{C}_6\text{H}_5)_2\text{P}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$  have been ordered  
 in terms of their *cis*-to-bromine dissociation.<sup>129</sup> A possible  
 explanation for the *cis*-to-bromine dissociation was offered  
 by the carbonyl bromide  $(\text{C}_6\text{H}_5)_3\text{P}(\text{C}_6\text{H}_5)_2\text{Au}^+\text{Br}^-$  and the carbonyl  
 a carbonyl bromide by a carbonyl bromide a carbonyl bromide  
 carbonyl bromide.

Using the ideas of the cis-labilizing effect the series of  $M(CO)_5X$  complexes can be extended to include the compounds presently being considered e.g.  $M(CO)_5X$  with  $X = Ni(CO)_4$  or  $M(CO)_4(M^+X^-)$  etc. Thus the initial formation of  $1,2-M_2(CO)_8(M^+X^-)$  rather than  $1,1-M_2(CO)_8(M^+X^-)$  occurs since the group  $M(CO)_4$  has a greater cis-labilizing effect than the accumulated cis-labilization of  $M(CO)_5$  and  $M^+X^-$ . Similarly the rate constant for substitution on  $1,1-M_2(CO)_8(M^+X^-)$  is greater than that for substitution on  $1,2-M_2(CO)_8(M^+X^-)$  and so the cis-labilizing effect of the group  $M(CO)_4$  is greater than the cis-labilizing effect of  $M(CO)_5$  and  $M^+X^-$  combined. Thus the order of decreasing cis-labilizing effect is

$$M(CO)_5(M^+X^-) > M(CO)_4(M^+X^-) > M(CO)_5$$

and other results suggest an analogous series for the rhodium complexes. Unfortunately this work does not allow for the ligands  $CO$  and  $M^+X^-$  to be placed in a sequence relative to the rate of substitution as it details a mechanism for the metal carbonyls and indeed suggests that  $CO$  and  $M(CO)_4$  groups have approximately equal cis-labilizing effects. From electronic considerations alone it is expected that isocyanides,  $RNC$ , should have a greater cis-labilizing effect than the carbonyl ligand. Work on carbonyl substitution of  $M(CO)_5L$  by isocyanide in which the rate

of second substitution is far greater than the rate of first substitution confirms this ordering, but further experiments are necessary to place all these groups (ligands or metal derivatives) in a single ordering scheme.

Of the substituted dimers  $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{X})_2$  only the manganese dimer was seen to undergo isomerization at under  $120^\circ\text{C}$ . The structural isomers could be differentiated by detailed study of their infrared spectra but the difference was small and the infrared spectra were complicated by the fact the isomer has a mass of 53 very nearly equivalent to three carbonyl groups ( $\text{M} = 54$ ). This problem can be avoided in future work by judicious choice of isocyanide e.g.  $\text{MeC}(\text{CN})_2$ . The various experiments performed show this isomerization to be both intramolecular and intermolecular. The mechanism proposed is consistent with the evidence for the  $\text{M}_2(\text{CO})_7(\text{MeNC})_3$  complex.<sup>186</sup> This involves the synchronous movement of ligands during which two ligands (carbonyls or isocyanides) move into a bridging position and then onto the second metal. The isomerization mechanism would be critically dependent upon the metal-metal bond length and the increased bond length is thought to be the reason why  $\text{M}_2(\text{CO})_8(\text{Bu}^t\text{X})_2$  was not seen to isomerize at temperatures below  $120^\circ\text{C}$ .

### 3.4 Experimental

#### 3.4.1 Kinetic Studies

All reactions were carried out in the dark under an inert atmosphere in n-hexane, or in 1-octane for reactions requiring temperatures greater than 60°C. Before use the solvents were redistilled, dried and degassed. Samples were removed through a suba-seal using a syringe and the spectra were obtained using a NaCl windowed cell and a Pye-Unicam 580B infrared spectrophotometer interfaced to an Apple II microcomputer. The spectra were collected in the transmittance mode and then converted to absorbance units before integration of the selected peaks was performed. Stirring rate was constant throughout and temperature stability of the reaction flask was estimated to be within 1°C of the tabulated values. Rate constants were obtained for the following reactions:



The uncatalysed substitution of  $\text{Re}_2(\text{CO})_{10}$  or  $\text{Re}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$  with  $\text{Bu}^t\text{NC}$  was not observed even after following each reaction for 6 hours at  $110^\circ\text{C}$ . In each reaction pseudo-first-order kinetics was used, this being justified by the isonitrile concentration always being far in excess of that of the metal dimer.

#### 3.4.2 Synthesis of 1,2- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

$\text{Mn}_2(\text{CO})_{10}$  (1mmol) and  $\text{Bu}^t\text{NC}$  (2.1mmol) in benzene (30ml) with  $\text{Pd}$  catalyst (20mg) was stirred at room temperature ( $25^\circ\text{C}$ ) for 60 min. The reaction could be followed by infrared spectroscopy or thin layer chromatography (silica, hexane). After solvent removal a crude product remained which was purified by column chromatography (silica, hexane/benzene mixtures) and recrystallization of the disubstituted product from a refrigerated hexane solution gave orange crystals in approx. 65% yields. These were identified by microanalysis as  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$ , analysis found C=42.94%, H=3.28%, N=5.35%;  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Mn}_2$  requires C=43.20%, H=3.62%, N=5.60%. Mass spectrometry distinguished the structural isomers. Other physical and spectral data are presented in Tables 3.1 and 3.2.

#### 3.4.3 Synthesis of 1,1- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$

Pure 1,2- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  (1mmol), synthesized as above was heated to  $55^\circ\text{C}$  in benzene (30ml) for 2 hours. The solution containing the equilibrium mixture of the

isomers so produced was filtered and solvent removed under vacuum. The crude product was taken up in a minimum amount of hexane and refrigerated. The required isomer was collected as orange crystals after 48 hours. The solution could then be reheated to obtain the equilibrium mixture of isomers again. Using the technique of fractional crystallization reasonable yields (~ 40%) of the 1,1-isomer could be obtained. This product was fully characterized, microanalysis found C=43.14%, H=3.70%, N=5.58%;  $C_{18}H_{18}O_8N_2Mn_2$  requires C=43.20%, H=3.62% and N=5.60%. A crystal structure determination<sup>209</sup> confirmed the isonitrile arrangement. Physical and spectral data are presented in Tables 3.1 and 3.2.

#### 3.4.4 Synthesis of 1,2-Re<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub>

Re<sub>2</sub>(CO)<sub>10</sub> (1mmol) and Bu<sup>t</sup>NC (2.2mmol) were stirred in benzene (50ml) with PdO catalyst (20mg) at room temperature for 4 hours. The reaction was followed by thin layer chromatography (silica, hexane-benzene (9:1)). The crude product was purified by column chromatography and identified initially by a comparison of the infrared spectrum with that of 1,2-Mn<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub>. Microanalysis found C=29.12%, H=2.55%, N=3.62%;  $C_{18}H_{18}O_8N_2Re_2$  requires C=28.35%, H=2.36%, N=3.67%. Other physical and spectral

data are given in Tables 3.1 and 3.2. Generally high yields (~ 82%) of the off-white powder were obtained.

#### 3.4.5 Synthesis of 1,1-Re<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub>

Re(CO)<sub>5</sub>I was synthesized from Re<sub>2</sub>(CO)<sub>10</sub> and I<sub>2</sub> in refluxing benzene (see later), and its purity was judged by its infrared spectrum which showed no Re<sub>2</sub>(CO)<sub>10</sub>.<sup>56</sup> Bu<sup>t</sup>NC (2.3mmol) was added to a refluxing solution of Re(CO)<sub>5</sub>I (1mmol) in benzene (30ml) with Pd/CaCO<sub>3</sub> (10%) (5mg) catalyst. The reaction was monitored by infrared spectroscopy and judged to be complete within 15 mins. The product, a yellow powder, was obtained in 82% yield and microanalysis found C=28.01, H=3.26, N=4.88, I=21.09%; C<sub>13</sub>H<sub>14.3</sub>N<sub>2</sub>ReI required C=27.72, H=3.20%, N=4.97% and I=22.53%. Other spectral data are given in Table 3.3.

Re(CO)<sub>3</sub>(Bu<sup>t</sup>NC)<sub>2</sub>I (1mmol) was added dropwise as a thf solution (2 ml) to a solution of NaRe(CO)<sub>5</sub><sup>218</sup> in thf (30ml). The reaction mixture was stirred under an inert atmosphere, at 60°C for 24 hours after which time the solution appeared slightly darker. After filtering and solvent removal the required product was obtained by recrystallization from a refrigerated hexane solution.

data are given in Tables 3.1 and 3.2. Generally high yields (82%) of the off-white powder were obtained.

#### 3.4.5 Synthesis of 1,1-Re<sub>2</sub>(CO)<sub>8</sub>(Bu<sup>t</sup>NC)<sub>2</sub>

Re(CO)<sub>5</sub>I was synthesized from Re<sub>2</sub>(CO)<sub>10</sub> and I<sub>2</sub> in refluxing benzene (see later), and its purity was judged by its infrared spectrum which showed no Re<sub>2</sub>(CO)<sub>10</sub>.<sup>56</sup> Bu<sup>t</sup>NC (2.3mmol) was added to a refluxing solution of Re(CO)<sub>5</sub>I (1mmol) in benzene (30ml) with Pd/CaCO<sub>3</sub> (10%) (5mg) catalyst. The reaction was monitored by infrared spectroscopy and judged to be complete within 15 mins. The product, a yellow powder, was obtained in 82% yield and microanalysis found C=28.01, H=3.26, N=4.88, I=21.09; C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>ReI required C=27.72, H=3.20%, N=4.97% and I=22.53%. Other spectral data are given in Table 3.3.

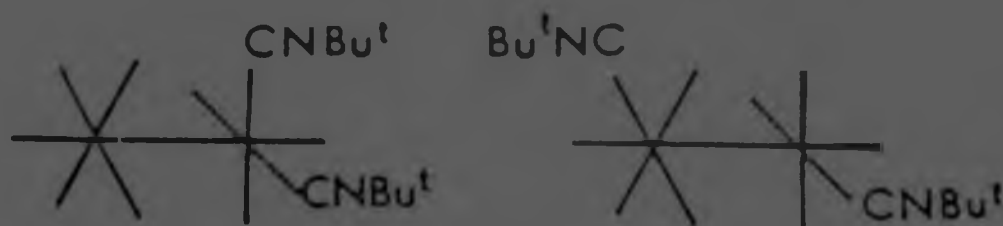
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Only low product yields ( $\sim 30\%$ ) were obtained and microanalysis found  $C=28.51\%$ ,  $H=2.52\%$ ,  $N=3.71\%$ ;  $C_{10}H_{12}N_2O_2$  requires  $C=28.35\%$ ,  $H=2.36\%$ ,  $N=3.67\%$ . The physical and spectral data are presented in Tables 3.1 and 3.2.

#### 3.4.6 Isomerisation of $M_2(CO)_8(Bu^tNC)_2$ ( $M=Mn$ or $Re$ )

All isomerisation studies were done in *i*-octane solutions under an inert atmosphere at a known constant stirring rate. Pure samples of the 1,1 and 1,2-disubstituted dimanganese and dirhenium compounds were obtained as described earlier.

Figure 3.6 Structural Isomers of  $M_2(CO)_8(Bu^tNC)_2$



$1,2-Mn_2(CO)_8(Bu^tNC)_2$  (0.1 mmol) was heated in *i*-octane at a variety of temperatures (see Table 3.7). The isomerisation was monitored by infrared spectrophotometry over a period of  $\sim 6$  hours during which time equilibrium was reached. A similar study of the isomerisation of

1,1-dimethyl-2,2,2-trifluoroethane showed that an identical equilibrium mixture was obtained (at the same temperature) irrespective of the initial amount of reagent.

Solutions of other 1,1 or 1,2-disubstituted ethanes were heated up to 110°C for 2-6 hours but neither showed any evidence of isomerization under these conditions.

#### 4. CARBONYL SUBSTITUTION REACTIONS OF THE MIXED METAL DIMERS $MnCo(CO)_8$ AND $FeCo(CO)_7$

##### 4.1 Introduction

The synthesis of  $MnCo(CO)_8$  from  $Mn(CO)_5Cl$  and  $Co(CO)_2Cl$  was first presented by Veselovsky *et al.*<sup>55</sup> and later repeated by Kasper *et al.*<sup>56</sup> The infrared spectrum of the heteronuclear dimer was reported by Kasper,<sup>57</sup> who also showed that the reported infrared spectrum of Veselovsky's product<sup>210</sup> was that of a mixture of  $Co_2(CO)_8$  and  $Fe_2(CO)_9$ . Kasper *et al.*<sup>58</sup> also showed that the alternative approach to the synthesis of  $MnCo(CO)_8$  from  $Mn(CO)_5Br$  and  $Co(CO)_2Cl$  only gave a mixture of the homonuclear dimers,  $Co_2(CO)_8$  and  $Fe_2(CO)_9$ . Since this early work a complete infrared spectral assignment of  $MnCo(CO)_8$  has been reported,<sup>59,60,61,62,63,64</sup> which included a study of the far-infrared region of the spectrum to obtain the metal-metal stretching frequency.<sup>61</sup>

Alternative thermal<sup>62</sup> or photochemical<sup>59,61,62,63</sup> syntheses of the mixed metal carbonyl,  $MnCo(CO)_8$ , have since been reported starting from  $Co_2(CO)_8$  and  $Fe_2(CO)_9$ . The low yields of  $MnCo(CO)_8$  obtained by these methods have been improved slightly by varying the initial carbonyl ratio<sup>72</sup> or the mode of irradiation.<sup>105</sup> The synthesis of  $MnCo(CO)_8$  in moderate yields has also been reported<sup>64</sup> from the reaction of  $[Mn(CO)_5]^-$  with  $[Co(CO)_2]^+$  at  $-80^\circ C$ .

The chemistry of  $\text{MnRe}(\text{CO})_{10}$  has been largely neglected over the years and the few reactions that have been reported are listed below. The direct synthesis of derivatives from  $\text{InRe}(\text{CO})_{10}$  have either involved reactions at a carbonyl <sup>221</sup> or substitution of a carbonyl by  $\text{PR}_3$  ( $R=\text{Ph}$ ,  $\text{OPh}$  or  $\text{Bu}^n$ ) to give a carbene or  $\text{MnRe}(\text{CO})_{10-n}(\text{PR}_3)_n$ . <sup>151, 152, 154, 162, 162, 222, 223</sup> Indirect methods from  $\text{NaIn}(\text{CO})_4$  and  $(o\text{-phen})\text{Re}(\text{CO})_4 \cdot \text{Zn}_2\text{Cl}_6$  or from  $\text{Re}(\text{CO})_5(\text{DAB})\text{X}$  ( $\text{X}=\text{halide}$ ) and  $\text{Mn}(\text{CO})_5^-$  ( $\text{Na}$  or  $\text{K}$  salt) have also been used to obtain  $\text{MnRe}(\text{CO})_{10}$  derivatives <sup>64, 224-226</sup> such as  $\text{MnRe}(\text{CO})_9(o\text{-phen})$  <sup>227</sup> and  $\text{InRe}(\text{CO})_9(\text{DAB})$ . <sup>228</sup>

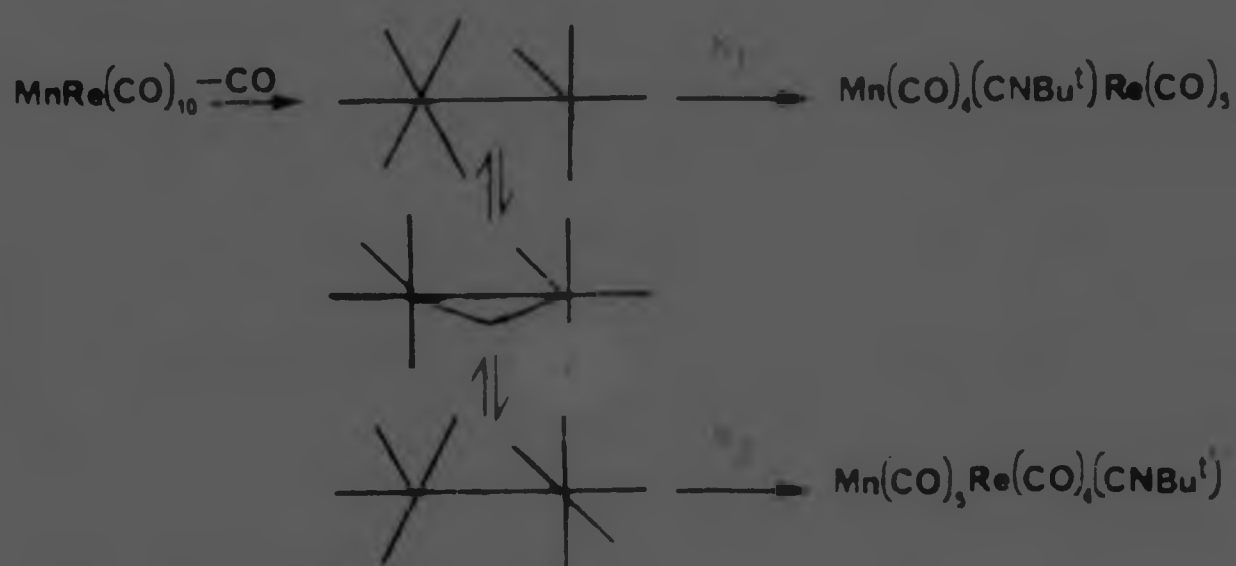
The electrochemical reduction of  $\text{InRe}(\text{CO})_{10}$  was studied by Gross *et al.* <sup>71</sup> and the reduction potential was found to be intermediate to that of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  (as expected) but the metal-metal bond dissociation energy was found to be greater than that for either  $\text{In}_2(\text{CO})_{10}$  or  $\text{Re}_2(\text{CO})_{10}$ . <sup>151, 152</sup>  $\text{InRe}(\text{CO})_{10}$  was seen to undergo a phase transition in the solid state at  $70^\circ\text{C}$  <sup>151</sup> very similar to that undergone by  $\text{In}_2(\text{CO})_{10}$  ( $68^\circ\text{C}$ ) <sup>151</sup> and  $\text{Re}_2(\text{CO})_{10}$  ( $63^\circ\text{C}$ ). <sup>231</sup>

Kinetic studies of the substitution reactions of  $\text{InRe}(\text{CO})_{10}$  with phosphines have been reported. <sup>151, 152, 225, 227</sup> Replacement of one carbonyl ligand was found to give predominantly a product in which the ligand is introduced into the axial site on the rhenium atom. <sup>229</sup> (Figure 4.1)





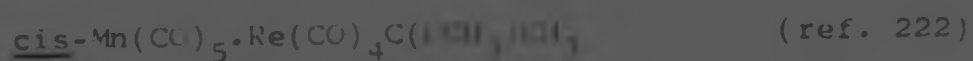
Scheme 4.1



The following study was undertaken in the hope of clarifying this little understood reaction mechanism. The reaction between  $\text{MnRe(CO)}_{10}$  and  $\text{Bu}^t\text{NC}$  was studied, the  $\text{Bu}^t\text{NC}$  being chosen as the substituting ligand as it has a small cone angle<sup>233</sup> and thus steric factors in the course of the substitution reaction should be minimized. Further, RNC can act as a bridging ligand (like CO) and the possibility of the transfer of unsaturation between metal centres can be further investigated.

During the course of this synthetic and kinetic investigation the monosubstituted product  $\text{MnRe(CO)}_9(\text{Bu}^t\text{NC})$  was isolated and its crystal and molecular structure

determined. Prior to this work the structures of only three complexes containing a manganese-rhenium bond have been determined, they are:



#### 4.2 Results and Discussion

The physical and spectral properties of the complexes

$\text{MM}'(\text{CO})_9(\text{Bu}^t\text{NC})$  ( $\text{M}, \text{M}' = \text{Mn}, \text{Re}$ ) and the complexes

$\text{MnRe(CO)}_9(\text{RNC})$  ( $\text{R} = \text{Bu}^t, \text{Pr}^i, \text{Xy}, \text{Cy}$ ) are given in Tables 4.1 and 4.2 respectively.

$\text{MnRe(CO)}_9$  was obtained in yields approaching 70%. Although this product did contain some  $\text{Mn}_2(\text{CO})_{10}$  impurity it could be purified by fractional sublimation, the  $\text{Mn}_2(\text{CO})_{10}$  subliming at room temperatures with pressures of  $\sim 10^{-4}$  atm. Sufficiently pure material was obtained so that the CO substitution reaction could be followed clearly by infrared spectroscopy. Occasionally traces of  $\text{Mn}_2(\text{CO})_{10}$  were found as an impurity in the heteronuclear dimer; this reacted rapidly and generally, substituted products  $\text{MnRe(CO)}_9(\text{RNC})$  and  $\text{Mn}_2(\text{CO})_{10-n}(\text{RNC})_n$  ( $n=1,2$ ) could be separated by column chromatography (silica). The reaction

TABLE 1.1

Physical and Spectral Data for the Monosubstituted

metal dimers  $\text{Co}(\text{CO})_2(\mu\text{M}^2\text{L})$  ( $\text{M}^2\text{L} = \text{dm, Me}$ )

| Compound                                          | $\nu(\text{C}=\text{O})/\text{cm}^{-1}$ <sup>a</sup> | $\nu(\text{C}=\text{O})/\text{cm}^{-1}$ <sup>b</sup> | $\nu(\text{C}=\text{O})/\text{cm}^{-1}$ <sup>c</sup> |
|---------------------------------------------------|------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|
| $\text{Co}_2(\text{CO})_8(\mu\text{M}^2\text{L})$ | 2173(s)                                              | 2173(s)                                              | 1955(s)                                              |
| $\text{Co}_2(\text{CO})_8(\mu\text{M}^2\text{L})$ | 2173(s)                                              | 2173(s)                                              | 1955(s)                                              |
| $\text{Co}(\text{CO})_2(\mu\text{M}^2\text{L})$   | 2173(s)                                              | 2173(s)                                              | 1955(s)                                              |
| $\text{Co}(\text{CO})_2(\mu\text{M}^2\text{L})$   | 2173(s)                                              | 2173(s)                                              | 1955(s)                                              |
| $\text{Co}(\text{CO})_2(\mu\text{M}^2\text{L})$   | 2173(s)                                              | 2173(s)                                              | 1955(s)                                              |

<sup>a</sup> Recorded in benzene. <sup>b</sup> Recorded in benzene. <sup>c</sup> Recorded in benzene relative to helium standard (0.00).

<sup>d</sup> Recorded in  $\text{C}_6\text{H}_6$  relative to TMS (5.1).

Table 4.2. Physical and Spectral Data for the Complexes

| Complex                                                     | Yield (%) <sup>a</sup> | Infrared Spectra (cm <sup>-1</sup> ) <sup>b</sup> |         | NMR <sup>c</sup>  |
|-------------------------------------------------------------|------------------------|---------------------------------------------------|---------|-------------------|
|                                                             |                        | Yield                                             | Yield   |                   |
| $\text{Co}(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3$ | 100-102                | 2102(w)                                           | 2082(w) | 11977(s) 11957(s) |
| $\text{Co}(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3$ | 71-72                  | 2107(w)                                           | 2082(w) | 11978(s) 11957(s) |
| $\text{Co}(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3$ | 100-102                | 2154(w)                                           | 2082(w) | 11957(s) 11957(s) |
| $\text{Co}(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3$ | 71-72                  | 2102(w)                                           | 2082(w) | 11957(s) 11957(s) |

<sup>a</sup> Yield in benzene. <sup>b</sup> Recorded in  $\text{C}_6\text{H}_6$  relative to TMS ( $\delta$ ). <sup>c</sup> Signal ratio 6:1.

<sup>d</sup> Normal ratio 2:1. <sup>e</sup> Yield 80-100. <sup>f</sup> Complex multimer.

of  $\text{MnRe}(\text{CO})_{10}$  with  $\text{Bu}^t\text{NC}$ , (4.1), gave only one monosubstituted product  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$  as detected by thin layer chromatography (silica, hexane) and infrared spectroscopy. This product was taken up in a minimum volume of hexane and refrigerated, and after 48 hours orange crystals suitable for diffraction studies were obtained. This reaction (4.1) was



repeated on a smaller scale using hexane as a solvent and followed at  $25^\circ\text{C}$  by infrared spectroscopy to obtain a rate constant which is compared to those obtained for the homonuclear dimers in Table 4.3. This product was shown conclusively by an X-ray diffraction structure determination to have the  $\text{Bu}^t\text{NC}$  bonded to the rhenium atom (see later). This rhenium substituted isomer could not be converted thermally to the manganese substituted isomer ( $95^\circ\text{C}$ , 8 hours) as determined by infrared spectroscopy. The reverse isomerization i.e. from the manganese substituted isomer (independently synthesized) to the rhenium substituted isomer was also not observed at  $90^\circ\text{C}$  over a period of 8 hours.

Thus, initial substitution of manganese followed by ligand isomerisation to give the rhenium substituted dimer can be ruled out as a possible mechanism for the first substitution of  $\text{MnRe}(\text{CO})_{10}$  by  $\text{Bu}^t\text{NC}$ . Metal-metal bond



substitution reaction with  $\text{Bu}^t\text{NC}$  would then be performed in hexane solution in a sealed container under a nitrogen atmosphere. Low pressure mass spectrometry would then be used to identify the isotopic abundance in the substituted carbonyl i.e. the free carbon monoxide. The presence of  $^{13}\text{C}$  would confirm the mechanism of Atwood and its absence would strongly suggest a free radical mechanism, as suggested earlier.

The rate constant for  $\text{O}^-$  substitution (Table 4.3) was found to be  $16.0 \times 10^{-3} \text{ s}^{-1}$ . Making a statistical correction for the number of carbonyl groups in possible reaction sites, for substitution, the rate constant for loss of a CO group (dissociative mechanism) at rhenium in  $\text{MnRe(CO)}_{10}$  is 1.3 times that for CO dissociation in  $\text{Re}_2(\text{CO})_{10}$ . This suggests that the Re-C bond strength is weaker in  $\text{MnRe(CO)}_{10}$  than in  $\text{Re}_2(\text{CO})_{10}$ .

As Re is considerably more electropositive than Mn, illustrated by the increased stability of the higher oxidation states for rhenium, compared to manganese, the metal-metal bond electron cloud would be unsymmetrical. The decrease in electron density at rhenium means much less back bonding to the carbonyls will occur so reducing the Re-C bond strength, with the reverse occurring at manganese. Since no disubstituted products were observed for the reaction of  $\text{MnRe(CO)}_{10}$  with  $\text{Bu}^t\text{NC}$  before complete reaction of  $\text{MnRe(CO)}_{10}$  was observed, it is clear that the rate for the second

TABLE 4.3      Kinetic Data for Transubstitution of  
 $\text{Cr}(\text{CO})_5$  ( $[\text{Cr}(\text{CO})_5]_0 = 10^{-4} \text{M}$ ) with  $\text{Ru}^{\text{I}}\text{SC}$   
 using  $\text{Pd}$  catalyst at  $25^\circ\text{C}$

| Complex                       | $[\text{Cr}(\text{CO})_5]_0^a$ | $[\text{Ru}^{\text{I}}\text{SC}]_0^a$ | $k^b$ | $t_{1/2}^c$ | $k^d$ |
|-------------------------------|--------------------------------|---------------------------------------|-------|-------------|-------|
| $\text{Ru}_2(\text{CO})_{10}$ | 0.4385                         | 3.888                                 | 26.80 | 6.2(4.8)    | 3.01  |
| $\text{Ru}_3(\text{CO})_{12}$ | 0.2645                         | 13.790                                | 21.99 | 5.9(4.5)    | 2.75  |
| $\text{Ru}_4(\text{CO})_{14}$ | 0.2645                         | 8.863                                 | 10.91 | 11.7(3.0)   | 4.20  |

<sup>a</sup> Initial concentrations in mol  $\text{l}^{-1}$  (x  $10^{-2}$ ).

<sup>b</sup> Pseudo-first-order rate constant in  $\text{s}^{-1}$  (x  $10^3$ ).

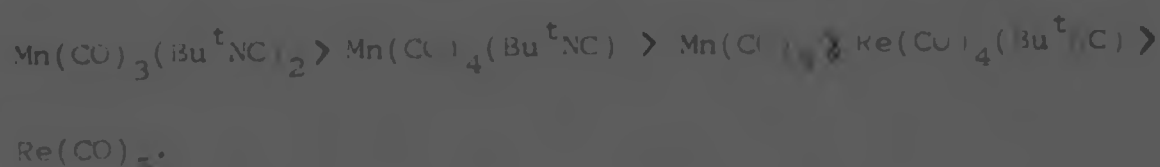
<sup>c</sup> Half-life for reaction (s) and number of half-lives the reaction was followed for in parentheses.

<sup>d</sup> Rate constant per equatorial carbonyl.

substitution is much slower than that observed for first substitution. A cis-labilizing ability, would be ordered

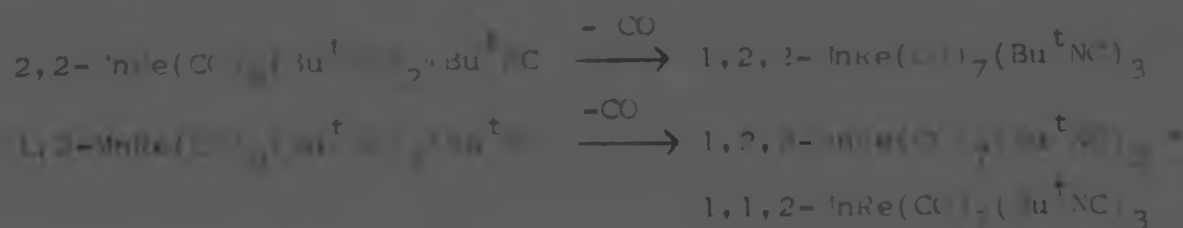


which combines with the data presented in Chapter 2 to give an overall ordering:



Unlike the cis-labilization data presented for the complexes  $\text{M}(\text{CO})_4\text{Br}$  ( $\text{M} = \text{Mn, Re}; \text{L} = \text{CO}, \text{NC}_5\text{H}_5, \text{PPh}_3, \text{P(OPh)}_3$ )<sup>128,129</sup> steric factors are negligible and the series is a result of only (or predominantly) electronic effects.

Subsequent work in this laboratory<sup>235</sup> has produced a mixture of disubstituted products from the reaction of  $(\text{CO})_5\text{MnRe}(\text{CO})_4(\text{Bu}^t\text{NC})$  and  $\text{Bu}^t\text{NC}$ , but with a dominance of  $(\text{CO})_5\text{MnRe}(\text{CO})_4(\text{Bu}^t\text{NC})_2$  and a lesser amount of  $(\text{CO})_4(\text{Bu}^t\text{NC})\text{MnRe}(\text{CO})_4(\text{Bu}^t\text{NC})$ . This confirms the ordering presented above with  $\text{Mn}(\text{CO})_5$  having a greater cis-labilizing effect than  $\text{Re}(\text{CO})_4(\text{Bu}^t\text{NC})$ . Study of the reaction of the disubstituted complexes with isonitrile ( $\text{RNC}$ ) is in progress and a comparison, using the reactions:



of rate constants and product ratios will lead to being able to place  $\text{Re}(\text{CO})_3(\text{Bu}^t\text{NC})_2$  in the above order.

#### 4.3. X-ray Crystallography of $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$

Single orange plate shaped crystals were obtained after a period of 48 hours from a refrigerated hexane solution of  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$ . Using oscillation and Weissenberg photographs, recorded with  $\text{Cu-K}\alpha$  radiation, the space group and unit cell dimensions were determined. The crystallographic and physical data for this complex are recorded in Table 4.4. The intensity data was collected using a Philips PW1100 four-circle diffractometer, using nickel monochromated  $\text{Cu-K}\alpha$  radiation. Accurate unit cell parameters and crystal face dimensions were obtained to make absorption corrections to the data at the later stages of structure refinement. After each group of 67 reflections three standard reflections were measured. These were seen to be decreasing slightly with time. The data was corrected for Lorentz and polarization effects; absorption corrections were only made after all non-hydrogen atoms had been positioned.

The vectors corresponding to the two rhenium atoms, in the asymmetric unit, were located on a Patterson map and the subsequent two Fourier syntheses revealed the positions of all the non-hydrogen atoms. The structure was first refined by full-matrix least squares with isotropic temperature

TABLE 4.4 Crystallographic and Physical Data  
for the Complex  $\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_4(\text{Bu}^t\text{NC})$

| Crystal Data                             |                                                 |
|------------------------------------------|-------------------------------------------------|
| Formula                                  | $\text{C}_{14}\text{H}_9\text{NO}_9\text{MnRe}$ |
| Molecular Weight                         | 576.36                                          |
| Melting Point                            | $103^\circ\text{C}$                             |
| Crystallisation Solvent                  | hexane                                          |
| Crystal System                           | monoclinic                                      |
| Space Group                              | $\text{P2}_1/\text{n}$                          |
| $a/\text{\AA}$                           | 15.262(3)                                       |
| $b/\text{\AA}$                           | 2.856(5)                                        |
| $c/\text{\AA}$                           | 12.051(3)                                       |
| $\beta/^\circ$                           | 91.54(6)                                        |
| $V/\text{\AA}^3$                         | 3839.45                                         |
| $Z$                                      | 8                                               |
| $D_c/\text{gcm}^{-3}$                    | 1.094                                           |
| $D_m$ (by floatation)/ $\text{gcm}^{-3}$ | 1.90                                            |
| $\mu(\text{Cu-K}\alpha)$                 | 166.09                                          |
| $F(000)$                                 | 2175.55                                         |
| Data Collection                          |                                                 |
| Crystal Dimensions/ $\text{mm}^3$        | $0.15 \times 0.15 \times 0.3 \text{ mm}^3$      |
| Scan Mode                                | $\omega - \theta$                               |
| Scan Speed/ $^\circ\text{s}^{-1}$        | 0.048                                           |
| Scan Width/ $^\circ$                     | 1.20                                            |
| Range Scanned/ $^\circ$                  | 5 - 60                                          |
| Number of Reflections Collected          | 4174                                            |
| Number of Observed Reflections           | 571                                             |
| Significance Test                        | $F_o > \sigma(F_c)$                             |
| Stability of standard reflection         | 0.4                                             |

factors. The calculations were carried out on a C D C Cyber 174 computer of the C.S.I.R. with the Shelx-76 package of computer programmes.<sup>236</sup>

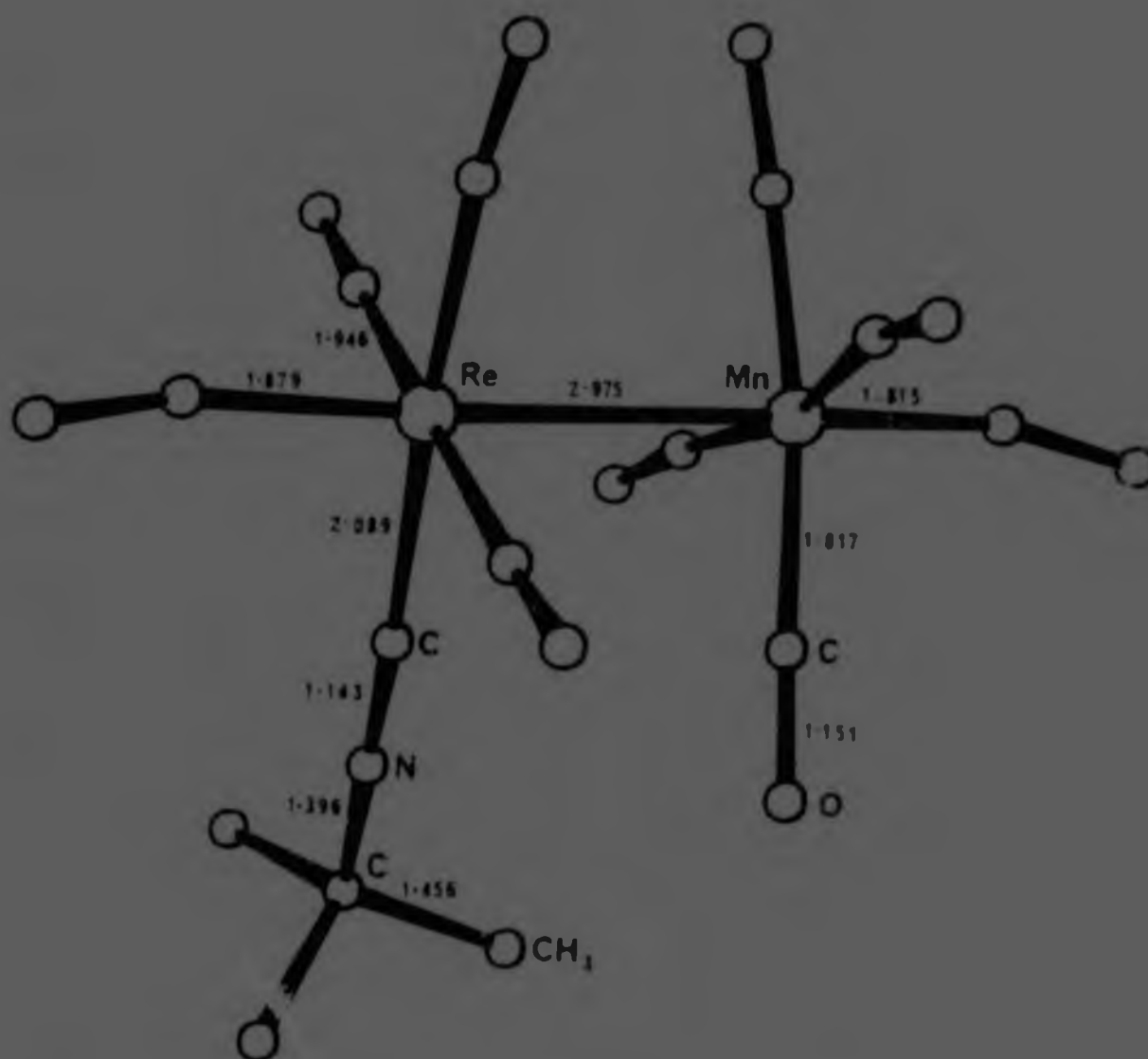
The structure was refined using a unit weighting scheme and only isotropic temperature factors to  $R_p = 13.24\%$ . Inclusion of absorption corrections reduced this to  $R_p = 9.89\%$  ( $R_w = 8.76\%$ ). The final coordinates of all the non-hydrogen atoms in the asymmetric unit are given in Tables 4.5 and 4.6. An Ortep diagram<sup>237</sup> of the molecule is given in Fig. 4.2 and the packing diagram is given in Appendix C. Average selected bond angles and bond lengths are given in Tables 4.7 and 4.8 and tables of isotropic and anisotropic temperature factors along with observed and calculated structure factors are given in Appendix D.

#### 4.4 DISCUSSION

The crystal structure of  $\text{MnReCl}_4(\text{Bu}^t\text{NC})_2$  makes interesting comparisons with two other groups of previously reported structures: 1) those heterometallic complexes containing a Mn-Re bond and 2) those complexes with the general formula  $\text{M}_2(\text{Cl})_4(\text{PR})_2$  ( $\text{M} = \text{In, Re}; n = 3-4$ ).

Only three other structures have been published that have contained a manganese-rhenium bond and pertinent structural details are given in Table 4.9. The Re-Mn bond length determined here is  $2.71 \text{ \AA}$  longer than the average Mn-Re bond previously reported and both the manganese-

Figure 4.2      Crystal Structure of  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})^*$



\* Selected bond lengths given in Å.

TABLE 4.5      Fractional Coordinates of Atoms  
in Molecule 1.

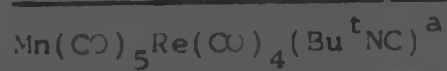
|     | x/A        | y/B       | z/C        |
|-----|------------|-----------|------------|
| Mn  | .1265(5)   | .3453(4)  | .3066(6)   |
| Re  | .2556(2)   | .4251(4)  | .1890(9)   |
| C1  | .0477(25)  | .2968(20) | .3793(32)  |
| C2  | .2233(16)  | .3124(15) | .3766(26)  |
| C3  | .1256(25)  | .4140(11) | .3992(24)  |
| C4  | .0479(18)  | .3871(20) | .2166(25)  |
| C5  | .1454(31)  | .2844(15) | .2028(26)  |
| C6  | .1881(22)  | .4036(20) | .0547(19)  |
| C7  | .3140(23)  | .4446(19) | .3305(17)  |
| C8  | .3297(22)  | .3505(12) | .1698(29)  |
| C9  | .3335(19)  | .4784(15) | .1135(30)  |
| C10 | .1727(19)  | .5035(11) | .2124(26)  |
| C11 | .0706(18)  | .5981(12) | .2372(24)  |
| C12 | .0662(35)  | .6371(24) | .1372(33)  |
| C13 | -.0165(24) | .5715(25) | .2518(41)  |
| C14 | .1053(33)  | .6399(22) | .3247(35)  |
| O1  | -.0045(21) | .2662(18) | .4221(30)  |
| O2  | .2831(14)  | .2942(13) | .4267(22)  |
| O3  | .1222(24)  | .4541(12) | .4642(21)  |
| O4  | -.0021(16) | .4125(16) | .1583(22)  |
| O5  | .1483(22)  | .2474(11) | .1372(18)  |
| O6  | .1596(17)  | .3861(14) | -.0290(14) |
| O7  | .3483(20)  | .4483(15) | .1162(16)  |
| O8  | .3667(17)  | .3038(10) | .1548(24)  |
| O9  | .3827(16)  | .5132(13) | .0742(23)  |
| N   | .1276(17)  | .5465(11) | .2233(22)  |

TABLE 4.6      Fractional Coordinates of Atoms  
in Molecule 2.

|     | x/A       | y/B       | z/C        |
|-----|-----------|-----------|------------|
| Mn  | .6991(4)  | .3525(3)  | .1278(6)   |
| Re  | .6946(3)  | .3776(5)  | .3707(7)   |
| C1  | .7077(50) | .3363(30) | -.0194(13) |
| C2  | .7609(23) | .4270(11) | .1237(30)  |
| C3  | .8070(12) | .3169(17) | .1474(25)  |
| C4  | .6581(26) | .2734(11) | .1628(31)  |
| C5  | .5918(12) | .3907(16) | .1312(32)  |
| C6  | .8143(11) | .4087(17) | .3655(27)  |
| C7  | .5732(12) | .3489(22) | .3704(32)  |
| C8  | .7399(29) | .2916(11) | .3985(34)  |
| C9  | .6959(29) | .3913(22) | .5246(12)  |
| C10 | .6526(25) | .4696(9)  | .3258(28)  |
| C11 | .6126(21) | .5842(10) | .2771(22)  |
| C12 | .6813(27) | .6287(21) | .3126(38)  |
| C13 | .5904(33) | .5917(25) | .1597(25)  |
| C14 | .5350(28) | .6044(29) | .3351(44)  |
| O1  | .6892(27) | .3391(13) | -.1124(22) |
| O2  | .7910(15) | .4775(7)  | .1204(19)  |
| O3  | .8713(12) | .2905(14) | .1677(25)  |
| O4  | .6161(21) | .2285(14) | .1785(25)  |
| O5  | .5230(12) | .4132(15) | .1307(22)  |
| O6  | .8849(11) | .4276(15) | .3648(22)  |
| O7  | .5033(12) | .3283(17) | .3688(23)  |
| O8  | .7613(21) | .2386(8)  | .4082(24)  |
| O9  | .6870(33) | .3997(14) | .6183(18)  |
| N   | .6304(18) | .5210(8)  | .3076(20)  |

TABLE 4.7

## Average Bond Angles for the Molecule




---

|                                    |            |
|------------------------------------|------------|
| Re-Mn-C1                           | 178.4 (16) |
| Re-Mn-C <sub>eq</sub> <sup>b</sup> | 84.5 (11)  |
| Mn-Re-C <sub>eq</sub> <sup>c</sup> | 88.4 (11)  |
| Mn-Re-C7                           | 89.8 (10)  |
| Mn-Re-C9                           | 177.6 (9)  |
| Mn-Re-C10                          | 86.7 (8)   |
| Mn-C1-O1                           | 177.4 (7)  |
| Mn-C <sub>eq</sub> <sup>b</sup> -O | 173.9 (6)  |
| Re-C <sub>eq</sub> <sup>c</sup> -O | 173.9 (7)  |
| Re-C7-O7                           | 173.8 (6)  |
| Re-C9-O9                           | 173.9 (7)  |
| Re-C10-N                           | 177.4 (5)  |
| C10-N-C11                          | 175.7 (6)  |
| N-C11-C <sup>d</sup>               | 110.1 (6)  |
| C-C11-C <sup>d</sup>               | 108.7 (6)  |

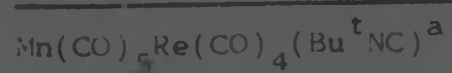
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<sup>a</sup> Measured in degrees, e.s.d. in parentheses.

<sup>b</sup> Average for equatorial carbonyls.

<sup>c</sup> Average for C6 and C8.

<sup>d</sup> Average for C12, C13 and C14.

TABLE 4.8      Average Bond Lengths for the Molecule

|                                 |           |
|---------------------------------|-----------|
| Mn-Re                           | 2.975 (4) |
| Mn-C1                           | 1.815 (9) |
| Mn-C <sub>eq</sub> <sup>b</sup> | 1.817 (5) |
| Re-C <sub>eq</sub> <sup>c</sup> | 1.946 (5) |
| Re-C9                           | 1.879 (9) |
| Re-C10                          | 2.089 (9) |
| C10-N                           | 1.143 (9) |
| N-C11                           | 1.396 (9) |
| C11-C <sup>d</sup>              | 1.456 (5) |
| C-O                             | 1.151 (3) |

<sup>a</sup> Measured in A with e.s.d. in parentheses.

<sup>b</sup> Average for C2-C5.

<sup>c</sup> Average for C6-C8.

<sup>d</sup> Average for C12-C14.

TABLE 4.9  
A Comparison of Structural Data for Manganese - Rhenium Dimers<sup>a</sup>

| Complex                                                                                                  | Bond Lengths <sup>b</sup> |           |           | Bond Angles <sup>c</sup> |          |
|----------------------------------------------------------------------------------------------------------|---------------------------|-----------|-----------|--------------------------|----------|
|                                                                                                          | Re-Mn                     | Re-C      | Mn-C      | Re-Mn-C                  | Mn-Re-C  |
| $\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_4(\text{th}^t\text{NC})^d$                                   | 2.975(7)                  | 1.929(7)  | 1.817(7)  | 84.5(11)                 | 86.7(12) |
| $\text{cis-Mn}(\text{CO})_5\text{Re}(\text{CO})_4\text{C}(\text{CH}_3)_3\text{CH}_3^e$                   | 2.972(1)                  | 1.980(26) | 1.843(27) | 87.3(4)                  | 84.3(7)  |
| $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnRe}(\text{CO})_4(\mu\text{-C}(\text{Ph})(\text{CO}))^f$ | 2.817(3)                  | 1.96(5)   | 1.84(6)   | -                        | -        |
| $\text{S}_2\text{Re}(\text{CO})_4\text{Re}(\text{CO})_5^g$                                               | 2.960(3)                  | 1.953(30) | 1.823(30) | 87.2(11)                 | 85.3(14) |

<sup>a</sup> Bond lengths in Å and bond angles in degrees, e.s.d. in parentheses<sup>b</sup> Average for carbonyls.<sup>c</sup> Average for equatorial carbonyls.<sup>d</sup> structure presented in this chapter.<sup>e</sup> ref. 222.<sup>f</sup> ref. 54.<sup>g</sup> ref. 234.

carbonyl and rhenium-carbonyl bond lengths are slightly shorter. The metal-metal bond length is thus typical for the expected single bond and the molecule exhibits octahedral geometry at the metal-ligand-metal-ligand bond angles in the range  $84.5^\circ - 95.7^\circ$ .

More interesting comparisons are made between the structure of  $\text{Re}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$  and other substituted dimers of the formula  $\text{Re}_2(\text{CO})_{10-n}(\text{XNC})_n$  ( $n = 1, 2, 3, 4$ ) and relevant structural data is listed in Table 1. The structure showed the isonitrile to occupy an equatorial site on the rhenium atom. The structure was found to be distorted with dihedral angles between  $41.1^\circ$  and  $46.7^\circ$ . This feature of staggered equatorial ligands has been found in all the structures reported for complexes of the general formula  $\text{Re}_2(\text{CO})_{10-n}(\text{XNC})_n$  ( $n = 1, 2, 3, 4$ ). The metal-metal bond length in the axial ligand complex is within one estimated standard deviation of that which might have been predicted by averaging the metal-metal bond lengths for the complexes  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}(\text{Bu}^t\text{NC})$ .

The metal-carbonyl bond lengths are consistently longer for the equatorial carbonyls than for the axial carbonyls, a feature found in all these complexes apart from  $\text{Re}_2(\text{CO})_{10}(\text{XNC})_4$ , which may be due to the fact that in  $\text{Re}_2(\text{CO})_{10}(\text{XNC})_4$  all the equatorial carbonyls are trans-to an isonitrile. It appears the rhenium-carbonyl bond lengths are consistently longer than the rhenium-carbonyl bond

TABLE 4.10 Structural Data for the Complexes  $M(CO)_{10-6}(HNC)_n$  ( $M, M' = Mn, Re; n=0-4$ )<sup>a</sup>

| Complex                      | M-H      | M-C <sub>alk</sub>                               | M-C <sub>eq</sub>                              | M-C <sub>iso</sub> | H-H-C <sub>alk</sub>                           | H-H-C <sub>eq</sub>                           | H-H-C <sub>iso</sub> | M-C-O                                            | M-C-N                  | C-N-C     |
|------------------------------|----------|--------------------------------------------------|------------------------------------------------|--------------------|------------------------------------------------|-----------------------------------------------|----------------------|--------------------------------------------------|------------------------|-----------|
| $Mn_2(CO)_{10}$ <sup>b</sup> | 2.904(1) | 1.811(3)                                         | 1.856(2)                                       | -                  | 177.0(1)                                       | 86.4(1)                                       | -                    | 178.9(3)                                         | -                      | -         |
| $Re_2(CO)_{10}$ <sup>b</sup> | 3.041(1) | 1.959(7)                                         | 1.987(6)                                       | -                  | 176.3(2)                                       | 86.4(2)                                       | -                    | 178.8(8)                                         | -                      | -         |
| $Re_2(CO)_9(Re^tNC)^C$       | 3.048(1) | 1.952(10)                                        | 1.955(22)                                      | 2.068(15)          | 177.0(6)                                       | 86.6(5)                                       | 87.5(4)              | 176.1(16)                                        | 175.5(13)              | 175.7(18) |
| $Mn_2(CO)_8(Al^tNC)_2^d$     | 2.924(1) | 1.784(5)                                         | 1.832(6)                                       | 1.944(4)           | 176.4(2)                                       | 84.5(1)                                       | 90.0(1)              | 178.1(6)                                         | 177.6(4)               | 176.7(4)  |
| $Re_2(CO)_8(Xe^tNC)_2^E$     | 1.047(1) | 1.924(6)                                         | 1.976(7)                                       | 2.050(6)           | 177.9(2)                                       | 86.2(1)                                       | 88.2(1)              | 178.0(6)                                         | 177.4(5)               | 171.0(5)  |
| $Re_2(CO)_7(Me^tNC)_3^C$     | 3.046(1) | 1.889(16)                                        | 1.929(20)                                      | 2.124(17)          | 178.8(5)                                       | 84.8(4)                                       | 86.3(4)              | 177.3(21)                                        | 174.1(14)              | 171.3(22) |
| $Mn_2(CO)_6(Xe^tNC)_4^E$     | 2.946(6) | 1.720(26)                                        | 1.610(26)                                      | 1.900(20)          | 173.0(10)                                      | 83.0(10)                                      | 90.0(10)             | 176.0(25)                                        | 176.0(20)              | 176.0(20) |
| $Re_2(CO)_6(Xe^tNC)_4^E$     | 3.081(2) | 1.968(20)                                        | 1.952(20)                                      | 2.020(20)          | 176.3(8)                                       | 85.1(8)                                       | 87.9(8)              | 174.2(22)                                        | 176.2(18)              | 176.8(21) |
| $MnRe(CO)_9(Co^tNC)$         | 2.975(4) | 1.815(10) <sup>f</sup><br>1.879(10) <sup>f</sup> | 1.817(9) <sup>f</sup><br>1.946(6) <sup>f</sup> | 2.085(9)           | 178.4(2) <sup>f</sup><br>177.6(9) <sup>f</sup> | 84.5(1) <sup>f</sup><br>89.3(12) <sup>f</sup> | 86.7(8) <sup>f</sup> | 174.6(35) <sup>f</sup><br>173.9(40) <sup>f</sup> | 171.4(28) <sup>f</sup> | 175.7(31) |

<sup>a</sup> Bond lengths in Å and angles in degrees, e.s.d. in parentheses.

<sup>b</sup> Ref. 15. <sup>c</sup> Ref. 197. <sup>d</sup> Ref. 200.

<sup>e</sup> M=Mn. <sup>f</sup> M=Re.

lengths. The chelate-bridged bond length was found to be 0.02 Å longer than the terminal-bridged bond length in  $\text{MnRe}(\text{CO})_{10}$ .

The equatorial ligands were all found to be bonded towards lower the centre of the metal-metal bond with this bond length being 0.10 Å shorter than the axial bond length (i.e. 90° angle) being more prominent on the manganese side. The axial bond was bent towards the centre of the metal-metal bond more than the equatorial carbonyls on rhenium but less than the equatorial carbonyls on manganese.

#### 4.5 Conclusions

The successful synthesis of  $\text{MnRe}(\text{CO})_{10}$  allowed a study of the carbonyl substitution reactions of this heteronuclear dimer to be undertaken. The reactivity of  $\text{MnRe}(\text{CO})_{10}$  is analogous to that of the homonuclear dimers (see earlier) and thus to obtain substituted derivatives in fair to good yields fairly rapid a catalyst must be used. No attempt to obtain a catalyst or conditions to replace either of the carbonyl groups in  $\text{MnRe}(\text{CO})_{10}$  or monosubstituted complexes could be obtained using the experimental conditions employed (see later).

The rate of the carbonyl substitution reaction of  $\text{MnRe}(\text{CO})_{10}$  with  $\text{Me}^t\text{CN}$  is slower than the rate observed

for either of the homonuclear dimers. If direct substitution on the rhenium atom is assumed\* then the rate of substitution per equatorial carbonyl is more rapid than either of the homonuclear dimers. This is strongly supportive of the mechanism suggested earlier in which the group X ( $X = \text{Re}(\text{CO})_5$ ) causes a labilization of the cis-carbonyls in  $\text{XRe}(\text{CO})_5$  relative to  $\text{Re}_2(\text{CO})_{10}$  ( $X = \text{Re}(\text{CO})_5$ ).

The structure of the monosubstituted heteronuclear dimer  $[\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})]_2$  was completely solved by X-ray crystallographic methods. This showed conclusively that the catalysed carbonyl substitution reaction of  $\text{MnRe}(\text{CO})_{10}$  gives a product substituted at the rhenium atom. The structure shows no unusual features when comparisons are made with other known structures of the type  $\text{M}_2(\text{CO})_{10-n}(\text{RNC})_n$  ( $n = 0-4$ ;  $\text{M} = \text{Mn, Re}$ ;  $\text{R} = \text{Et, Bu}^t, \dots$ ).

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\* No isomerisation of  $[\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})]_2$  was observed when either the manganese or the rhenium substituted dimer was heated in *i*-octane solution to 90° for 8 hours.

## 4.6 Experimental

### 4.6.1 Synthesis of $\text{MnRe}(\text{CO})_{11}$

A sodium amalgam (Na, 4mmoles; Hg, 5ml) was prepared under an inert atmosphere in a two-necked flask equipped with a side-arm which was fitted with a tap.  $\text{Mn}_2(\text{CO})_{10}$  (1mmol) was added dropwise as a tetrahydrofuran solution (30ml), and a rapid colour change (yellow to green) was observed. stirring at room temperature was continued for a further hour after which the amalgam was poured off through the side-arm and the reaction mixture washed with a further 3ml of clean mercury.

The solution of  $\text{NaMn}(\text{CO})_5$  was used in situ and yields were assumed to be 7%\*. An appropriate amount of  $\text{Re}(\text{CO})_5\text{Br}$  (1.4mmol) was then added to the  $\text{NaMn}(\text{CO})_5$  as a thf solution (70ml). This mixture was then stirred overnight at room temperature before solvent removal and ether extractions yielded the required product in approximately 70% yield. The complex was identified by comparison of its mp and infrared spectrum with the literature data.<sup>220</sup>

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\* Yields of  $\text{NaMn}(\text{CO})_5$  were probably greater than 70% but an excess  $\text{NaMn}(\text{CO})_5$  was preferable to an excess of  $\text{Re}(\text{CO})_5\text{Br}$  in the subsequent reaction.

#### 4.6.2 Substitution Reactions of $\text{MnRe}(\text{CO})_{10}$

In the presence of the catalyst  $\text{PdO}$ , a solution of  $\text{MnRe}(\text{CO})_{10}$  (1 mmol) and isonitrile (1.1 mmol), in hexane (50 ml) was stirred under nitrogen at room temperature and the reaction monitored by infrared spectroscopy or thin layer chromatography (silica, hexane/benzene). The reactions were usually complete within 4 hours (as judged by infrared spectroscopy). The monosubstituted complexes were purified by recrystallization from a hexane solution at  $-5^\circ\text{C}$ . Yields were between 65-75%.

The complexes were all shades of yellow. Other physical and spectral data for the complexes with  $\text{R}=\text{Bu}^t$ ,  $\text{Pr}^i$ , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_{11}$  are given in Table 4.2.

#### 4.6.3 Synthesis of $\text{Mn}(\text{CO})_4(\text{Bu}^t\text{NC})\text{Re}(\text{CO})_5(\text{eq})$

1,2- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  was prepared from  $\text{Mn}_2(\text{CO})_{10}$  and 2.2 equivalents of  $\text{Bu}^t\text{NC}$  using  $\text{PdO}$  catalyst as described earlier (Section 3.4.2). The required product was then synthesized in the same manner as  $\text{MnRe}(\text{CO})_{10}$  (Section 4.6.1) using 1,2- $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  in place of  $\text{Mn}_2(\text{CO})_{10}$ . The required product was obtained as orange crystals from a refrigerated hexane solution and was fully characterized by spectroscopic and analytical techniques (Table 4.1).

#### 4.6.4 Isomerisation of $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$

Isomerisation studies were carried out as described earlier, 3.4.6. No isomerisation was observed at  $90-95^\circ\text{C}$  in under 8 hours.

## 5. SUBSTITUTION REACTIONS OF $[\text{CpRu}(\text{CO})_2]_2$

### 5.1 Introduction

Cyclopentadienyl metal complexes have been of special interest since the discovery of ferrocene. Since then many cyclopentadienyl metal carbonyl complexes have been synthesised and their chemistry is intimately related to the development of organometallic chemistry. The presence of the cyclopentadienyl ligand can influence the chemistry of the metal carbonyl fragment, for example, it was recently proposed that the cyclopentadienyl ligand promotes an unexpected associative pathway for ligand substitution reactions in stable 18-electron organometallic complexes.<sup>137</sup> Indeed, modifying the cyclopentadienyl ring can have dramatic effects on both the rate and mechanism of the carbonyl substitution reactions.<sup>238-241</sup>

Studied in this chapter are the substitution reactions of  $[\text{CpRu}(\text{CO})_2]_2$  with isonitriles. This metal dimer first reported in 1962, has been largely neglected when compared to the analogous iron compound  $[\text{CpFe}(\text{CO})_2]_2$ . In order to place this work in context comparisons between these two dimers will be made throughout this chapter.

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It is interesting to note that recently the mixed metal dimer  $[\text{Cp}(\text{Ru}(\text{CO})_2)_2\text{Fe}(\text{CO})_2]_2$  has been synthesised<sup>243</sup> and a crystal structure showed two carbonyls to be terminal.<sup>244</sup>

The iron dimer has been prepared by several methods<sup>245, 246</sup>, which generally involve the reaction of an iron carbonyl with cyclopentadiene or one of its derivatives such as methylocyclopentadiene<sup>245</sup> or pentamethylocyclopentadiene.<sup>246</sup> The ruthenium dimer however, was first synthesised from  $[\text{Ru}(\text{CO})_5]_2$  and NaCp.<sup>247</sup> Since then other ruthenium carbonyl halides and sodium cyclopentadienides have also been used.<sup>247-249</sup> Quantitative yields of the ruthenium dimer have been reported when synthesised from  $\text{H}_2\text{Ru}(\text{CO})_{12}$  and cyclopentadiene<sup>250</sup> in the presence of air, whereas analogous reactions using other ruthenium carbonyls give lower yields.<sup>251, 252</sup>

The organic chemistry of the diruthenium centre stabilized by cyclopentadienyl and carbonyl ligands has only recently been reported,<sup>253</sup> but of importance in this dissertation are the substitution reactions of the ruthenium dimer. It will become clear from this study (see below) that the ruthenium dimer is relatively chemically inert compared to the iron dimer and this partially accounts for the limited available data on the chemistry of  $[\text{CpRu}(\text{CO})_2]_2$ .

The monosubstituted complexes  $\text{Cp}_2\text{Fe}_2(\text{CO})_4(\text{RNC})$  ( $\text{R} = \text{e}, \text{t}, \text{Pr}^i, \text{Bu}^i, \text{Ph}$ ) have been prepared by direct substitution on the dimer.<sup>254, 255</sup> The phenyl isonitrile complex has also been reported from the reduction of

$\text{Cp}_2\text{Fe}(\text{CO})(\text{Ph})\text{I}$  <sup>256</sup> under more forcing conditions the

more highly substituted complexes  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{RNC})_2$  (e.g.  $\text{R}=\text{Me}, \text{t-Bu}, \text{Ph}$ ) and  $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{RNC})_3$  ( $\text{R}=\text{Me}, \text{Et}, \text{Pr}^i$ ) have been prepared but only with lower or unreported yields. The synthesis of the completely substituted dimers  $\text{Cp}_2\text{Fe}_2(\text{RNC})_4$  has been reported<sup>257</sup> and recently a crystal structure determination and variable temperature  $^1\text{H}$  NMR study on complexes of this type has been performed.<sup>258</sup> Fewer isonitrile substituted derivatives of the ruthenium dimer have been prepared. Unspecified yields of the monosubstituted complexes  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$  ( $\text{R}=\text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^t$ ) were obtained by prolonged refluxing in xylene of  $[\text{CpRu}(\text{CO})_2]_2$  and isonitrile.<sup>255</sup> Only with isopropyl isonitrile has the disubstituted ruthenium dimer been obtained<sup>259</sup> and then only in low yields from a reaction involving prolonged heating. Other reactions of the dimer carbonyls  $[\text{CpM}(\text{CO})_2]_2$  which are relevant to this work include the reaction with halogenated hydrocarbons  $\text{CX}_4$  ( $\text{X}=\text{Cl}, \text{Br}$ ) to give the carbonyl halides  $\text{CpM}(\text{CO})_2\text{X}$  ( $\text{M}=\text{Fe},$ <sup>260</sup>  $\text{Ru}$ <sup>261, 262</sup>). The same carbonyl halides are produced by the thermal metal-metal bond cleavage of the dimers in the presence of the halogens  $\text{X}_2$  ( $\text{M}=\text{Fe},$ <sup>263, 264</sup>  $\text{Ru}$ <sup>252, 265</sup>).

There have been several reports of photochemical reactions of  $[\text{CpFe}(\text{CO})_2]_2$  with halocarbon solvents<sup>260, 261, 266</sup> but few with other ligands (in non-halogenated solvents). Until recently it was generally believed that the photo-

reactions of  $[\text{CpFe}(\text{CO})_2]_2$  occurred via the 17-electron radical intermediates  $\text{CpFe}(\text{CO})_2$ .<sup>262,266</sup> However, for the photochemical reaction of  $[\text{CpFe}(\text{CO})_2]_2$  with phosphines or chlorocarbons a recent paper has proposed an intermediate with no metal-metal bond but a bridging carbonyl:<sup>267</sup>



This substitution reaction is inhibited by a carbon monoxide atmosphere, the quantum efficiency dropping by 36%. The thermal reaction of the ruthenium dimer with phosphites,  $\text{P}(\text{OR})_3$ , gives a mixture of products  $\text{CpRu}(\text{CO})_2\text{H}$  and  $\text{CpRu}(\text{P}(\text{OR})_3)_2(\text{P}(\text{O})(\text{OR})_2)$ .<sup>268</sup> Under vigorous conditions (140°C, 48 hours) a mixture of  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$  and  $\text{CpRu}(\text{CO})(\text{PR}_3)\text{H}$  was obtained from  $[\text{CpRu}(\text{CO})_2]_2$  and phosphine  $\text{PR}_3$  ( $\text{R}_3 = \text{Pr}^n, \text{Me}_2\text{Ph}$ ) and when excess  $\text{PMe}_2\text{Ph}$  was used  $\text{CpRu}(\text{PMe}_2\text{Ph})_2\text{H}$  was prepared.<sup>268</sup> There have been few studies of photochemical reactions of the ruthenium dimer but one, which may be of importance in future studies of models for catalysis, is that with ethene.<sup>241</sup>

The iron dimer has been found to be a catalyst of some importance both in photoinduced radical reactions<sup>269</sup> and under strictly thermal conditions.<sup>270,271</sup> The catalytic role of the ruthenium dimer in substitution chemistry has to date been less well studied.<sup>272,273</sup>

The substituted derivatives of these dimers can be difficult to identify by spectroscopic means due to the number of structural isomers that may be present in solution. The proportion of each isomer present depends not only on the steric and electronic properties of the group, R, but also on the solvent and physical conditions under which the system is being studied. The difference in chemical shifts of the bridging and terminal ligands means that  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance can be used to distinguish between the structural isomers and hence help to determine their properties in solution. For example, the substituted iron dimer complexes  $\text{Cp}_2\text{Fe}_2(\text{CO})_{4-n}(\text{RNC})_n$  ( $n=1,2$ ) have been shown to exist in solution as a mixture of rapidly interconverting structural isomers.<sup>187,274</sup>

In this chapter the catalysed carbonyl substitution reactions,<sup>275</sup> as developed for other systems e.g.  $\text{Mn}_2(\text{CO})_{10}$ ,<sup>195</sup>  $\text{Re}_2(\text{CO})_{10}$ ,<sup>197</sup>  $\text{Fe}(\text{CO})_5$ <sup>276</sup> etc., were used to synthesise substituted derivatives of the ruthenium dimer with a variety of isonitrile ligands. This work represents a preliminary investigation of the  $[\text{CpRu}(\text{CO})_2]_2$  system, and will be elaborated on in future work.<sup>235</sup> The ultimate objectives of this work include the catalysed synthesis of the complexes in the series  $\text{Cp}_2\text{Ru}_2(\text{CO})_{4-n}(\text{RNC})_n$  ( $n=1-4$ ) and a study of both the chemistry of these substituted dimers

(e.g. reaction with electrophiles <sup>277</sup>) and their possible role as catalysts especially in those reactions in which  $[\text{CoRu}(\text{CO})_2]_2$  has already found a use. <sup>272,273</sup>

## 5.2 Results

The catalysed reactions of the dimer  $[\text{CoRu}(\text{CO})_2]_2$  with isonitrile occurs rapidly and could be readily followed by infrared spectroscopy and the extent of the reaction monitored by the disappearance of the starting material. In the absence of catalyst a molar equivalent solution of isonitrile e.g.  $\text{Bu}^t\text{NC}$  and dimer could be stirred in refluxing toluene for 24 hours before 50% completion was achieved. In this time considerable decomposition was observed even when the reaction was carried out in the dark and under an inert atmosphere. Using either  $[\text{MoFe}(\text{CO})_2]_2$  ( $\text{Mo}=\text{C}_5\text{H}_5$ ) or  $\text{PtO}_2$  as catalyst, yields > 50% of crude product  $\text{Co}_2\text{Ru}_2(\text{CO})_8(\text{HNC})$  were obtained, after only 6 hours stirring in refluxing toluene. Of the catalysts considered in this study the best was found to be  $\text{PdO}$  which for  $\text{Bu}^t\text{NC}$  gave yields of approximately 80% after only 2 hours stirring in refluxing toluene. Under the same conditions similar high yields were observed for other isonitriles e.g.  $\text{C}_6\text{H}_{11}\text{NC}$ , 80% yield after 1 hour and  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ , 90% yield after 5 hours (see Table 5.1).

Problems in purification of these products were found when column chromatography was used. After extensive investigation of numerous chromatographic materials grade IV alumina was found to cause least decomposition of the products. Even the use of flash chromatographic procedures (to reduce the time on the column and thus decomposition) gave only 40 - 50% yields of column purified products. Fractional crystallization is a superior alternative method of purification and may be useful in future work, especially when the more air-sensitive, di-, tri- and tetra- substituted derivatives are synthesized. The spectral data for the mono-substituted derivatives synthesized in this work are presented in Table 5.2. Microanalytical data for these complexes was obtained and found to be consistent with spectral characterisation. The complexity of the infrared spectra suggests a mixture of structural isomers is present for all complexes except  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{Bu}^t\text{C})$ . Indeed, the bridged isomer might be expected to be less favoured in the ruthenium dimer because of the increased metal-metal bond length, (as compared to the iron dimer). This however is not found in practice. It has been suggested that the need to bridge a longer metal-metal bond is more than compensated by relief of steric interaction between the cyclopentadienyl ligand and the alkyl substituent of the isonitrile.<sup>255</sup> The NMR

spectra are however simple which suggests that if a mixture of isomers is present that ligand scrambling is rapid on the NMR timescale. A mixture of bridged and non-bridged isomers was observed for the complexes  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$  ( $\text{R}=\text{Me}, \text{Et}, \text{Pr}^i$ ) using variable temperature  $^1\text{H}$  NMR but only terminal isomers for the tertiary butyl derivative were observed.<sup>255</sup>

The disubstituted complex  $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{Bu}^t\text{NC})_2$  was observed when excess  $\text{Bu}^t\text{NC}$  was reacted with  $[\text{CpRu}(\text{CO})_2]_2$  in the presence of  $\text{PdO}$  and after prolonged heating ( $110^\circ\text{C}$ , 6 hours). No attempt was made to isolate this complex and it was identified by comparison of its infrared spectrum with the known analogous complex  $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{Pr}^i\text{NC})_2$ .<sup>259</sup>

### 5.3 Conclusions

This work indicates that the use of catalysts to synthesize the monosubstituted derivatives  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$  is a viable synthetic strategy. The complexes were found to be moderately air-sensitive and separation procedures using column chromatography or thin layer chromatography were of limited use. No attempt to isolate more highly substituted derivatives was made here but the complex  $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{Bu}^t\text{NC})_2$

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\* NMR spectra may be broadened by the presence of paramagnetic decomposition products.

TABLE 5.1

Catalysis of  $[\text{CpRu}(\text{CO})_2]_2$   
 Carbonyl Substitution<sup>a</sup>

| Isonitrile                                    | Catalyst                       | Time(hours) | Yield(%) <sup>b</sup> |
|-----------------------------------------------|--------------------------------|-------------|-----------------------|
| $\text{Bu}^t\text{NC}$                        | NONE                           | 24          | 30                    |
| $\text{Bu}^t\text{NC}$                        | $[\text{MnFe}(\text{CO})_2]_2$ | 5           | 50                    |
| $\text{Bu}^t\text{NC}$                        | $\text{PtO}_2$                 | 6           | 55                    |
| $\text{Bu}^t\text{NC}$                        | $\text{PdO}$                   | 2           | 80                    |
| $\text{MeNC}$                                 | "                              | 4           | 65                    |
| $\text{Pr}^i\text{NC}$                        | "                              | 1           | 45                    |
| $\text{C}_6\text{H}_{11}\text{NC}$            | "                              | 1           | 80                    |
| $2,6\text{-e}_2\text{C}_6\text{H}_3\text{NC}$ | "                              | 5           | 90                    |

<sup>a</sup> All reactions done in refluxing toluene using a mole ratio of reactants  $[\text{CpRu}(\text{CO})_2]_2$  : RNC of approximately 1:1.1.

<sup>b</sup> Estimated by infrared spectroscopy.

TABLE 5.2  
Spectral Data for the Complexes  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$ 

| R               | Infrared ( $\text{cm}^{-1}$ ) <sup>a</sup>                  | Cp        | NMR <sup>b, c</sup>                 |
|-----------------|-------------------------------------------------------------|-----------|-------------------------------------|
| Me              | 2160(w) 2060(m) 2000(vs) 1960(s) 1800(m) 1755(m) 1730(s)    | 4.74      | - 3.05                              |
| Pr <sup>d</sup> | 2150(sh), 2130(m) 2005(vs) 1960(vs) 1800(m) 1775(s) 1710(m) | 4.83      | 3.42 <sup>d</sup> 1.10 <sup>e</sup> |
| Bu <sup>t</sup> | 2125(m) 2090(sh) 2045(sh) 1950(s) - 1765(vs) -              | 4.89      | - 0.90                              |
| Cy <sup>f</sup> | 2130(w) 2100(sh) 1990(vs) 1945(s) 1795(w) 1760(m) 1705(w)   | 4.92/4.75 | - 0.98-0.74 <sup>d</sup>            |
| Xy <sup>g</sup> | 2140(m) 2100(sh) 1990(vs) 1955(sh) 1805(w) 1789(m) 1775(m)  | 4.80      | 6.68 <sup>d</sup> 2.17              |

<sup>a</sup> Recorded in  $\text{CH}_2\text{Cl}_2$  ( $\text{cm}^{-1}$ ).<sup>b</sup> Recorded in  $\text{C}_6\text{D}_6$  relative to TMS ( $\delta$ ).<sup>c</sup>  $[\text{CpRu}(\text{CO})_2]_2$  gives a singlet,  $\delta = 4.76$  ppm.<sup>d</sup> Broad.<sup>e</sup> Doublet  $J = 3.5$  Hz.<sup>f</sup> Cy =  $\text{C}_6\text{H}_{11}$ .<sup>g</sup> Xy = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

was observed when a solution of  $[\text{CpRu}(\text{CO})_2]_2$  and 2 mole equivalents of  $\text{Bu}^t\text{NC}$  were subject to prolonged heating in the presence of catalyst. This catalysis of the substitution reactions shows potential as a method of obtaining more highly substituted dimers. Clearly there remains scope for improvement in choice of catalyst but the principle has been demonstrated.

#### 5.4 Experimental

##### 5.4.1 General

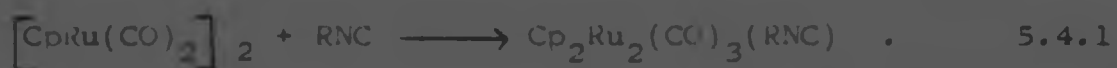
All solvents were routinely dried and distilled under nitrogen before use, and reactions were done under an inert atmosphere in normal laboratory lighting. Infrared spectra obtained on a Jasco IRA-1 infrared spectrophotometer were suitable for following reactions. The product characterisation was done using a Pye Unicam SP 300 infrared spectrophotometer and a Varian EM 360A NMR spectrophotometer. The catalysts used were either prepared by literature methods ( $[\text{MnFe}(\text{CO})_2]_2^{246}$ ) or obtained from chemical suppliers (see Appendix A).

##### 5.4.2 Synthesis of $[\text{CpRu}(\text{CO})_2]_2$

The crude product, was synthesized by the literature method<sup>252</sup> by Dr. M. O. Albers (N.C.R.L., C.S.I.R.) and further purified by column chromatography (silica). The first fraction (eluted with hexane) contained unreacted cyclopentadiene ligand which could be recovered and re-used.

Subsequent elution with dichloromethane gave the pure dimer in good yields. A less pure product could be obtained using repeated dichloromethane extractions of an aqueous solution of the crude product. The dimer is fairly stable in the solid state and when purified could be stored (at  $-5^{\circ}\text{C}$ ) for several weeks before noticeable decomposition occurred. The product was identified by infrared and  $^1\text{H}$  NMR spectroscopy and microanalysis found  $\text{C}=37.90\%$ ,  $\text{H}=2.41\%$ ;  $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Ru}_2$  requires  $\text{C}=37.83\%$ ,  $\text{H}=2.27\%$ .

#### 5.4.3 Synthesis of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$



Catalyst (20mg) and RNC (0.22 mmol) was added to a solution of  $[\text{CpRu}(\text{CO})_2]_2$  in toluene (30ml). The reaction mixture was stirred at reflux under an inert atmosphere and followed by infrared spectroscopy. Flash chromatography (silica, benzene/hexane) allowed isolation of the desired products in yields of approximately 50%. An alternative method of purification also used, was recrystallization from a degassed solution (benzene/hexane) at  $-5^{\circ}\text{C}$ .

## 6. MIXED METAL TRIMERS $M_2Fe(CO)_{14}$

### 6.1 Introduction

The logical extension of a study of substitution reactions of dimers is the extension to substitution reactions of linear trimers and eventually linear tetramers and oligomers. Subsequent to the work on the  $M_2(CO)_{10}$  ( $M=Mn, Re$ ) and the cyclopentadienyl rutheniumdicarbonyldimers, the complexes  $MM'Fe(CO)_{14}$  were chosen for study and the results of that study are presented in this chapter.

Complexes of the type  $MM'Fe(CO)_{14}$  ( $M, M'=Mn, Re$ ) were first synthesised by Hubert and Sheline<sup>86</sup> in 1965. Mercury lamp irradiation of a mixture of  $Fe(CO)_5$  and  $Mn_2(CO)_{10}$  in hexane for 45 minutes, followed by product work-up gave red crystals of  $Mn_2Fe(CO)_{14}$ . Small amounts of  $Mn_2Fe(CO)_{14}$  have subsequently been isolated as secondary products of the reaction between  $Li[(C_7H_7)Fe(CO)_3]$  and  $[Mn(CO)_4Br]_2$ .<sup>87</sup>

The analogous dirhenium complex  $Re_2Fe(CO)_{14}$  was synthesized in a similar manner two years later by Sheline et al.<sup>91</sup> A second product was also obtained from the reaction mixture. It was isolated as the tetraethylammonium salt and identified as the cluster  $[ReFe_2(CO)_{12}]^-$  by comparison of its infrared spectrum with that reported for  $[MnFe_2(CO)_{12}]^-$ .<sup>94</sup> The salt  $[(C_2H_5)_4N][MnFe_2(CO)_{12}]$

was obtained from the reaction between  $\text{Mn}(\text{CO})_5^-$  and  $\text{Fe}(\text{CO})_5$  and its structure was proposed to be that of a trigonal cluster analogous to  $[\text{HFe}_3(\text{CO})_{11}]^-$  with which it is isoelectronic.<sup>94</sup>

The third member of this series of trinuclear carbonyls (i.e.  $\text{MM}' = \text{Mn, Re}$ ) was synthesised in an analogous manner to the previous two, i.e. mercury lamp irradiation of a mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{MnRe}(\text{CO})_{10}$ .<sup>71</sup>

The infrared spectrum of the complexes  $\text{M}_2\text{Fe}(\text{CO})_{14}$  ( $\text{M}_2 = \text{Mn}_2, \text{Re}_2, \text{MnRe}$ ) were recorded in hexane solution and show 3, 4 and 5 terminal carbonyl bonds respectively.<sup>71, 86, 87, 220\*</sup> The low solubility of these complexes is well illustrated by the need to use a 3.0mm path length NaCl cell with saturated hexane solutions to record the infrared spectra.<sup>220</sup> An added problem related to product characterisation is the decomposition of these complexes in organic solvents.<sup>220</sup>

The high symmetry required for such simple infrared spectra and the lack of bridging carbonyls strongly suggested a linear trinuclear system. This was confirmed for  $\text{Mn}_2\text{Fe}(\text{CO})_{14}$  by an X-ray crystallographic structure determination,<sup>90, 278</sup> from which a mean Mn-Fe distance of  $2.815 \text{ \AA}$  was reported. Levy *et al*<sup>92</sup> have also refined crystallographic data for  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  in which the Re-Fe distances of

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\* No absorptions in the bridging carbonyl region were observed.

was obtained from the reaction between  $\text{Mn}(\text{CO})_5^-$  and  $\text{Fe}(\text{CO})_5$  and its structure was proposed to be that of a trigonal cluster analogous to  $[\text{HFe}_3(\text{CO})_{11}]^-$  with which it is isoelectronic.<sup>94</sup>

The third member of this series of trinuclear carbonyls (i.e.  $\text{MM}' = \text{Mn, Re}$ ) was synthesised in an analogous manner to the previous two, i.e. mercury lamp irradiation of a mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{MnRe}(\text{CO})_{10}$ .<sup>71</sup>

The infrared spectrum of the complexes  $\text{M}_2\text{Fe}(\text{CO})_{14}$  ( $\text{M}_2 = \text{Mn}_2, \text{Re}_2, \text{MnRe}$ ) were recorded in hexane solution and show 3, 4 and 5 terminal carbonyl bonds respectively.<sup>71, 86, 87, 220\*</sup> The low solubility of these complexes is well illustrated by the need to use a 3.0mm path length NaCl cell with saturated hexane solutions to record the infrared spectra.<sup>220</sup> An added problem related to product characterisation is the decomposition of these complexes in organic solvents.<sup>220</sup>

The high symmetry required for such simple infrared spectra and the lack of bridging carbonyls strongly suggested a linear trinuclear system. This was confirmed for  $\text{Mn}_2\text{Fe}(\text{CO})_{14}$  by an X-ray crystallographic structure determination,<sup>90, 97B</sup> from which a mean Mn-Fe distance of 2.815 Å was reported. Levy *et al.*<sup>92</sup> have also refined crystallographic data for  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  in which the Re-Fe distances of

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\* No absorptions in the bridging carbonyl region were observed.

2.876 $\overset{\circ}{\text{\AA}}$  and 2.849 $\overset{\circ}{\text{\AA}}$  were found. Few other details of this structure were however reported.

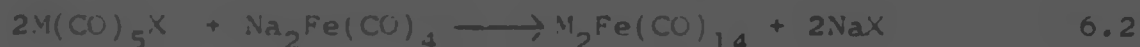
An investigation of the metal-metal stretching frequencies of the compounds  $\text{MM}'\text{Fe}(\text{CO})_{14}$  ( $\text{MM}'=\text{Mn}_2, \text{MnRe}$ ) established force constants for the metal-metal bonds.<sup>49</sup> The electronic structure of these trinuclear carbonyls was investigated by Gray *et al*<sup>88</sup> and compared to those of other trinuclear carbonyls such as  $\text{M}_3(\text{CO})_{12}$  ( $\text{M}=\text{Ru}, \text{Os}, \text{Fe}$ ). The lowest electronic excitation was predicted to be a  $\sigma - \sigma^*$  transition which would be polarized along the metal-metal axis and this was confirmed experimentally. The absorptions measured at 27°C were observed at 431nm, 380nm and 403nm for  $\text{MM}'\text{Fe}(\text{CO})_{14}$  ( $\text{MM}'=\text{Mn}_2, \text{Re}_2, \text{MnRe}$ ) respectively. With the structural<sup>90, 92, 278</sup> and spectral<sup>49, 71, 20</sup> data for these linear trinuclear carbonyls available a quantum-mechanical study was undertaken<sup>89</sup> to develop potential models and calculate atomic and average molecular polarizabilities.

There are no reported reactions of the linear trimers  $\text{MM}'\text{Fe}(\text{CO})_{14}$  ( $\text{M}, \text{M}'=\text{Mn}, \text{Re}$ ) either resulting in cleavage of a metal-metal bond or involving carbonyl ligand substitution, other than the reported decomposition in organic solvents.<sup>220</sup> No substituted derivatives have been synthesized indirectly either. No doubt the synthetic strategy presently used (i.e. photochemistry), which only gives the starting materials in low yields is at least partly responsible for this situation.

The following preliminary study was thus undertaken with two main aims, 1) the development of a synthesis of the trinuclear carbonyl complexes in at least moderate yields and 2) the initiation of a study of the substitution reactions of the trimers and their properties.

## 6.2 Results and Discussion

The synthesis of the trinuclear carbonyls  $M_2Fe(CO)_{14}$  from a metal carbonyl halide and a metal carbonyl anion can in theory be performed in two ways as represented by 6.1 and 6.2:



( $M = Mn, Re$ ;  $X = \text{halide}$ ).

Thus the situation is similar to that for the synthesis of  $MnRe(CO)_{11}$  (see Chapter 4) and as with the  $MnRe(CO)_{10}$  only one of the two possible routes was found to give the required product.<sup>57</sup> On the basis of nucleophilic strengths it might be expected that the reaction of the supernucleophile  $Na_2Fe(CO)_4$  with  $M(CO)_5X$  (6.2) would be most likely to give the desired products. Surprisingly this was not found to be the case and more success was had with the alternative route (6.1).

TABLE 6.1  
Physical and Spectral Data for the Complexes  $M_2Fe(CO)_{14}$ 

(M = Mn, Re) and some Derivatives

| Complex                         | Colour      | Mpt. <sup>a</sup> | Infrared Spectra <sup>b</sup>                             |
|---------------------------------|-------------|-------------------|-----------------------------------------------------------|
| $Re_2Fe(CO)_{14}$ <sup>c</sup>  | white       | 163-165           | 2097(m) 2020(s) 1983(m)                                   |
| $Mn_2Fe(CO)_{14}$               | red         | 115-117           | 2068(m) 2027(s) 1990(m)                                   |
| $Re_2Fe(CO)_{13}(Bu^tNC)^{d,e}$ | pale yellow | 145-149           | 2095(m) 2022(s) 2012(vs) 1998(sh) 1989(w) 1966(s) 1937(w) |
| $Re_2(CO)_8(Pr^iNC)_2^f$        | pale yellow | 122-125           | 2175(m) 2077(w) 2035(s) 1980(vs) 1930(s)                  |

<sup>a</sup> Uncorrected values in °C.<sup>b</sup> Recorded in hexane ( $cm^{-1}$ ).<sup>c</sup> Mass spectrometry gave a molecular ion of 822( $Re_2Fe(CO)_{14}$  requires  $M=821.99$ , based on  $^{187}Re$ ).<sup>d</sup> Mass spectrometry gave a molecular ion of 877( $Re_2Fe(CO)_{13}(Bu^tNC)$  requires  $M=877.11$ , based on  $^{187}Re$ ).<sup>e</sup>  $^1H$  NMR gives a singlet at 0.86 ppm in  $C_6D_6$ .<sup>f</sup>  $^1H$  NMR gives a multiplet at 2.87 ppm and a doublet at 0.69 ppm ( $J=6.5Hz$ ) in  $C_6D_6$ .

Although the compound  $\text{Mn}_2\text{Fe}(\text{CO})_{14}$  was successfully synthesized (route 6.1) and identified by spectroscopic means, problems of product decomposition in solution made purification of the product extremely difficult. As a consequence of the problems of work-up it was decided to concentrate on the synthesis and subsequent reactions of the analogous rhenium trimer,  $\text{Re}_2\text{Fe}(\text{CO})_{14}$ . The reaction of  $\text{NaRe}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4\text{I}_2$ , (6.1), ( $\text{M}=\text{Re}$ ;  $\text{X}=\text{I}$ ) gave the desired product  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  in moderate yields (20-40% based on  $\text{Re}_2(\text{CO})_{10}$ ). The alternative approach, (6.2), ( $\text{M}=\text{Re}$ ,  $\text{X}=\text{I}$ ) gave several unidentified products and since there were also other problems associated with this method\* the approach was not further investigated. The rhenium-iron trimer was purified by hexane extraction using Soxhlet extraction techniques and purified trimer could then be recrystallized from hexane by cooling. The physical and spectral data for the trimers  $\text{M}_2\text{Fe}(\text{CO})_{14}$  ( $\text{M}=\text{Mn}, \text{Re}$ ) is presented in Table 6.1.

Having devised a route to the trimer  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  an attempt was then made to investigate the chemistry of the linear trimer. In particular the reaction with isonitrile

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\*  $\text{Na}_2\text{Fe}(\text{CO})_4$  was synthesized by a modification of the literature method<sup>279</sup> and is an extremely air-sensitive complex and thus required special handling techniques such as Schlenk-type apparatus or glove-box techniques.

was chosen as a model reaction. We were primarily interested in obtaining information about the site of substitution and the possible isomerisation of the complexes  $\text{Re}_2\text{Fe}(\text{CO})_{11}(\text{RNC})$ . The reaction of the trimer with isonitrile in the presence of a catalyst was expected to give a substituted trimer,  $\text{M}_2\text{Fe}(\text{CO})_{13}(\text{RNC})$  and from a knowledge of the catalysed substitution reactions of  $\text{Fe}(\text{CO})_5$ <sup>276</sup> and  $\text{Re}_2(\text{CO})_{11}$ ,<sup>197</sup> the substitution might be expected to occur at the iron atom.

The reaction with  $\text{Bu}^t\text{NC}$  gave a yellow complex thought to be a substituted trimer. In order to further identify this complex, an attempt to synthesize the iron substituted complex was made using  $\text{Re}(\text{CO})_5\text{I}$  and  $\text{Na}_2\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})$  (synthesized by a modified literature procedure<sup>276</sup>). A yellow crystalline complex was obtained and both mass spectral and preliminary X-ray diffraction studies strongly suggest the isonitrile is located at one of the rhenium atoms in the substituted trimer. Mass spectral studies give a molecular ion of 877 ( $\text{Re}_2\text{Fe}(\text{CO})_{13}(\text{Bu}^t\text{NC})$  requires 877.11). Other important fragments that were observed are 168, ( $\text{Fe}(\text{CO})_4$ ,  $M=167.89$ ) and 382 ( $\text{Re}(\text{CO})_4(\text{Bu}^t\text{NC})$ ,  $M=382.16$ ). Crystallographic studies were incomplete because of problems encountered in collecting and correcting the data on a small crystal which was decomposing with time, best results obtained gave an Fe-Re distance of  $2.80(1) \text{ \AA}$  and showed the

isonitrile to be equatorial on a rhenium atom which is essentially octahedral. The exact correlation of infrared and NMR spectra data between this complex and the product of direct substitution on the trimer,  $\text{Re}_2\text{Fe}(\text{CO})_{14}$ , show the product of monosubstitution is the trimer derivative substituted at rhenium. The product of the indirect synthesis gave a substituted rhenium atom by a mechanism which remains presently inexplicable. This product could only have been produced in one of two ways: 1) initially the iron substituted trimer was prepared but rapidly and irreversibly isomerised to the rhenium substituted trimer or 2) the isonitrile was transferred before trimer formation possibly in an intermediate such as  $\text{NaFe}(\text{CO})_3(\text{Bu}^t\text{NC})\cdot\text{Re}(\text{CO})_5$ . Thus the substitution reaction of the unsubstituted trimer with  $\text{Bu}^t\text{NC}$  is thought to be occurring directly at a rhenium atom.

The reaction with isopropyl isonitrile gave a complex identified by comparison of spectral and physical properties (Table 6.1) with analogous complexes<sup>107</sup> to be  $\text{Re}_3(\text{CO})_8(\text{Pr}^i\text{NC})_2$ . A possible explanation for the observed product is: 1) substitution of one equatorial carbonyl ligand at each rhenium atom, 2) metal-metal bond cleavage, yielding a solution of " $\cdot\text{Re}(\text{CO})_4(\text{Pr}^i\text{NC})$ " and " $\cdot\text{Fe}(\text{CO})_4$ " and 3) rapid decomposition or reformation of metal-metal bonds giving  $1,2\text{-Re}_2(\text{CO})_8(\text{Pr}^i\text{NC})_2$  and other unidentified metal compounds.

Clearly further work is required to establish the viability of the catalysed substitution reaction on the trimer  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  and further examine this "decomposition" pathway. The data suggests this trimer system has inherent difficulties both in the synthesis and solubility of the starting materials and also the reaction with isonitrile can lead to product breakdown.

### 6.3 Conclusions

As an extension of the earlier work, on the substitution chemistry of metal carbonyl dimers, the trimers offer analogous possibilities. Thus information on selective site substitution (e.g. in heterometallic systems) as well as the possibility of pathways which may include metal atom re-arrangement may be studied using trimers. The work presented here illustrates the potential of such a study.

Further work depends upon the adequate development of synthetic strategies and purification procedures of the starting materials which has only presently been achieved for  $\text{Re}_2\text{Fe}(\text{CO})_{14}$ . The heterotrimetallic carbonyl  $\text{MnReFe}(\text{CO})_{14}$  can not be synthesized by the method used here but when available, an analogous study of the substitution chemistry could be undertaken.

It was hoped that the use of inert atmospheres and darkened reaction vessels would eliminate the anticipated problem

of metal-metal bond cleavage but clearly the result with isopropyl isonitrile shows such bond cleavage may not have been eliminated. The results of this preliminary study did not prove sufficiently rewarding to warrant further study.

#### 6.4 Experimental

##### 6.4.1 Synthesis of $\text{Fe}(\text{CO})_4\text{I}_2$ <sup>280</sup>

$\text{Fe}(\text{CO})_5$  (5mmol) was stirred in a two necked flask under an inert atmosphere in a cold bath ( $-10^\circ\text{C}$ ).  $\text{I}_2$  (5.2mmol) was then added dropwise as a cooled chloroform solution (50ml) over a period of 10 mins. Stirring at  $0^\circ\text{C}$  was continued for a further 45 mins. Excess iodine was removed using an aqueous sodium thiosulphate extraction and the chloroform solution was dried using anhydrous sodium sulphate. Filtration and solvent removal left a dark crystalline material in yields approaching 80%. The product was identified by infrared spectroscopy <sup>281</sup> and analysis found C=11.41%, I=57.65%;  $\text{C}_4\text{O}_4\text{FeI}_2$  requires C=11.39%, I=56.19. Before use,  $\text{Fe}(\text{CO})_4\text{I}_2$  was stored in the dark, under nitrogen and at  $-5^\circ\text{C}$ .

##### 6.4.2 Synthesis of $\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})\text{I}_2$

This was synthesized as above but replacing  $\text{Fe}(\text{CO})_5$  by  $\text{Fe}(\text{CO})_4(\text{Bu}^t\text{NC})$ , which was prepared by the catalytic method <sup>276</sup> from  $\text{Fe}(\text{CO})_5$  and  $\text{Bu}^t\text{NC}$ . The product, a black solid, was obtained in 45% yield based on  $\text{Fe}(\text{CO})_5$ , and was

identified by comparison of mpt ( $72-74^{\circ}\text{C}$ , decomp.) and infrared spectra ( $\nu_{\text{NC}}, 2200(\text{vs})\text{cm}^{-1}$ ;  $\nu_{\text{CO}}, 2100(\text{s}), 2065(\text{m}), 2045(\text{m})\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ) with those in the literature.<sup>281</sup>

#### 6.4.3 Synthesis of $\text{Re}(\text{CO})_5\text{I}$

See Chapter 4.

#### 6.4.4 Synthesis of $\text{Mn}(\text{CO})_5\text{I}$

A solution of  $\text{Mn}_2(\text{CO})_{10}$  (5mmol) in tetrahydrofuran (30ml) was added to a sodium amalgam (Hg 7ml/Na 12mmol) in a two-necked round-bottom flask equipped with a side-arm with a two-way tap. An inert atmosphere was maintained at all times up to the work-up of the product. The solution became green after 5 min stirring at room temperature ( $20^{\circ}\text{C}$ ). Stirring was continued for a further 30 mins. The amalgam was drained off using the side-arm and maintaining a positive pressure of nitrogen and the remaining solution washed with a further 5ml of mercury. Draining off all mercury leaves a solution of  $\text{NaMn}(\text{CO})_5$ .<sup>218</sup> A tetrahydrofuran solution of  $\text{I}_2$  (10.5mmol, 25ml) was then added dropwise to the  $\text{NaMn}(\text{CO})_5$ . After a further 15min stirring the crude product was dried, taken up in chloroform and filtered. An aqueous sodium thiosulphate extraction was used to remove any excess  $\text{I}_2$  and after drying the solution with anhydrous sodium sulphate, solvent removal

(rotary evaporator) left a semi-crystalline orange/red product, identified by infrared spectroscopy<sup>282,283</sup> and analysis found C=19.15%, I=38.95%;  $C_5O_5MnI$  requires C=18.66%, I=39.42%.

#### 6.4.5 Synthesis of $NaRe(CO)_5$ <sup>218</sup>

A solution of  $Re_2(CO)_{10}$  (1mmol) in tetrahydrofuran was added to a sodium amalgam (Hg 3ml/Na 2.5mmol) whilst maintaining an inert atmosphere. The reaction was stirred at room temperature ( $20^{\circ}C$ ) for a further 3 hours. The amalgam was drained off and the remaining solution washed with fresh mercury (2ml). The solution was then used in-situ and a quantitative yield of  $NaRe(CO)_5$  was assumed.

#### 6.4.6 Synthesis of $Na_2Fe(CO)_4$ <sup>279</sup>

A sodium sand (22mmol) was prepared in refluxing toluene under a nitrogen atmosphere in a Schlenk type apparatus. The toluene was removed using steel tubing and whilst maintaining an inert atmosphere, a benzophenone (1mmol) solution in tetrahydrofuran (50ml) was added. To the intense blue solution,  $Fe(CO)_5$  (10mmol) was added dropwise always maintaining the blue colour. When either all the  $Fe(CO)_5$  was added or the blue colour did not return within an hour, the reaction was assumed complete. The solvent was removed using a vacuum line and the cream powder washed twice with freshly distilled, dried and degassed hexane which was

transferred by means of steel tubing to the reaction. The product darkened and spontaneously inflamed with traces of air.  $\text{Na}_2\text{Fe}(\text{CO})_4$  was used in situ and the synthesis was assumed to be quantitative based on  $\text{Fe}(\text{CO})_5$ .

#### 6.4.7 Synthesis of $\text{Na}_2\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})$

$\text{Fe}(\text{CO})_4(\text{Bu}^t\text{NC})$  was synthesized from  $\text{Fe}(\text{CO})_5$  and  $\text{Bu}^t\text{NC}$ ,<sup>276</sup> this was then used as a tetrahydrofuran solution in the same manner as  $\text{Fe}(\text{CO})_5$  in the previously described synthesis of  $\text{Na}_2\text{Fe}(\text{CO})_4$ . Being even more air-sensitive than  $\text{Na}_2\text{Fe}(\text{CO})_4$ , the product  $\text{Na}_2\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})$  was used in situ and assumed to be produced in quantitative yields. The product when dried was seen to be pale pink powder which spontaneously inflamed in air.

#### 6.4.8 Synthesis of $\text{Re}_2\text{Fe}(\text{CO})_{14}$

##### a) Reaction of $\text{NaRe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{I}_2$

$\text{Fe}(\text{CO})_4\text{I}_2$  (1.5mmol) in tetrahydrofuran (30ml) was added dropwise to a solution of  $\text{NaRe}(\text{CO})_5$  (2.8mmol) in tetrahydrofuran (25ml) maintaining an inert atmosphere. The reaction was stirred for a further two hours at room temperature (20°C). Solvent removal left a brown crude reaction product. Hexane extraction removed a yellow fraction which was not identified. A Soxhlet extraction was then performed on the remaining brown powder using hexane.

After two days of continuous extraction using 250ml hexane at  $-60^{\circ}\text{C}$  the solvent was removed and on cooling to room temperature microcrystals formed. Cooling the solution in a dichloromethane slush ( $-77^{\circ}\text{C}$ ) a pale yellow powder was collected by decanting off the solvent at low temperature. This pale yellow powder was identified by infrared spectroscopy<sup>220</sup> and melting point  $163-165^{\circ}\text{C}$  (uncorrected; lit.  $163^{\circ}\text{C}$ <sup>91</sup>). The yield was estimated to be 24% based on  $\text{NaRe}(\text{CO})_5$ .

A tetrahydrofuran extraction of the remaining brown powder gave on solvent removal a yellow powder, which on continuous pumping became pink, this colour change was seen to be reversible on pumping or exposure to air or solvent.\* The spectral and physical data for the product,  $\text{Re}_2\text{Fe}(\text{CO})_{14}$ , is presented in Table 6.1.

b) Reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  and  $\text{Re}(\text{CO})_5\text{I}$

$\text{Re}(\text{CO})_5\text{I}$  (2mmol) in tetrahydrofuran (30ml) was added to  $\text{Na}_2\text{Fe}(\text{CO})_4$  (1.1mmol estimated) in tetrahydrofuran (30ml) whilst maintaining an inert atmosphere. Reaction was rapid with instant darkening of the solution. The reaction was stirred for a further 6 hours. A black solid remained after solvent removal but no hexane soluble fraction was obtained from the solid. A tetrahydrofuran extraction gave a red

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\* This product remains unidentified and is being further investigated.

solution which on long exposure to air (e.g. filtration) became green. The infrared spectra of the red and green solution were recorded and neither had any bridging carbonyls. The red product, B, and the green product, C, both gave crystals from refrigerated tetrahydrofuran/hexane solution but neither was identified. The crystalline compounds have physical and spectral properties as follows:

B) mpt, 105-107°C; i.r., 2145(w), 2090(w), 2065(w), 2040(vs), 2005(s), 1990(s), 1915(w) and analysis C, 12.30%; H, 1.57% and N, < 0.3%;

C) mpt, 97-100°C; i.r., 2073(m), 2045(m), 2020(vs), 1983(w), 1977(s) and analysis C, 18.04%; H, 2.02% and N, < 0.3% (melting points are uncorrected and i.r. were run in hexane).

#### 6.4.9 Synthesis of $\text{Re}_2\text{Fe}(\text{CO})_{13}(\text{Bu}^t\text{NC})$

##### a) Reaction of $\text{Re}_2\text{Fe}(\text{CO})_{14}$ with $\text{Bu}^t\text{NC}$

$\text{Bu}^t\text{NC}$  (0.1mmol) was added to  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  (0.09mmol) in tetrahydrofuran (50ml) with  $\text{PdO}$  (10mg) catalyst present. The reaction was followed by thin layer chromatography (silica, hexane(60)/benzene(40)) and was judged to be complete after 3 hours stirring at room temperature (20°C). The crude product was obtained by filtration and solvent removal. The off-white product had increased hexane solubility and the infrared, NMR and ultra-violet spectra of this new compound were recorded (Table 6.1). Yields of  $\text{Re}_2\text{Fe}(\text{CO})_{13}(\text{Bu}^t\text{NC})$  by both methods (a) and (b) were found to be 25 - 30%.

b) Reaction of  $\text{NaRe}(\text{CO})_5$  with  $\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})_2$

A solution of  $\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})_2$  (2.5mmol) in tetrahydrofuran was added dropwise to a  $\text{NaRe}(\text{CO})_5$  (5.0mmol, estimated) solution. The solution darkened rapidly and after a further 2 hours stirring the solvent was removed on a vacuum line. A hexane extraction of the crude product gave a yellow/orange solution which gave yellow crystals after 3 days refrigeration. These crystals were found suitable for crystallographic study and a crystal structure determination was initiated. The physical and spectral data for this complex correspond exactly to that obtained from the reaction of  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  and  $\text{Bu}^t\text{NC}$  (6.4.9a), and are presented in Table 6.1.

6.4.1) Synthesis of  $\text{Mn}_2\text{Fe}(\text{CO})_{14}$

$\text{Mn}(\text{CO})_5\text{I}$  (2mmol) was added dropwise as a tetrahydrofuran solution to a solution of  $\text{Na}_2\text{Fe}(\text{CO})_4$  (1mmol, estimated). After 2 hours stirring at room temperature, filtration and solvent removal on a vacuum line, a brown powder was obtained. Hexane extraction removed a yellow powder identified as  $\text{Mn}_2(\text{CO})_{10}$ . Use of a continuous Soxhlet extraction on the brown powder (hexane at  $\pm 60^\circ\text{C}$ ) resulted in isolation of a single product (as determined by thin layer chromatography). Filtration and solvent removal left a red powder in low yield. This was identified by mpt  $115-117^\circ\text{C}$  (Lit.  $112^\circ\text{C}$ ,<sup>86</sup>) and infrared spectroscopy (Table 6.1), (yield 15-20%).

#### 6.4.11 Reaction of $\text{Fe}_2(\text{CO})_{10}$ and $\text{Ir}^+\text{NC}$

The reaction described earlier (6.4.9a) was repeated using isopropyl isonitrile in place of  $\text{Bu}^+\text{NC}$ .

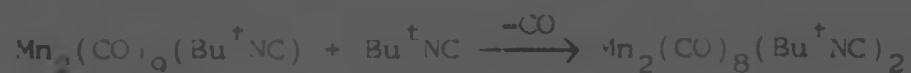
The tetrahydrofuran solution containing both reactants and  $\text{PbO}$  catalyst was followed by thin layer chromatography (silica, hexane(60)/benzene(40)). Stirring was continued for 4 hours at room temperature and the crude product isolated by filtration and solvent removal. Recrystallization from hexane gave an off-white product whose physical and spectral properties are given in Table 6.1. By comparison with other isonitrile substituted derivatives of  $\text{Fe}_2(\text{CO})_{10}$ <sup>197</sup> the product was identified as  $1,2\text{-Fe}_2(\text{CO})_8(\text{Ir}^+\text{NC})_2$  and was isolated in 42% yield.

## CONCLUSIONS

As discussed in earlier chapters the understanding of reactions of transition metal complexes, such as ligand substitution, is pertinent to the development of synthetic and industrial chemical processes. A complete understanding of a mechanism can be difficult to obtain and may involve not only kinetic investigations but also structural and synthetic work, all of which have been used in the course of this study. The conclusions that can be drawn from this work with a few possible interpretations and suggestions for future work will now be discussed.

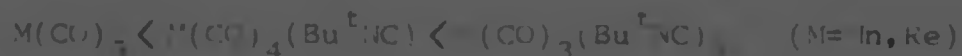
A study of the reactions of the complexes  $M_n(CO)_{10-n}(RNC)_n$  ( $M=Mn, Re; n=0-2$ ) with isocyanides, resulted in a comprehensive set of rate constants for both the catalysed and uncatalysed (when  $t_1 < 4$  hours, at  $120^\circ C$ ) carbonyl substitution reactions. Some of the more interesting observations resulting from this study will now be discussed. Lower temperatures were required for the uncatalysed carbonyl substitution reaction of  $Mn_2(CO)_{10}$  by  $Bu^tNC$  than for the equivalent reaction with either phosphines or labelled carbon monoxide ( $^{13}CO$ ). This would suggest that either the substitution reaction with  $Bu^tNC$  contains an associative term (which seems unlikely as no ligand dependence was observed) or that previous reactions have not involved a

'pure' dissociative reaction. As there is no evidence to support either of these possibilities, the reasons for this effect are presently unknown. Catalysts such as PdO provide a high yield route to the substituted complexes  $M_n(CO)_{10-n}(RNC)_n$  ( $M=Mn, Fe; n=1-4$ ) which proceed rapidly at ambient temperatures, whereas the uncatalysed reactions required prolonged heating. The Arrhenius plots for the reaction:



confirm that the activation energy barrier for the catalysed reaction is only about half of that for the uncatalysed thermal reaction. Further reductions in the activation energy barrier would be expected when more effective catalysts are discovered. Homogeneous catalysts have largely been neglected here and indeed their study may provide more effective catalysts for the future, although then problems of product isolation must be overcome for synthetic utility. The initially formed disubstituted dimer is the 1,2-isomer (the kinetic product) in both the catalysed and uncatalysed reactions. The isomerisation between the 1,2- and 1,1-disubstituted dimers is unaffected by catalyst or excess isonitrile and studies have shown that the 1,2-disubstituted dimer is also the thermodynamically favoured product. The

slow rate of isomerisation of the structural isomers of  $M_2(CO)_8(Bu^tNC)_2$  rules out the possibility of initial formation of the 1,1-isomer followed by isomerisation as the reaction mechanism. Indeed the rhenium analogues of  $Mn_2(CO)_8(Bu^tNC)_2$  could not be interconverted at temperatures up to 120°C. Thus an alternative mechanism involving direct substitution onto the unsubstituted metal atom of the dimer  $M_2(CO)_8(Bu^tNC)$  was proposed (see earlier). This mechanism can be used to explain all the kinetic data for the substitution of  $M_2(CO)_{10-n}(Bu^tNC)_n$  ( $M=Mn, Re; n=0-2$ ) by isonitriles presented in this dissertation, as well as previously reported data on other phosphine and isonitrile derivatives. Thus an order for degree of labilization of cis-carbonyls by a group X ( $X=M(CO)_n(Bu^tNC)_n$ ) was determined. The results presented earlier suggest orders of increasing cis-labilization are:



and



If the work on the substitution of  $M_2(CO)_{10}$  by larger ligands (e.g. phosphines) is considered, then it is suggested that substitution occurs initially at an equatorial site and steric factors encourage rapid rearrangement to give axial substituted derivatives. Indeed most reported data on

$\text{Mn}_2(\text{CO})_{10-n}\text{L}_n$  (L=phosphine;  $n=1,2$ ) are consistent with axial phosphine substitution,<sup>151</sup> whereas the di-rhenium analogues are known with both axial and equatorially substituted phosphines.<sup>150, 284</sup> Such observations are consistent with the proposed importance of steric factors, as the metal-metal bond length is approximately  $0.2\text{\AA}$ <sup>0</sup> longer in the rhenium dimers.

The movement of ligands (RNC, CO) between metal atoms was observed for the complex  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  but not for the rhenium analogue or for the mixed metal dimer  $\text{InRe}(\text{CO})_9(\text{Bu}^t\text{NC})$ . This is also thought to be related to the increase in metal-metal bond length, although increased metal-isonitrile bond strength may be the reason why no isomerisation is observed. The rearrangement process for  $\text{Mn}_2(\text{CO})_8(\text{Bu}^t\text{NC})_2$  was found to be intramolecular and unimolecular and a mechanism involving two bridging ligands, analogous to that widely accepted for  $[\text{CpFe}(\text{CO})_2]_2$ <sup>187</sup>, was proposed.

Catalysed substitution of carbonyls was found useful for the synthesis of the monosubstituted derivatives of the mixed metal dimer,  $\text{MnRe}(\text{CO})_{10}$ . These derivatives,  $\text{InRe}(\text{CO})_9(\text{RNC})$  were fully characterised and the question of site of substitution was solved conclusively for the molecule  $\text{InRe}(\text{CO})_9(\text{Bu}^t\text{NC})$  by X-ray crystal structure

determination. Indeed the molecule  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$  was found to be substituted at rhenium, with the isonitrile in an equatorial site. This is a little surprising when metal-carbonyl bond strengths are considered but may be easily rationalised by the mechanism proposed earlier. The determined bond lengths for this molecule are comparable to those reported for other similar systems e.g.  $d_{\text{Mn-Re}} = 2.975 \text{ \AA}$ ,  $d_{\text{Mn-CO}} = 1.916 \text{ \AA}$ ,  $d_{\text{Re-CO}} = 1.896 \text{ \AA}$  etc. A bending of the equatorial ligands was observed with an average metal-metal-equatorial carbonyl angle of  $86.4^\circ$ , similar to data reported for the analogous homonuclear dimers. The manganese substituted complex  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$  was synthesised indirectly and an X-ray crystal structure determination on this dimer is to be performed in the near future.

The reactions of  $[\text{CpRu}(\text{CO})_2]_2$  with a variety of isonitriles to give  $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{RNC})$  were performed using Pd as a catalyst. These complexes had previously been prepared by low yield methods which involved prolonged heating and so the catalysed method offers a convenient alternative route. This study is to be followed up with attempted synthesis and isolation of the di-, tri- and tetrasubstituted complexes. These complexes are expected to be more air-sensitive and thus problems of purification may be more significant. Results of this study suggest recrystallization may be a

superior method of purification than chromatography.

The mixed metal trimer  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  was prepared from  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Fe}(\text{CO})_5$  via  $\text{NaRe}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4\text{I}_2$  and this method affords better yields than present literature methods. Unfortunately purification involved solvent extraction which was not suitable for the analogous manganese complex which was far less stable in solution. The first substitution reactions of the linear trimer  $\text{Re}_2\text{Fe}(\text{CO})_{14}$  were carried out using isonitriles and a palladium catalyst. Such substitution resulted in isolation of a monosubstituted trimer complex or products of metal-metal bond cleavage.

Appendix ATHE SOURCES OF CHEMICALS USED IN THIS STUDY

Chemicals used that required no further purification were purchased from Chemical Suppliers as listed below:-

(a) B. D. H. Laboratory Reagents,

$\text{Pd/C}$  (5%)

(b) B. Owen Jones,

$\text{Na}$  (metal).

(c) Fluka A. G. Chemicals,

$\text{Bu}^t\text{NC}$ ,  $\text{Pr}^i\text{NC}$ ,  $\text{C}_6\text{H}_{11}\text{NC}$ , 2,6-Me $_2\text{C}_6\text{H}_3\text{NC}$ .

(d) Johnson Matthey Chemicals Limited,

$\text{Pd}$ ,  $\text{PtO}_2$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .

(e) Merck Chemicals,

$\text{Pd/CaCO}_3$  (10%), molecular sieve (type 4A),  $\text{KI}$ ,

benzophenone, silica gel and alumina.

(f) Protea Laboratory Services,

$\text{I}_2$ , sodium thiosulphate.

(g) SAAR Chem. Pty. Ltd.,

$\text{Br}_2$ .

(h) Strem Chemicals Incorporated,

$\text{Fe(CO)}_5$ ,  $\text{In}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$ .

Appendix BGENERAL EXPERIMENTAL DETAILS(a) Chemicals

The chemicals used in this study were either obtained from the sources indicated in Appendix A or synthesised by the methods indicated in the relevant chapters.

(b) Solvents

The solvents used were obtained from a variety of sources and were generally of "Chemical Purity" or of Analytical Grade. Solvents were dried and distilled under a nitrogen atmosphere prior to use.

Benzene and tetrahydrofuran were distilled from a sodium benzophenone ketyl solution. Toluene, n-octane, i - octane and xylene were distilled over molten sodium. Hexane was distilled from calcium hydride.

(c) Experimental Details

An inert atmosphere was generally maintained for all reactions and additionally all kinetic work was done in foil covered glassware to prevent radical involvement. Reaction temperatures were generally maintained at a constant value ( $\pm 0.5^{\circ}\text{C}$ ) using thermostat controlled oil-baths. To monitor reactions, samples were removed using a syringe through a Suba-seal. Thin layer chromatography was performed

on silica gel (Kieselgel 60, F254) or alumina (aluminium oxide 150, F254, type J). Column chromatography was generally carried out under air (except in Chapter 5) using silica gel (Kieselgel 60, 63-200 m) or neutral alumina (aluminium oxide 90, 63-200 m). Other grade alumina was prepared from neutral alumina following the manufacturers recommendations.

Recrystallizations were generally performed in the dark under an inert atmosphere at  $-5^{\circ}\text{C}$ , either from hexane or a mixture of hexane and other organic solvents.

#### Instrumentation

Infrared spectra were recorded using NaCl cells of either 1.1 or 0.15 mm pathlength on either a Jasco IAA-1, a Pye Unicam SP 3 or a Perkin Elmer 580B instrument. When problems of low solubility were encountered or spectra of particularly important compounds were involved, the spectra were obtained on a Bruker 85 Infrared Spectrophotometer at N.C.R.I., C.S.I.R., Pretoria, under the instruction of Dr. M. O. Albers.

All nuclear magnetic resonance spectra were recorded using a Varian A360A NMR spectrophotometer or a Bruker WM 80 FT NMR spectrophotometer.

U.V. - Visible spectra were recorded using a Varian 634 Series U.V. - Visible Spectrophotometer. Mass spectra were obtained by Dr. T. Doshoff using a Varian Mat CH7 mass spectrometer or by Dr. L. Fourie at Potchefstroom University.\*

Microanalyses were performed by Microanalytical Division of N.P.S.L., C.S.I.R., Pretoria or for air-sensitive complexes by the Galbraith Laboratories Inc., Knoxville, Tennessee, U.S.A.

The oscillation, zero layer and first layer diffraction photographs for the crystal structure were obtained using a Seifert Iso-Delverflex 1001 fully stabilized X-ray generator. The intensity data was collected by Dr. J. Albani at the N.P.S.L., C.S.I.R., Pretoria.

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\* Mass spectra were obtained with a 70eV ionizing voltage and the source temperature was between 100°C and 200°C.

Appendix CX-RAY CRYSTAL STRUCTURE DATA

Tables for the final atomic coordinates of the atoms in the molecule  $\text{MnRe(CO)}_9(\text{Bu}^t\text{NC})$  along with average bond lengths and bond angles were given in Chapter 4.

Isotropic and anisotropic temperature factor and structure factor tables are listed below. Table C1 gives the isotropic temperature factors for the protons in the methyl group of the isonitrile for molecule 1 and molecule 2. Tables C2 and C3 give the anisotropic temperature factors for the non-hydrogen atoms in molecule 1 and molecule 2 respectively,\* and Table C4 presents the observed and calculated values for the structure factors. The molecule packing in the unit cell is illustrated by Figure C1.

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\* C12, C13, and C14 were resolved as  $\text{CH}_3$  groups and only an isotropic temperature factor was determined.

TABLE C1      Isotropic Temperature Factors for  
Methyl Group Protons

| Methyl Group<br>Carbon Atom | <u>Isotropic Temperature Factor</u> |            |
|-----------------------------|-------------------------------------|------------|
|                             | Molecule 1                          | Molecule 2 |
| C12                         | 0.0907                              | 0.1162     |
| C13                         | 0.1320                              | 0.0505     |
| C14                         | 0.0730                              | 0.1301     |

Figure C1      Unit Cell Molecular Packing Diagram  
for  $\text{MnRe}(\text{CO})_9(\text{Bu}^t\text{NC})$

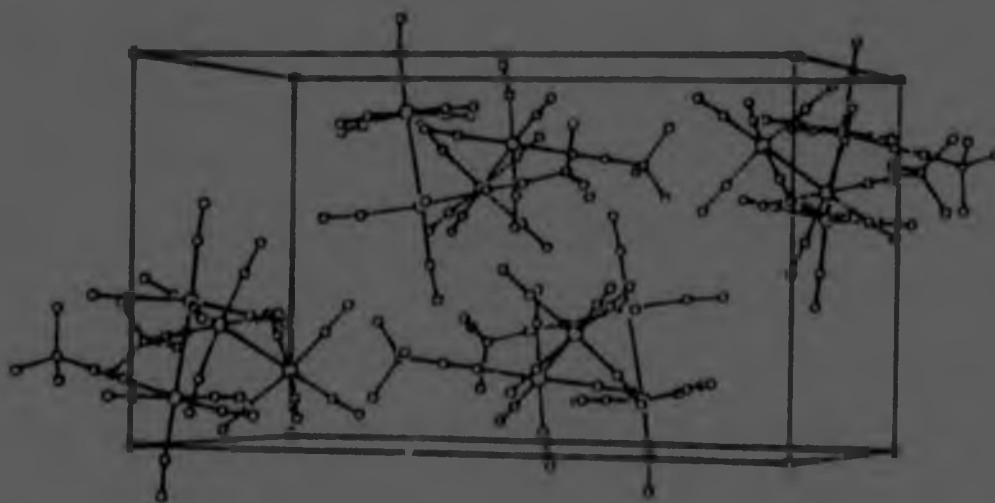


TABLE C2      Anisotropic Temperature Factors  
for Molecule 1

|     | U11    | U22    | U33    | U23     | U13     | U12     |
|-----|--------|--------|--------|---------|---------|---------|
| Mn  | 0.0438 | 0.0339 | 0.0366 | -0.0008 | 0.0124  | -0.0020 |
| Re  | 0.0491 | 0.0485 | 0.0556 | 0.0002  | 0.0056  | 0.0054  |
| C1  | 0.1175 | 0.0603 | 0.1028 | -0.0149 | -0.0436 | 0.0041  |
| C2  | 0.0660 | 0.0787 | 0.0714 | -0.0168 | -0.0142 | 0.0162  |
| C3  | 0.0448 | 0.0226 | 0.1441 | 0.0394  | -0.0053 | -0.0037 |
| C4  | 0.0574 | 0.1053 | 0.0837 | -0.0232 | 0.0641  | -0.0398 |
| C5  | 0.1152 | 0.0255 | 0.1349 | -0.0122 | 0.0380  | 0.0480  |
| C6  | 0.0081 | 0.1462 | 0.0795 | -0.0045 | -0.0060 | -0.0291 |
| C7  | 0.0089 | 0.1061 | 0.0995 | 0.0115  | -0.0211 | 0.0279  |
| C8  | 0.0925 | 0.0088 | 0.0845 | 0.0173  | 0.0101  | -0.0190 |
| C9  | 0.0632 | 0.0195 | 0.1122 | 0.0046  | -0.0449 | 0.0131  |
| C10 | 0.0333 | 0.0472 | 0.0605 | 0.0097  | 0.0006  | 0.0106  |
| C11 | 0.0410 | 0.0581 | 0.0525 | 0.0018  | -0.0003 | 0.0073  |
| C12 | 0.1293 |        |        |         |         |         |
| C13 | 0.1124 |        |        |         |         |         |
| C14 | 0.1094 |        |        |         |         |         |
| O1  | 0.1130 | 0.1261 | 0.1243 | 0.0232  | 0.0338  | -0.0289 |
| O2  | 0.0852 | 0.0629 | 0.0976 | -0.0020 | -0.0059 | -0.0174 |
| O3  | 0.1228 | 0.0952 | 0.0887 | -0.0069 | 0.0381  | -0.0021 |
| O4  | 0.0508 | 0.1113 | 0.0995 | -0.0055 | 0.0127  | 0.0002  |
| O5  | 0.1325 | 0.0468 | 0.1143 | 0.0018  | 0.0110  | 0.0372  |
| O6  | 0.0597 | 0.1200 | 0.0537 | 0.0040  | -0.0121 | -0.0329 |
| O7  | 0.0771 | 0.1081 | 0.1123 | -0.0025 | -0.0420 | 0.0164  |
| O8  | 0.0744 | 0.0547 | 0.1113 | -0.0010 | -0.0056 | 0.0063  |
| O9  | 0.0572 | 0.0865 | 0.1081 | 0.0024  | -0.0022 | -0.0084 |
| N   | 0.0510 | 0.0454 | 0.0626 | 0.0032  | 0.0015  | 0.0116  |

TABLE C3      Anisotropic Temperature Factors  
for Molecule 2

|     | U11    | U22    | U33    | U23     | U13     | U12     |
|-----|--------|--------|--------|---------|---------|---------|
| Mn  | 0.0462 | 0.0283 | 0.0375 | 0.0029  | 0.0081  | -0.0031 |
| Re  | 0.0517 | 0.0497 | 0.0551 | 0.0036  | 0.0090  | -0.0001 |
| C1  | 0.0642 | 0.0365 | 0.0165 | 0.0291  | -0.0404 | -0.0558 |
| C2  | 0.0313 | 0.0517 | 0.0928 | -0.0237 | 0.0030  | -0.0390 |
| C3  | 0.0117 | 0.0717 | 0.0580 | -0.0312 | 0.0038  | 0.0138  |
| C4  | 0.1606 | 0.0091 | 0.0665 | -0.0100 | 0.0146  | -0.0462 |
| C5  | 0.0454 | 0.0566 | 0.0808 | -0.0063 | 0.0226  | -0.0205 |
| C6  | 0.0457 | 0.0590 | 0.0490 | 0.0054  | -0.0052 | -0.0053 |
| C7  | 0.0804 | 0.0832 | 0.0604 | 0.0196  | -0.0110 | -0.0240 |
| C8  | 0.1282 | 0.0877 | 0.0236 | 0.0320  | 0.0170  | -0.1017 |
| C9  | 0.1599 | 0.0663 | 0.0081 | 0.0363  | 0.0040  | -0.0329 |
| C10 | 0.1105 | 0.0283 | 0.0434 | 0.0084  | -0.0055 | -0.0838 |
| C11 | 0.0558 | 0.0601 | 0.0595 | -0.0225 | 0.0405  | 0.0040  |
| C12 | 0.1030 |        |        |         |         |         |
| C13 | 0.1053 |        |        |         |         |         |
| C14 | 0.1421 |        |        |         |         |         |
| O1  | 0.2477 | 0.0304 | 0.0794 | 0.0082  | 0.0035  | 0.0149  |
| O2  | 0.0566 | 0.0695 | 0.0583 | 0.0042  | 0.0055  | 0.0242  |
| O3  | 0.0379 | 0.0943 | 0.1258 | 0.0195  | 0.0117  | 0.0047  |
| O4  | 0.1093 | 0.0916 | 0.0918 | 0.0110  | -0.0187 | -0.0358 |
| O5  | 0.0590 | 0.1096 | 0.0854 | 0.0071  | 0.0228  | 0.0048  |
| O6  | 0.0557 | 0.0979 | 0.0886 | 0.0050  | 0.0024  | -0.0259 |
| O7  | 0.0513 | 0.1419 | 0.0880 | -0.0244 | 0.0092  | -0.0327 |
| O8  | 0.1145 | 0.0628 | 0.0999 | 0.0163  | 0.0170  | 0.0167  |
| O9  | 0.1405 | 0.0767 | 0.0534 | 0.0118  | 0.0230  | -0.0781 |
| N   | 0.0694 | 0.0106 | 0.0538 | -0.0110 | 0.0161  | 0.0029  |

| DECEMBER AND CALCULATED STRENGTH FACTORS FOR DURE |     |   |       |     |     |   |      |     |     | PAGE 3 |     |     |     |
|---------------------------------------------------|-----|---|-------|-----|-----|---|------|-----|-----|--------|-----|-----|-----|
| M                                                 | N   | L | FC    | H   | K   | L | FC   | H   | K   | L      | FC  | M   | N   |
| 1                                                 | 1   | 0 | 674   | 14  | 2   | 0 | 38   | 14  | 2   | 0      | 354 | 1   | 1   |
| 2                                                 | 2   | 0 | 777   | 15  | 3   | 0 | 55   | 15  | 3   | 0      | 41  | 2   | 2   |
| 3                                                 | 3   | 0 | 877   | 16  | 4   | 0 | 102  | 16  | 4   | 0      | 240 | 3   | 3   |
| 4                                                 | 4   | 0 | 977   | 17  | 5   | 0 | 152  | 17  | 5   | 0      | 56  | 4   | 4   |
| 5                                                 | 5   | 0 | 1077  | 18  | 6   | 0 | 200  | 18  | 6   | 0      | 120 | 5   | 5   |
| 6                                                 | 6   | 0 | 1177  | 19  | 7   | 0 | 250  | 19  | 7   | 0      | 161 | 6   | 6   |
| 7                                                 | 7   | 0 | 1277  | 20  | 8   | 0 | 300  | 20  | 8   | 0      | 222 | 7   | 7   |
| 8                                                 | 8   | 0 | 1377  | 21  | 9   | 0 | 350  | 21  | 9   | 0      | 286 | 8   | 8   |
| 9                                                 | 9   | 0 | 1477  | 22  | 10  | 0 | 400  | 22  | 10  | 0      | 354 | 9   | 9   |
| 10                                                | 10  | 0 | 1577  | 23  | 11  | 0 | 450  | 23  | 11  | 0      | 41  | 10  | 10  |
| 11                                                | 11  | 0 | 1677  | 24  | 12  | 0 | 500  | 24  | 12  | 0      | 56  | 11  | 11  |
| 12                                                | 12  | 0 | 1777  | 25  | 13  | 0 | 550  | 25  | 13  | 0      | 120 | 12  | 12  |
| 13                                                | 13  | 0 | 1877  | 26  | 14  | 0 | 600  | 26  | 14  | 0      | 161 | 13  | 13  |
| 14                                                | 14  | 0 | 1977  | 27  | 15  | 0 | 650  | 27  | 15  | 0      | 222 | 14  | 14  |
| 15                                                | 15  | 0 | 2077  | 28  | 16  | 0 | 700  | 28  | 16  | 0      | 286 | 15  | 15  |
| 16                                                | 16  | 0 | 2177  | 29  | 17  | 0 | 750  | 29  | 17  | 0      | 354 | 16  | 16  |
| 17                                                | 17  | 0 | 2277  | 30  | 18  | 0 | 800  | 30  | 18  | 0      | 41  | 17  | 17  |
| 18                                                | 18  | 0 | 2377  | 31  | 19  | 0 | 850  | 31  | 19  | 0      | 56  | 18  | 18  |
| 19                                                | 19  | 0 | 2477  | 32  | 20  | 0 | 900  | 32  | 20  | 0      | 120 | 19  | 19  |
| 20                                                | 20  | 0 | 2577  | 33  | 21  | 0 | 950  | 33  | 21  | 0      | 161 | 20  | 20  |
| 21                                                | 21  | 0 | 2677  | 34  | 22  | 0 | 1000 | 34  | 22  | 0      | 222 | 21  | 21  |
| 22                                                | 22  | 0 | 2777  | 35  | 23  | 0 | 1050 | 35  | 23  | 0      | 286 | 22  | 22  |
| 23                                                | 23  | 0 | 2877  | 36  | 24  | 0 | 1100 | 36  | 24  | 0      | 354 | 23  | 23  |
| 24                                                | 24  | 0 | 2977  | 37  | 25  | 0 | 1150 | 37  | 25  | 0      | 41  | 24  | 24  |
| 25                                                | 25  | 0 | 3077  | 38  | 26  | 0 | 1200 | 38  | 26  | 0      | 56  | 25  | 25  |
| 26                                                | 26  | 0 | 3177  | 39  | 27  | 0 | 1250 | 39  | 27  | 0      | 120 | 26  | 26  |
| 27                                                | 27  | 0 | 3277  | 40  | 28  | 0 | 1300 | 40  | 28  | 0      | 161 | 27  | 27  |
| 28                                                | 28  | 0 | 3377  | 41  | 29  | 0 | 1350 | 41  | 29  | 0      | 222 | 28  | 28  |
| 29                                                | 29  | 0 | 3477  | 42  | 30  | 0 | 1400 | 42  | 30  | 0      | 286 | 29  | 29  |
| 30                                                | 30  | 0 | 3577  | 43  | 31  | 0 | 1450 | 43  | 31  | 0      | 354 | 30  | 30  |
| 31                                                | 31  | 0 | 3677  | 44  | 32  | 0 | 1500 | 44  | 32  | 0      | 41  | 31  | 31  |
| 32                                                | 32  | 0 | 3777  | 45  | 33  | 0 | 1550 | 45  | 33  | 0      | 56  | 32  | 32  |
| 33                                                | 33  | 0 | 3877  | 46  | 34  | 0 | 1600 | 46  | 34  | 0      | 120 | 33  | 33  |
| 34                                                | 34  | 0 | 3977  | 47  | 35  | 0 | 1650 | 47  | 35  | 0      | 161 | 34  | 34  |
| 35                                                | 35  | 0 | 4077  | 48  | 36  | 0 | 1700 | 48  | 36  | 0      | 222 | 35  | 35  |
| 36                                                | 36  | 0 | 4177  | 49  | 37  | 0 | 1750 | 49  | 37  | 0      | 286 | 36  | 36  |
| 37                                                | 37  | 0 | 4277  | 50  | 38  | 0 | 1800 | 50  | 38  | 0      | 354 | 37  | 37  |
| 38                                                | 38  | 0 | 4377  | 51  | 39  | 0 | 1850 | 51  | 39  | 0      | 41  | 38  | 38  |
| 39                                                | 39  | 0 | 4477  | 52  | 40  | 0 | 1900 | 52  | 40  | 0      | 56  | 39  | 39  |
| 40                                                | 40  | 0 | 4577  | 53  | 41  | 0 | 1950 | 53  | 41  | 0      | 120 | 40  | 40  |
| 41                                                | 41  | 0 | 4677  | 54  | 42  | 0 | 2000 | 54  | 42  | 0      | 161 | 41  | 41  |
| 42                                                | 42  | 0 | 4777  | 55  | 43  | 0 | 2050 | 55  | 43  | 0      | 222 | 42  | 42  |
| 43                                                | 43  | 0 | 4877  | 56  | 44  | 0 | 2100 | 56  | 44  | 0      | 286 | 43  | 43  |
| 44                                                | 44  | 0 | 4977  | 57  | 45  | 0 | 2150 | 57  | 45  | 0      | 354 | 44  | 44  |
| 45                                                | 45  | 0 | 5077  | 58  | 46  | 0 | 2200 | 58  | 46  | 0      | 41  | 45  | 45  |
| 46                                                | 46  | 0 | 5177  | 59  | 47  | 0 | 2250 | 59  | 47  | 0      | 56  | 46  | 46  |
| 47                                                | 47  | 0 | 5277  | 60  | 48  | 0 | 2300 | 60  | 48  | 0      | 120 | 47  | 47  |
| 48                                                | 48  | 0 | 5377  | 61  | 49  | 0 | 2350 | 61  | 49  | 0      | 161 | 48  | 48  |
| 49                                                | 49  | 0 | 5477  | 62  | 50  | 0 | 2400 | 62  | 50  | 0      | 222 | 49  | 49  |
| 50                                                | 50  | 0 | 5577  | 63  | 51  | 0 | 2450 | 63  | 51  | 0      | 286 | 50  | 50  |
| 51                                                | 51  | 0 | 5677  | 64  | 52  | 0 | 2500 | 64  | 52  | 0      | 354 | 51  | 51  |
| 52                                                | 52  | 0 | 5777  | 65  | 53  | 0 | 2550 | 65  | 53  | 0      | 41  | 52  | 52  |
| 53                                                | 53  | 0 | 5877  | 66  | 54  | 0 | 2600 | 66  | 54  | 0      | 56  | 53  | 53  |
| 54                                                | 54  | 0 | 5977  | 67  | 55  | 0 | 2650 | 67  | 55  | 0      | 120 | 54  | 54  |
| 55                                                | 55  | 0 | 6077  | 68  | 56  | 0 | 2700 | 68  | 56  | 0      | 161 | 55  | 55  |
| 56                                                | 56  | 0 | 6177  | 69  | 57  | 0 | 2750 | 69  | 57  | 0      | 222 | 56  | 56  |
| 57                                                | 57  | 0 | 6277  | 70  | 58  | 0 | 2800 | 70  | 58  | 0      | 286 | 57  | 57  |
| 58                                                | 58  | 0 | 6377  | 71  | 59  | 0 | 2850 | 71  | 59  | 0      | 354 | 58  | 58  |
| 59                                                | 59  | 0 | 6477  | 72  | 60  | 0 | 2900 | 72  | 60  | 0      | 41  | 59  | 59  |
| 60                                                | 60  | 0 | 6577  | 73  | 61  | 0 | 2950 | 73  | 61  | 0      | 56  | 60  | 60  |
| 61                                                | 61  | 0 | 6677  | 74  | 62  | 0 | 3000 | 74  | 62  | 0      | 120 | 61  | 61  |
| 62                                                | 62  | 0 | 6777  | 75  | 63  | 0 | 3050 | 75  | 63  | 0      | 161 | 62  | 62  |
| 63                                                | 63  | 0 | 6877  | 76  | 64  | 0 | 3100 | 76  | 64  | 0      | 222 | 63  | 63  |
| 64                                                | 64  | 0 | 6977  | 77  | 65  | 0 | 3150 | 77  | 65  | 0      | 286 | 64  | 64  |
| 65                                                | 65  | 0 | 7077  | 78  | 66  | 0 | 3200 | 78  | 66  | 0      | 354 | 65  | 65  |
| 66                                                | 66  | 0 | 7177  | 79  | 67  | 0 | 3250 | 79  | 67  | 0      | 41  | 66  | 66  |
| 67                                                | 67  | 0 | 7277  | 80  | 68  | 0 | 3300 | 80  | 68  | 0      | 56  | 67  | 67  |
| 68                                                | 68  | 0 | 7377  | 81  | 69  | 0 | 3350 | 81  | 69  | 0      | 120 | 68  | 68  |
| 69                                                | 69  | 0 | 7477  | 82  | 70  | 0 | 3400 | 82  | 70  | 0      | 161 | 69  | 69  |
| 70                                                | 70  | 0 | 7577  | 83  | 71  | 0 | 3450 | 83  | 71  | 0      | 222 | 70  | 70  |
| 71                                                | 71  | 0 | 7677  | 84  | 72  | 0 | 3500 | 84  | 72  | 0      | 286 | 71  | 71  |
| 72                                                | 72  | 0 | 7777  | 85  | 73  | 0 | 3550 | 85  | 73  | 0      | 354 | 72  | 72  |
| 73                                                | 73  | 0 | 7877  | 86  | 74  | 0 | 3600 | 86  | 74  | 0      | 41  | 73  | 73  |
| 74                                                | 74  | 0 | 7977  | 87  | 75  | 0 | 3650 | 87  | 75  | 0      | 56  | 74  | 74  |
| 75                                                | 75  | 0 | 8077  | 88  | 76  | 0 | 3700 | 88  | 76  | 0      | 120 | 75  | 75  |
| 76                                                | 76  | 0 | 8177  | 89  | 77  | 0 | 3750 | 89  | 77  | 0      | 161 | 76  | 76  |
| 77                                                | 77  | 0 | 8277  | 90  | 78  | 0 | 3800 | 90  | 78  | 0      | 222 | 77  | 77  |
| 78                                                | 78  | 0 | 8377  | 91  | 79  | 0 | 3850 | 91  | 79  | 0      | 286 | 78  | 78  |
| 79                                                | 79  | 0 | 8477  | 92  | 80  | 0 | 3900 | 92  | 80  | 0      | 354 | 79  | 79  |
| 80                                                | 80  | 0 | 8577  | 93  | 81  | 0 | 3950 | 93  | 81  | 0      | 41  | 80  | 80  |
| 81                                                | 81  | 0 | 8677  | 94  | 82  | 0 | 4000 | 94  | 82  | 0      | 56  | 81  | 81  |
| 82                                                | 82  | 0 | 8777  | 95  | 83  | 0 | 4050 | 95  | 83  | 0      | 120 | 82  | 82  |
| 83                                                | 83  | 0 | 8877  | 96  | 84  | 0 | 4100 | 96  | 84  | 0      | 161 | 83  | 83  |
| 84                                                | 84  | 0 | 8977  | 97  | 85  | 0 | 4150 | 97  | 85  | 0      | 222 | 84  | 84  |
| 85                                                | 85  | 0 | 9077  | 98  | 86  | 0 | 4200 | 98  | 86  | 0      | 286 | 85  | 85  |
| 86                                                | 86  | 0 | 9177  | 99  | 87  | 0 | 4250 | 99  | 87  | 0      | 354 | 86  | 86  |
| 87                                                | 87  | 0 | 9277  | 100 | 88  | 0 | 4300 | 100 | 88  | 0      | 41  | 87  | 87  |
| 88                                                | 88  | 0 | 9377  | 101 | 89  | 0 | 4350 | 101 | 89  | 0      | 56  | 88  | 88  |
| 89                                                | 89  | 0 | 9477  | 102 | 90  | 0 | 4400 | 102 | 90  | 0      | 120 | 89  | 89  |
| 90                                                | 90  | 0 | 9577  | 103 | 91  | 0 | 4450 | 103 | 91  | 0      | 161 | 90  | 90  |
| 91                                                | 91  | 0 | 9677  | 104 | 92  | 0 | 4500 | 104 | 92  | 0      | 222 | 91  | 91  |
| 92                                                | 92  | 0 | 9777  | 105 | 93  | 0 | 4550 | 105 | 93  | 0      | 286 | 92  | 92  |
| 93                                                | 93  | 0 | 9877  | 106 | 94  | 0 | 4600 | 106 | 94  | 0      | 354 | 93  | 93  |
| 94                                                | 94  | 0 | 9977  | 107 | 95  | 0 | 4650 | 107 | 95  | 0      | 41  | 94  | 94  |
| 95                                                | 95  | 0 | 10077 | 108 | 96  | 0 | 4700 | 108 | 96  | 0      | 56  | 95  | 95  |
| 96                                                | 96  | 0 | 10177 | 109 | 97  | 0 | 4750 | 109 | 97  | 0      | 120 | 96  | 96  |
| 97                                                | 97  | 0 | 10277 | 110 | 98  | 0 | 4800 | 110 | 98  | 0      | 161 | 97  | 97  |
| 98                                                | 98  | 0 | 10377 | 111 | 99  | 0 | 4850 | 111 | 99  | 0      | 222 | 98  | 98  |
| 99                                                | 99  | 0 | 10477 | 112 | 100 | 0 | 4900 | 112 | 100 | 0      | 286 | 99  | 99  |
| 100                                               | 100 | 0 | 10577 | 113 | 101 | 0 | 4950 | 113 | 101 | 0      | 354 | 100 | 100 |

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR GUR

| PAGE 2 |    |   |     |      |   |   |   |     |     |
|--------|----|---|-----|------|---|---|---|-----|-----|
| H      | K  | L | FO  | FC   | H | K | L | FO  | FC  |
| 14     | 12 | 0 | 45  | -31  | 1 | 1 | 1 | 121 | -91 |
| 13     | 13 | 0 | 57  | -53  | 1 | 1 | 0 | 101 | -80 |
| 12     | 13 | 0 | 54  | -26  | 1 | 1 | 0 | 108 | -93 |
| 13     | 13 | 0 | 54  | 77   | 1 | 1 | 0 | 80  | 54  |
| 4      | 13 | 0 | 54  | -61  | 1 | 1 | 0 | 79  | -57 |
| 13     | 13 | 0 | 40  | 75   | 1 | 1 | 0 | 62  | -55 |
| 13     | 13 | 0 | 41  | -33  | 1 | 1 | 0 | 73  | -54 |
| 13     | 13 | 0 | 54  | -39  | 1 | 1 | 0 | 30  | 30  |
| 13     | 13 | 0 | 54  | -40  | 1 | 1 | 0 | 32  | -49 |
| 13     | 13 | 0 | 30  | 40   | 1 | 1 | 0 | 39  | -24 |
| 13     | 13 | 0 | 70  | -53  | 1 | 1 | 0 | 40  | -30 |
| 14     | 13 | 0 | 70  | 146  | 1 | 1 | 0 | 37  | -42 |
| 0      | 14 | 0 | 145 | -128 | 1 | 1 | 0 | 35  | -33 |
| 1      | 14 | 0 | 145 | -119 | 1 | 1 | 0 | 25  | -36 |
| 1      | 14 | 0 | 145 | -47  | 1 | 1 | 0 | 24  | -38 |
| 1      | 14 | 0 | 108 | -100 | 1 | 1 | 0 | 56  | -55 |
| 1      | 14 | 0 | 132 | -101 | 1 | 1 | 0 | 52  | -45 |
| 1      | 14 | 0 | 132 | -60  | 1 | 1 | 0 | 72  | -62 |
| 1      | 14 | 0 | 132 | -30  | 1 | 1 | 0 | 69  | -47 |
| 1      | 14 | 0 | 132 | 30   | 1 | 1 | 0 | 65  | -95 |
| 1      | 14 | 0 | 132 | -74  | 1 | 1 | 0 | 62  | -44 |
| 1      | 14 | 0 | 132 | -59  | 1 | 1 | 0 | 62  | -73 |
| 1      | 14 | 0 | 132 | -59  | 1 | 1 | 0 | 61  | -40 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 41  | -28 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 49  | -31 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 49  | -22 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 52  | -47 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 52  | -24 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 52  | -25 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 52  | -78 |
| 1      | 14 | 0 | 132 | -52  | 1 | 1 | 0 | 52  | -20 |

| OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DUBI |     |   |     |     |    |    |   |     |     |     |     |   |     | PAGE 3 |  |  |  |
|----------------------------------------------------|-----|---|-----|-----|----|----|---|-----|-----|-----|-----|---|-----|--------|--|--|--|
| H                                                  | K   | L | FO  | EC  | H  | K  | L | FO  | EC  | H   | K   | L | FO  | EC     |  |  |  |
| 2                                                  | 2   | 1 | 104 | 104 | 1  | 1  | 1 | 104 | 104 | 5   | 5   | 1 | 104 | 104    |  |  |  |
| 3                                                  | 3   | 1 | 104 | 104 | 2  | 2  | 1 | 104 | 104 | 6   | 6   | 1 | 104 | 104    |  |  |  |
| 4                                                  | 4   | 1 | 104 | 104 | 3  | 3  | 1 | 104 | 104 | 7   | 7   | 1 | 104 | 104    |  |  |  |
| 5                                                  | 5   | 1 | 104 | 104 | 4  | 4  | 1 | 104 | 104 | 8   | 8   | 1 | 104 | 104    |  |  |  |
| 6                                                  | 6   | 1 | 104 | 104 | 5  | 5  | 1 | 104 | 104 | 9   | 9   | 1 | 104 | 104    |  |  |  |
| 7                                                  | 7   | 1 | 104 | 104 | 6  | 6  | 1 | 104 | 104 | 10  | 10  | 1 | 104 | 104    |  |  |  |
| 8                                                  | 8   | 1 | 104 | 104 | 7  | 7  | 1 | 104 | 104 | 11  | 11  | 1 | 104 | 104    |  |  |  |
| 9                                                  | 9   | 1 | 104 | 104 | 8  | 8  | 1 | 104 | 104 | 12  | 12  | 1 | 104 | 104    |  |  |  |
| 10                                                 | 10  | 1 | 104 | 104 | 9  | 9  | 1 | 104 | 104 | 13  | 13  | 1 | 104 | 104    |  |  |  |
| 11                                                 | 11  | 1 | 104 | 104 | 10 | 10 | 1 | 104 | 104 | 14  | 14  | 1 | 104 | 104    |  |  |  |
| 12                                                 | 12  | 1 | 104 | 104 | 11 | 11 | 1 | 104 | 104 | 15  | 15  | 1 | 104 | 104    |  |  |  |
| 13                                                 | 13  | 1 | 104 | 104 | 12 | 12 | 1 | 104 | 104 | 16  | 16  | 1 | 104 | 104    |  |  |  |
| 14                                                 | 14  | 1 | 104 | 104 | 13 | 13 | 1 | 104 | 104 | 17  | 17  | 1 | 104 | 104    |  |  |  |
| 15                                                 | 15  | 1 | 104 | 104 | 14 | 14 | 1 | 104 | 104 | 18  | 18  | 1 | 104 | 104    |  |  |  |
| 16                                                 | 16  | 1 | 104 | 104 | 15 | 15 | 1 | 104 | 104 | 19  | 19  | 1 | 104 | 104    |  |  |  |
| 17                                                 | 17  | 1 | 104 | 104 | 16 | 16 | 1 | 104 | 104 | 20  | 20  | 1 | 104 | 104    |  |  |  |
| 18                                                 | 18  | 1 | 104 | 104 | 17 | 17 | 1 | 104 | 104 | 21  | 21  | 1 | 104 | 104    |  |  |  |
| 19                                                 | 19  | 1 | 104 | 104 | 18 | 18 | 1 | 104 | 104 | 22  | 22  | 1 | 104 | 104    |  |  |  |
| 20                                                 | 20  | 1 | 104 | 104 | 19 | 19 | 1 | 104 | 104 | 23  | 23  | 1 | 104 | 104    |  |  |  |
| 21                                                 | 21  | 1 | 104 | 104 | 20 | 20 | 1 | 104 | 104 | 24  | 24  | 1 | 104 | 104    |  |  |  |
| 22                                                 | 22  | 1 | 104 | 104 | 21 | 21 | 1 | 104 | 104 | 25  | 25  | 1 | 104 | 104    |  |  |  |
| 23                                                 | 23  | 1 | 104 | 104 | 22 | 22 | 1 | 104 | 104 | 26  | 26  | 1 | 104 | 104    |  |  |  |
| 24                                                 | 24  | 1 | 104 | 104 | 23 | 23 | 1 | 104 | 104 | 27  | 27  | 1 | 104 | 104    |  |  |  |
| 25                                                 | 25  | 1 | 104 | 104 | 24 | 24 | 1 | 104 | 104 | 28  | 28  | 1 | 104 | 104    |  |  |  |
| 26                                                 | 26  | 1 | 104 | 104 | 25 | 25 | 1 | 104 | 104 | 29  | 29  | 1 | 104 | 104    |  |  |  |
| 27                                                 | 27  | 1 | 104 | 104 | 26 | 26 | 1 | 104 | 104 | 30  | 30  | 1 | 104 | 104    |  |  |  |
| 28                                                 | 28  | 1 | 104 | 104 | 27 | 27 | 1 | 104 | 104 | 31  | 31  | 1 | 104 | 104    |  |  |  |
| 29                                                 | 29  | 1 | 104 | 104 | 28 | 28 | 1 | 104 | 104 | 32  | 32  | 1 | 104 | 104    |  |  |  |
| 30                                                 | 30  | 1 | 104 | 104 | 29 | 29 | 1 | 104 | 104 | 33  | 33  | 1 | 104 | 104    |  |  |  |
| 31                                                 | 31  | 1 | 104 | 104 | 30 | 30 | 1 | 104 | 104 | 34  | 34  | 1 | 104 | 104    |  |  |  |
| 32                                                 | 32  | 1 | 104 | 104 | 31 | 31 | 1 | 104 | 104 | 35  | 35  | 1 | 104 | 104    |  |  |  |
| 33                                                 | 33  | 1 | 104 | 104 | 32 | 32 | 1 | 104 | 104 | 36  | 36  | 1 | 104 | 104    |  |  |  |
| 34                                                 | 34  | 1 | 104 | 104 | 33 | 33 | 1 | 104 | 104 | 37  | 37  | 1 | 104 | 104    |  |  |  |
| 35                                                 | 35  | 1 | 104 | 104 | 34 | 34 | 1 | 104 | 104 | 38  | 38  | 1 | 104 | 104    |  |  |  |
| 36                                                 | 36  | 1 | 104 | 104 | 35 | 35 | 1 | 104 | 104 | 39  | 39  | 1 | 104 | 104    |  |  |  |
| 37                                                 | 37  | 1 | 104 | 104 | 36 | 36 | 1 | 104 | 104 | 40  | 40  | 1 | 104 | 104    |  |  |  |
| 38                                                 | 38  | 1 | 104 | 104 | 37 | 37 | 1 | 104 | 104 | 41  | 41  | 1 | 104 | 104    |  |  |  |
| 39                                                 | 39  | 1 | 104 | 104 | 38 | 38 | 1 | 104 | 104 | 42  | 42  | 1 | 104 | 104    |  |  |  |
| 40                                                 | 40  | 1 | 104 | 104 | 39 | 39 | 1 | 104 | 104 | 43  | 43  | 1 | 104 | 104    |  |  |  |
| 41                                                 | 41  | 1 | 104 | 104 | 40 | 40 | 1 | 104 | 104 | 44  | 44  | 1 | 104 | 104    |  |  |  |
| 42                                                 | 42  | 1 | 104 | 104 | 41 | 41 | 1 | 104 | 104 | 45  | 45  | 1 | 104 | 104    |  |  |  |
| 43                                                 | 43  | 1 | 104 | 104 | 42 | 42 | 1 | 104 | 104 | 46  | 46  | 1 | 104 | 104    |  |  |  |
| 44                                                 | 44  | 1 | 104 | 104 | 43 | 43 | 1 | 104 | 104 | 47  | 47  | 1 | 104 | 104    |  |  |  |
| 45                                                 | 45  | 1 | 104 | 104 | 44 | 44 | 1 | 104 | 104 | 48  | 48  | 1 | 104 | 104    |  |  |  |
| 46                                                 | 46  | 1 | 104 | 104 | 45 | 45 | 1 | 104 | 104 | 49  | 49  | 1 | 104 | 104    |  |  |  |
| 47                                                 | 47  | 1 | 104 | 104 | 46 | 46 | 1 | 104 | 104 | 50  | 50  | 1 | 104 | 104    |  |  |  |
| 48                                                 | 48  | 1 | 104 | 104 | 47 | 47 | 1 | 104 | 104 | 51  | 51  | 1 | 104 | 104    |  |  |  |
| 49                                                 | 49  | 1 | 104 | 104 | 48 | 48 | 1 | 104 | 104 | 52  | 52  | 1 | 104 | 104    |  |  |  |
| 50                                                 | 50  | 1 | 104 | 104 | 49 | 49 | 1 | 104 | 104 | 53  | 53  | 1 | 104 | 104    |  |  |  |
| 51                                                 | 51  | 1 | 104 | 104 | 50 | 50 | 1 | 104 | 104 | 54  | 54  | 1 | 104 | 104    |  |  |  |
| 52                                                 | 52  | 1 | 104 | 104 | 51 | 51 | 1 | 104 | 104 | 55  | 55  | 1 | 104 | 104    |  |  |  |
| 53                                                 | 53  | 1 | 104 | 104 | 52 | 52 | 1 | 104 | 104 | 56  | 56  | 1 | 104 | 104    |  |  |  |
| 54                                                 | 54  | 1 | 104 | 104 | 53 | 53 | 1 | 104 | 104 | 57  | 57  | 1 | 104 | 104    |  |  |  |
| 55                                                 | 55  | 1 | 104 | 104 | 54 | 54 | 1 | 104 | 104 | 58  | 58  | 1 | 104 | 104    |  |  |  |
| 56                                                 | 56  | 1 | 104 | 104 | 55 | 55 | 1 | 104 | 104 | 59  | 59  | 1 | 104 | 104    |  |  |  |
| 57                                                 | 57  | 1 | 104 | 104 | 56 | 56 | 1 | 104 | 104 | 60  | 60  | 1 | 104 | 104    |  |  |  |
| 58                                                 | 58  | 1 | 104 | 104 | 57 | 57 | 1 | 104 | 104 | 61  | 61  | 1 | 104 | 104    |  |  |  |
| 59                                                 | 59  | 1 | 104 | 104 | 58 | 58 | 1 | 104 | 104 | 62  | 62  | 1 | 104 | 104    |  |  |  |
| 60                                                 | 60  | 1 | 104 | 104 | 59 | 59 | 1 | 104 | 104 | 63  | 63  | 1 | 104 | 104    |  |  |  |
| 61                                                 | 61  | 1 | 104 | 104 | 60 | 60 | 1 | 104 | 104 | 64  | 64  | 1 | 104 | 104    |  |  |  |
| 62                                                 | 62  | 1 | 104 | 104 | 61 | 61 | 1 | 104 | 104 | 65  | 65  | 1 | 104 | 104    |  |  |  |
| 63                                                 | 63  | 1 | 104 | 104 | 62 | 62 | 1 | 104 | 104 | 66  | 66  | 1 | 104 | 104    |  |  |  |
| 64                                                 | 64  | 1 | 104 | 104 | 63 | 63 | 1 | 104 | 104 | 67  | 67  | 1 | 104 | 104    |  |  |  |
| 65                                                 | 65  | 1 | 104 | 104 | 64 | 64 | 1 | 104 | 104 | 68  | 68  | 1 | 104 | 104    |  |  |  |
| 66                                                 | 66  | 1 | 104 | 104 | 65 | 65 | 1 | 104 | 104 | 69  | 69  | 1 | 104 | 104    |  |  |  |
| 67                                                 | 67  | 1 | 104 | 104 | 66 | 66 | 1 | 104 | 104 | 70  | 70  | 1 | 104 | 104    |  |  |  |
| 68                                                 | 68  | 1 | 104 | 104 | 67 | 67 | 1 | 104 | 104 | 71  | 71  | 1 | 104 | 104    |  |  |  |
| 69                                                 | 69  | 1 | 104 | 104 | 68 | 68 | 1 | 104 | 104 | 72  | 72  | 1 | 104 | 104    |  |  |  |
| 70                                                 | 70  | 1 | 104 | 104 | 69 | 69 | 1 | 104 | 104 | 73  | 73  | 1 | 104 | 104    |  |  |  |
| 71                                                 | 71  | 1 | 104 | 104 | 70 | 70 | 1 | 104 | 104 | 74  | 74  | 1 | 104 | 104    |  |  |  |
| 72                                                 | 72  | 1 | 104 | 104 | 71 | 71 | 1 | 104 | 104 | 75  | 75  | 1 | 104 | 104    |  |  |  |
| 73                                                 | 73  | 1 | 104 | 104 | 72 | 72 | 1 | 104 | 104 | 76  | 76  | 1 | 104 | 104    |  |  |  |
| 74                                                 | 74  | 1 | 104 | 104 | 73 | 73 | 1 | 104 | 104 | 77  | 77  | 1 | 104 | 104    |  |  |  |
| 75                                                 | 75  | 1 | 104 | 104 | 74 | 74 | 1 | 104 | 104 | 78  | 78  | 1 | 104 | 104    |  |  |  |
| 76                                                 | 76  | 1 | 104 | 104 | 75 | 75 | 1 | 104 | 104 | 79  | 79  | 1 | 104 | 104    |  |  |  |
| 77                                                 | 77  | 1 | 104 | 104 | 76 | 76 | 1 | 104 | 104 | 80  | 80  | 1 | 104 | 104    |  |  |  |
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| 81                                                 | 81  | 1 | 104 | 104 | 80 | 80 | 1 | 104 | 104 | 84  | 84  | 1 | 104 | 104    |  |  |  |
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| 83                                                 | 83  | 1 | 104 | 104 | 82 | 82 | 1 | 104 | 104 | 86  | 86  | 1 | 104 | 104    |  |  |  |
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| 87                                                 | 87  | 1 | 104 | 104 | 86 | 86 | 1 | 104 | 104 | 90  | 90  | 1 | 104 | 104    |  |  |  |
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| 90                                                 | 90  | 1 | 104 | 104 | 89 | 89 | 1 | 104 | 104 | 93  | 93  | 1 | 104 | 104    |  |  |  |
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| 93                                                 | 93  | 1 | 104 | 104 | 92 | 92 | 1 | 104 | 104 | 96  | 96  | 1 | 104 | 104    |  |  |  |
| 94                                                 | 94  | 1 | 104 | 104 | 93 | 93 | 1 | 104 | 104 | 97  | 97  | 1 | 104 | 104    |  |  |  |
| 95                                                 | 95  | 1 | 104 | 104 | 94 | 94 | 1 | 104 | 104 | 98  | 98  | 1 | 104 | 104    |  |  |  |
| 96                                                 | 96  | 1 | 104 | 104 | 95 | 95 | 1 | 104 | 104 | 99  | 99  | 1 | 104 | 104    |  |  |  |
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| 100                                                | 100 | 1 | 104 | 104 | 99 | 99 | 1 | 104 | 104 | 103 | 103 | 1 | 104 | 104    |  |  |  |

UNREFINED AND CALCULATED STRUCTURE FACTORS FOR DIBI

| PAGE 4 |    |    |    |     |    |    |    |     |    |
|--------|----|----|----|-----|----|----|----|-----|----|
| H      | K  | L  | FC | H   | K  | L  | FC | H   | K  |
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APPROVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

| PAGE 8 |     |   |      |      |     |   |   |      |      |
|--------|-----|---|------|------|-----|---|---|------|------|
| M      | N   | L | FO   | FC   | H   | K | L | FO   | FC   |
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| 28     | 30  | 2 | 72   | 31   | 6   | 6 | 2 | 140  | 14   |
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| 34     | 36  | 2 | 57   | 82   | 12  | 6 | 2 | 179  | 41   |
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| 38     | 40  | 2 | 47   | 116  | 16  | 6 | 2 | 205  | 59   |
| 40     | 42  | 2 | 42   | 133  | 18  | 6 | 2 | 218  | 68   |
| 42     | 44  | 2 | 37   | 150  | 20  | 6 | 2 | 231  | 77   |
| 44     | 46  | 2 | 32   | 167  | 22  | 6 | 2 | 244  | 86   |
| 46     | 48  | 2 | 27   | 184  | 24  | 6 | 2 | 257  | 95   |
| 48     | 50  | 2 | 22   | 201  | 26  | 6 | 2 | 270  | 104  |
| 50     | 52  | 2 | 17   | 218  | 28  | 6 | 2 | 283  | 113  |
| 52     | 54  | 2 | 12   | 235  | 30  | 6 | 2 | 296  | 122  |
| 54     | 56  | 2 | 7    | 252  | 32  | 6 | 2 | 309  | 131  |
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| 60     | 62  | 2 | -8   | 303  | 38  | 6 | 2 | 348  | 158  |
| 62     | 64  | 2 | -13  | 320  | 40  | 6 | 2 | 361  | 167  |
| 64     | 66  | 2 | -18  | 337  | 42  | 6 | 2 | 374  | 176  |
| 66     | 68  | 2 | -23  | 354  | 44  | 6 | 2 | 387  | 185  |
| 68     | 70  | 2 | -28  | 371  | 46  | 6 | 2 | 400  | 194  |
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| 74     | 76  | 2 | -43  | 422  | 52  | 6 | 2 | 439  | 221  |
| 76     | 78  | 2 | -48  | 439  | 54  | 6 | 2 | 452  | 230  |
| 78     | 80  | 2 | -53  | 456  | 56  | 6 | 2 | 465  | 239  |
| 80     | 82  | 2 | -58  | 473  | 58  | 6 | 2 | 478  | 248  |
| 82     | 84  | 2 | -63  | 490  | 60  | 6 | 2 | 491  | 257  |
| 84     | 86  | 2 | -68  | 507  | 62  | 6 | 2 | 504  | 266  |
| 86     | 88  | 2 | -73  | 524  | 64  | 6 | 2 | 517  | 275  |
| 88     | 90  | 2 | -78  | 541  | 66  | 6 | 2 | 530  | 284  |
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| 96     | 98  | 2 | -98  | 609  | 74  | 6 | 2 | 582  | 320  |
| 98     | 100 | 2 | -103 | 626  | 76  | 6 | 2 | 595  | 329  |
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| 112    | 114 | 2 | -138 | 745  | 90  | 6 | 2 | 686  | 392  |
| 114    | 116 | 2 | -143 | 762  | 92  | 6 | 2 | 699  | 401  |
| 116    | 118 | 2 | -148 | 779  | 94  | 6 | 2 | 712  | 410  |
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| 126    | 128 | 2 | -173 | 864  | 104 | 6 | 2 | 777  | 455  |
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| 134    | 136 | 2 | -193 | 932  | 112 | 6 | 2 | 829  | 491  |
| 136    | 138 | 2 | -198 | 949  | 114 | 6 | 2 | 842  | 500  |
| 138    | 140 | 2 | -203 | 966  | 116 | 6 | 2 | 855  | 509  |
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| 142    | 144 | 2 | -213 | 1000 | 120 | 6 | 2 | 881  | 527  |
| 144    | 146 | 2 | -218 | 1017 | 122 | 6 | 2 | 894  | 536  |
| 146    | 148 | 2 | -223 | 1034 | 124 | 6 | 2 | 907  | 545  |
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| 150    | 152 | 2 | -233 | 1068 | 128 | 6 | 2 | 933  | 563  |
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| 158    | 160 | 2 | -253 | 1136 | 136 | 6 | 2 | 985  | 599  |
| 160    | 162 | 2 | -258 | 1153 | 138 | 6 | 2 | 998  | 608  |
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| 174    | 176 | 2 | -293 | 1272 | 152 | 6 | 2 | 1089 | 671  |
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| 184    | 186 | 2 | -318 | 1357 | 162 | 6 | 2 | 1154 | 716  |
| 186    | 188 | 2 | -323 | 1374 | 164 | 6 | 2 | 1167 | 725  |
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| 190    | 192 | 2 | -333 | 1408 | 168 | 6 | 2 | 1193 | 743  |
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| 194    | 196 | 2 | -343 | 1442 | 172 | 6 | 2 | 1219 | 761  |
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| 202    | 204 | 2 | -363 | 1510 | 180 | 6 | 2 | 1271 | 797  |
| 204    | 206 | 2 | -368 | 1527 | 182 | 6 | 2 | 1284 | 806  |
| 206    | 208 | 2 | -373 | 1544 | 184 | 6 | 2 | 1297 | 815  |
| 208    | 210 | 2 | -378 | 1561 | 186 | 6 | 2 | 1310 | 824  |
| 210    | 212 | 2 | -383 | 1578 | 188 | 6 | 2 | 1323 | 833  |
| 212    | 214 | 2 | -388 | 1595 | 190 | 6 | 2 | 1336 | 842  |
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| 216    | 218 | 2 | -398 | 1629 | 194 | 6 | 2 | 1362 | 860  |
| 218    | 220 | 2 | -403 | 1646 | 196 | 6 | 2 | 1375 | 869  |
| 220    | 222 | 2 | -408 | 1663 | 198 | 6 | 2 | 1388 | 878  |
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| 252    | 254 | 2 | -488 | 1935 | 230 | 6 | 2 | 1596 | 1022 |
| 254    | 256 | 2 | -493 | 1952 | 232 | 6 | 2 | 1609 | 1031 |
| 256    | 258 | 2 | -498 | 1969 | 234 | 6 | 2 | 1622 | 1040 |
| 258    | 260 | 2 | -503 | 1986 | 236 | 6 | 2 | 1635 | 1049 |
| 260    | 262 | 2 | -508 | 2003 | 238 | 6 | 2 | 1648 | 1058 |
| 262    | 264 | 2 | -513 | 2020 | 240 | 6 | 2 | 1661 | 1067 |
| 264    | 266 | 2 | -518 | 2037 | 242 | 6 | 2 | 1674 | 1076 |
| 266    | 268 | 2 | -523 | 2054 | 244 | 6 | 2 | 1687 | 1085 |
| 268    | 270 | 2 | -528 | 2071 | 246 | 6 | 2 | 1700 | 1094 |
| 270    | 272 | 2 | -533 | 2088 | 248 | 6 | 2 | 1713 | 1103 |
| 272    | 274 | 2 | -538 | 2105 | 250 | 6 | 2 | 1726 | 1112 |
| 274    | 276 | 2 | -543 | 2122 | 252 | 6 | 2 | 1739 | 1121 |
| 276    | 278 | 2 | -548 | 2139 | 254 | 6 | 2 | 1752 | 1130 |
| 278    | 280 | 2 | -553 | 2156 | 256 | 6 | 2 | 1765 | 1139 |
| 280    | 282 | 2 | -558 | 2173 | 258 | 6 | 2 | 1778 | 1148 |
| 282    | 284 | 2 | -563 | 2190 | 260 | 6 | 2 | 1791 | 1157 |
| 284    | 286 | 2 | -568 | 2207 | 262 | 6 | 2 | 1804 | 1166 |
| 286    | 288 | 2 | -573 | 2224 | 264 | 6 | 2 | 1817 | 1175 |
| 288    | 290 | 2 | -578 | 2241 | 266 | 6 | 2 | 1830 | 1184 |
| 290    | 292 | 2 | -583 | 2258 | 268 | 6 | 2 | 1843 | 1193 |
| 292    | 294 | 2 | -588 | 2275 | 270 | 6 | 2 | 1856 | 1202 |
| 294    | 296 | 2 | -593 | 2292 | 272 | 6 | 2 | 1869 | 1211 |
| 296    | 298 | 2 | -598 | 2309 | 274 | 6 | 2 | 1882 | 1220 |
| 298    | 300 | 2 | -603 | 2326 | 276 | 6 | 2 | 1895 | 1229 |
| 300    | 302 | 2 | -608 | 2343 | 278 | 6 | 2 | 1908 | 1238 |
| 302    | 304 | 2 | -613 | 2360 | 280 | 6 | 2 | 1921 | 1247 |
| 304    | 306 | 2 | -618 | 2377 | 282 | 6 | 2 | 1934 | 1256 |
| 306    | 308 | 2 | -623 | 2394 | 284 | 6 | 2 | 1947 | 1265 |
| 308    | 310 | 2 | -628 | 2411 | 286 | 6 | 2 | 1960 | 1274 |
| 310    | 312 | 2 | -633 | 2428 | 288 | 6 | 2 | 1973 | 1283 |
| 312    | 314 | 2 | -638 | 2445 | 290 | 6 | 2 | 1986 | 1292 |
| 314    | 316 | 2 | -643 | 2462 | 292 | 6 | 2 | 1999 | 1301 |
| 316    | 318 | 2 | -648 | 2479 | 294 | 6 | 2 | 2012 | 1310 |
| 318    | 320 | 2 | -653 | 2496 | 296 | 6 | 2 | 2025 |      |

CREATED AND CALCULATED STRUCTURE FACTORS FOR DRE

| M  | N  | L | FC  | EC   | H   | K  | L | FO  | FC   | H   | K  | L | FO  | FC   | M  | N  | L | FC  | EC   | H   | K  | L | FO  | FC   |
|----|----|---|-----|------|-----|----|---|-----|------|-----|----|---|-----|------|----|----|---|-----|------|-----|----|---|-----|------|
| -1 | 10 | 2 | 21  | 13   | -13 | 12 | 2 | 47  | -40  | -13 | 12 | 2 | 31  | -33  | -1 | 10 | 2 | 21  | 13   | -13 | 12 | 2 | 31  | -33  |
| -4 | 10 | 2 | 25  | 35   | -13 | 12 | 2 | 32  | 36   | -13 | 12 | 2 | 35  | -41  | -4 | 10 | 2 | 25  | 35   | -13 | 12 | 2 | 35  | -41  |
| -2 | 10 | 2 | 53  | -61  | -11 | 12 | 2 | 91  | -85  | -11 | 12 | 2 | 71  | -70  | -2 | 10 | 2 | 53  | -61  | -11 | 12 | 2 | 71  | -70  |
| -1 | 10 | 2 | 63  | -82  | -6  | 12 | 2 | 96  | 41   | -6  | 12 | 2 | 105 | -88  | -1 | 10 | 2 | 63  | -82  | -6  | 12 | 2 | 105 | -88  |
| 1  | 10 | 2 | 25  | -35  | -5  | 12 | 2 | 35  | -41  | -5  | 12 | 2 | 100 | -60  | 1  | 10 | 2 | 25  | -35  | -5  | 12 | 2 | 100 | -60  |
| 3  | 10 | 2 | 32  | -190 | -3  | 12 | 2 | 28  | -127 | -3  | 12 | 2 | 120 | -113 | 3  | 10 | 2 | 32  | -190 | -3  | 12 | 2 | 120 | -113 |
| 4  | 10 | 2 | 81  | -190 | -2  | 12 | 2 | 55  | 151  | -2  | 12 | 2 | 120 | -113 | 4  | 10 | 2 | 81  | -190 | -2  | 12 | 2 | 120 | -113 |
| 5  | 10 | 2 | 152 | 147  | -1  | 12 | 2 | 53  | -43  | -1  | 12 | 2 | 120 | -113 | 5  | 10 | 2 | 152 | 147  | -1  | 12 | 2 | 120 | -113 |
| 6  | 10 | 2 | 149 | -154 | 0   | 12 | 2 | 101 | -106 | 0   | 12 | 2 | 120 | -113 | 6  | 10 | 2 | 149 | -154 | 0   | 12 | 2 | 120 | -113 |
| 7  | 10 | 2 | 100 | -109 | 1   | 12 | 2 | 120 | -110 | 1   | 12 | 2 | 120 | -110 | 7  | 10 | 2 | 100 | -109 | 1   | 12 | 2 | 120 | -110 |
| 8  | 10 | 2 | 44  | -62  | 2   | 12 | 2 | 126 | -49  | 2   | 12 | 2 | 126 | -49  | 8  | 10 | 2 | 44  | -62  | 2   | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 65  | -63  | 5   | 12 | 2 | 109 | 104  | 5   | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 65  | -63  | 5   | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 27  | 22   | 5   | 12 | 2 | 48  | 104  | 5   | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 27  | 22   | 5   | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 07  | -36  | 7   | 12 | 2 | 81  | -79  | 7   | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 07  | -36  | 7   | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 25  | -55  | -3  | 12 | 2 | 50  | -73  | -3  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 25  | -55  | -3  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 79  | -47  | 0   | 12 | 2 | 96  | 91   | 0   | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 79  | -47  | 0   | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 20  | -17  | 10  | 12 | 2 | 31  | -38  | 10  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 20  | -17  | 10  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 70  | -17  | 12  | 12 | 2 | 99  | -65  | 12  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 70  | -17  | 12  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 29  | 125  | -13 | 12 | 2 | 174 | -79  | -13 | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 29  | 125  | -13 | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 164 | -175 | -10 | 12 | 2 | 109 | 113  | -10 | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 164 | -175 | -10 | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 32  | -125 | -10 | 12 | 2 | 126 | -49  | -10 | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 32  | -125 | -10 | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 139 | 149  | -7  | 12 | 2 | 126 | -49  | -7  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 139 | 149  | -7  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 31  | 164  | -7  | 12 | 2 | 126 | -49  | -7  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 31  | 164  | -7  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 74  | -44  | -6  | 12 | 2 | 193 | 178  | -6  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 74  | -44  | -6  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 67  | -77  | -5  | 12 | 2 | 193 | 178  | -5  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 67  | -77  | -5  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 60  | -40  | -5  | 12 | 2 | 193 | 178  | -5  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 60  | -40  | -5  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 20  | -22  | -2  | 12 | 2 | 23  | -142 | -2  | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 20  | -22  | -2  | 12 | 2 | 126 | -49  |
| 11 | 10 | 2 | 20  | -22  | -10 | 12 | 2 | 23  | 39   | -10 | 12 | 2 | 126 | -49  | 11 | 10 | 2 | 20  | -22  | -10 | 12 | 2 | 126 | -49  |

UNRECOVERED AND CALCULATED STRUCTURE FACTORS FOR DJR1

| PAGE |  | A |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  | H |  | FC |  | FO |  | L |  | K |  |
|------|--|---|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|---|--|----|--|----|--|---|--|---|--|
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## OBSERVED AND CALC/LATF STRUCTURE FACTORS FOR DJR1

PAGE 21

| M   | N  | I | FO  | FC   | M   | K  | L | FO  | FC   | M  | K  | L | FO  | FC   | M  | K  | L | FO | FC  | M  | K  | L | FO | FC  |
|-----|----|---|-----|------|-----|----|---|-----|------|----|----|---|-----|------|----|----|---|----|-----|----|----|---|----|-----|
| -2  | 1  | 1 | 48  | -51  | 11  | 12 | 0 | 35  | 29   | -3 | 10 | 0 | 32  | 71   | 7  | 12 | 0 | 22 | -43 | 7  | 12 | 0 | 22 | -43 |
| 1   | 2  | 1 | 34  | -31  | -12 | 3  | 0 | 14  | -154 | 3  | 10 | 0 | 47  | -40  | 9  | 13 | 0 | 23 | 28  | 9  | 13 | 0 | 23 | 28  |
| 2   | 3  | 1 | 74  | 73   | -12 | 4  | 0 | 62  | 66   | 4  | 10 | 0 | 26  | -27  | -8 | 13 | 0 | 30 | 55  | -8 | 13 | 0 | 30 | 55  |
| 3   | 4  | 1 | 94  | -95  | -8  | 5  | 0 | 29  | 63   | 5  | 10 | 0 | 41  | 81   | -7 | 13 | 0 | 34 | -61 | -7 | 13 | 0 | 34 | -61 |
| 4   | 5  | 1 | 66  | -71  | -7  | 6  | 0 | 19  | -20  | 6  | 10 | 0 | 80  | -101 | -6 | 13 | 0 | 40 | -50 | -6 | 13 | 0 | 40 | -50 |
| 5   | 6  | 1 | 24  | 22   | -6  | 7  | 0 | 38  | -42  | -4 | 10 | 0 | 10  | 95   | -5 | 13 | 0 | 29 | -48 | -5 | 13 | 0 | 29 | -48 |
| 6   | 7  | 1 | 47  | -42  | -5  | 8  | 0 | 19  | 20   | -2 | 10 | 0 | 30  | -35  | -2 | 13 | 0 | 29 | -34 | -2 | 13 | 0 | 29 | -34 |
| 10  | 11 | 1 | 34  | -39  | -4  | 9  | 0 | 35  | -48  | 1  | 10 | 0 | 10  | -35  | 1  | 13 | 0 | 18 | 0   | 1  | 13 | 0 | 18 | 0   |
| 11  | 12 | 1 | 44  | -41  | -3  | 10 | 0 | 35  | -48  | -1 | 11 | 0 | 40  | -53  | 2  | 13 | 0 | 33 | 4   | 2  | 13 | 0 | 33 | 4   |
| -12 | 13 | 1 | 44  | 30   | -2  | 11 | 0 | 33  | -46  | -1 | 11 | 0 | 36  | -42  | 3  | 13 | 0 | 20 | 3   | -1 | 13 | 0 | 20 | 3   |
| -13 | 14 | 1 | 34  | 43   | -1  | 12 | 0 | 25  | -15  | -1 | 11 | 0 | 26  | -45  | 4  | 13 | 0 | 35 | -53 | -1 | 13 | 0 | 35 | -53 |
| -14 | 15 | 1 | 72  | -79  | 0   | 13 | 0 | 81  | 76   | -2 | 11 | 0 | 40  | -53  | 5  | 13 | 0 | 35 | -53 | 5  | 13 | 0 | 35 | -53 |
| -15 | 16 | 1 | 34  | -26  | 1   | 14 | 0 | 72  | 77   | -1 | 11 | 0 | 42  | -47  | 6  | 13 | 0 | 25 | 43  | 6  | 13 | 0 | 25 | 43  |
| -16 | 17 | 1 | 97  | -97  | 2   | 15 | 0 | 105 | -105 | 2  | 11 | 0 | 34  | -61  | 7  | 13 | 0 | 17 | 28  | 7  | 13 | 0 | 17 | 28  |
| -17 | 18 | 1 | 35  | 27   | 3   | 16 | 0 | 50  | -50  | 3  | 11 | 0 | 32  | -51  | -9 | 14 | 0 | 50 | -51 | -9 | 14 | 0 | 50 | -51 |
| -18 | 19 | 1 | 98  | -80  | 4   | 17 | 0 | 76  | -85  | 4  | 11 | 0 | 32  | -51  | -8 | 14 | 0 | 40 | -56 | -8 | 14 | 0 | 40 | -56 |
| -19 | 20 | 1 | 82  | -80  | 5   | 18 | 0 | 59  | -65  | 5  | 11 | 0 | 35  | -45  | -7 | 14 | 0 | 32 | -46 | -7 | 14 | 0 | 32 | -46 |
| -20 | 21 | 1 | 159 | 16   | 7   | 19 | 0 | 27  | -30  | 6  | 11 | 0 | 35  | -45  | -6 | 14 | 0 | 30 | -34 | -6 | 14 | 0 | 30 | -34 |
| -21 | 22 | 1 | 127 | -16  | 10  | 20 | 0 | 24  | -77  | 10 | 11 | 0 | 28  | -31  | -3 | 14 | 0 | 18 | -31 | -3 | 14 | 0 | 18 | -31 |
| -22 | 23 | 1 | 127 | -16  | 11  | 21 | 0 | 27  | -31  | 11 | 11 | 0 | 32  | -52  | -2 | 14 | 0 | 23 | -52 | -2 | 14 | 0 | 23 | -52 |
| -23 | 24 | 1 | 112 | -16  | -11 | 22 | 0 | 20  | 22   | -7 | 12 | 0 | 31  | -52  | -1 | 14 | 0 | 23 | -52 | -1 | 14 | 0 | 23 | -52 |
| -24 | 25 | 1 | 77  | -16  | -10 | 23 | 0 | 46  | -37  | -5 | 12 | 0 | 37  | -70  | 0  | 14 | 0 | 33 | -70 | 0  | 14 | 0 | 33 | -70 |
| -25 | 26 | 1 | 90  | -95  | -9  | 24 | 0 | 28  | -37  | -4 | 12 | 0 | 29  | -72  | 2  | 14 | 0 | 39 | -51 | 2  | 14 | 0 | 39 | -51 |
| -26 | 27 | 1 | 104 | -104 | -7  | 25 | 0 | 40  | -33  | -3 | 12 | 0 | 29  | -72  | 4  | 14 | 0 | 39 | -51 | 4  | 14 | 0 | 39 | -51 |
| -27 | 28 | 1 | 130 | -120 | -6  | 26 | 0 | 47  | -38  | -2 | 12 | 0 | 29  | -72  | 5  | 14 | 0 | 37 | -45 | -2 | 14 | 0 | 37 | -45 |
| -28 | 29 | 1 | 71  | -66  | -5  | 27 | 0 | 70  | -78  | -1 | 12 | 0 | 67  | -141 | 6  | 14 | 0 | 49 | -45 | -1 | 14 | 0 | 49 | -45 |
| -29 | 30 | 1 | 98  | -84  | -4  | 28 | 0 | 58  | -81  | 0  | 12 | 0 | 100 | -124 | 7  | 14 | 0 | 34 | -43 | 0  | 14 | 0 | 34 | -43 |
| -30 | 31 | 1 | 29  | -81  | -3  | 29 | 0 | 173 | -155 | 1  | 12 | 0 | 59  | -70  | 8  | 14 | 0 | 34 | -43 | 1  | 14 | 0 | 34 | -43 |
| -31 | 32 | 1 | 101 | -95  | -2  | 30 | 0 | 169 | -155 | 2  | 12 | 0 | 33  | -72  | -4 | 15 | 0 | 33 | -40 | -4 | 15 | 0 | 33 | -40 |
| -32 | 33 | 1 | 101 | -95  | -1  | 31 | 0 | 169 | -155 | 3  | 12 | 0 | 33  | -72  | -2 | 15 | 0 | 29 | -33 | 3  | 15 | 0 | 29 | -33 |
| -33 | 34 | 1 | 140 | -140 | -1  | 32 | 0 | 169 | -155 | 4  | 12 | 0 | 33  | -72  | 0  | 15 | 0 | 27 | -33 | 4  | 15 | 0 | 27 | -33 |
| -34 | 35 | 1 | 140 | -140 | 0   | 33 | 0 | 169 | -155 | 4  | 12 | 0 | 33  | -72  | -2 | 15 | 0 | 27 | -33 | 4  | 15 | 0 | 27 | -33 |

| PAGE 22                                             |    |   |    |     |     |   |   |     |      |    |   |   |     |
|-----------------------------------------------------|----|---|----|-----|-----|---|---|-----|------|----|---|---|-----|
| CROSSOVER AND CALCULATED STRUCTURE FACTORS FOR DJR1 |    |   |    |     |     |   |   |     |      |    |   |   |     |
| L                                                   | M  | L | F0 | FC  | H   | K | L | F0  | FC   | H  | K | L | F0  |
| 1                                                   | 15 | 1 | 19 | 4   | 5   | 2 | 9 | 57  | 50   | -4 | 4 | 9 | 49  |
| 2                                                   | 15 | 1 | 39 | -27 | 7   | 2 | 9 | 57  | -113 | -2 | 4 | 9 | 64  |
| 3                                                   | 15 | 1 | 25 | -35 | 9   | 2 | 9 | 111 | -113 | -2 | 4 | 9 | 39  |
| 4                                                   | 15 | 1 | 40 | 33  | 10  | 2 | 9 | 143 | 145  | -1 | 4 | 9 | 56  |
| 5                                                   | 15 | 1 | 37 | 110 | 11  | 2 | 9 | 128 | 136  | 1  | 4 | 9 | 31  |
| 6                                                   | 15 | 1 | 47 | 91  | 12  | 2 | 9 | 47  | -55  | 2  | 4 | 9 | 52  |
| 7                                                   | 15 | 1 | 27 | 74  | 11  | 3 | 9 | 33  | 34   | 3  | 4 | 9 | 74  |
| 8                                                   | 15 | 1 | 34 | 63  | -11 | 3 | 9 | 70  | 84   | 4  | 4 | 9 | 45  |
| 9                                                   | 15 | 1 | 34 | 48  | -10 | 3 | 9 | 51  | -12  | 5  | 4 | 9 | 90  |
| 10                                                  | 15 | 1 | 50 | 52  | -7  | 3 | 9 | 45  | -16  | 8  | 4 | 9 | 62  |
| 11                                                  | 15 | 1 | 44 | 20  | -7  | 3 | 9 | 75  | 70   | 8  | 4 | 9 | 111 |
| 12                                                  | 15 | 1 | 44 | 55  | -4  | 3 | 9 | 56  | -15  | 9  | 4 | 9 | 105 |
| 13                                                  | 15 | 1 | 44 | 62  | -3  | 3 | 9 | 44  | -15  | 10 | 4 | 9 | 144 |
| 14                                                  | 15 | 1 | 44 | 21  | -3  | 3 | 9 | 42  | -16  | 7  | 4 | 9 | 81  |
| 15                                                  | 15 | 1 | 44 | 18  | -2  | 3 | 9 | 47  | -17  | 6  | 4 | 9 | 67  |
| 16                                                  | 15 | 1 | 29 | 19  | 1   | 3 | 9 | 52  | -18  | 5  | 4 | 9 | 45  |
| 17                                                  | 15 | 1 | 35 | 26  | 10  | 3 | 9 | 56  | -19  | 8  | 4 | 9 | 53  |
| 18                                                  | 15 | 1 | 32 | 10  | -11 | 3 | 9 | 59  | -20  | 10 | 4 | 9 | 38  |
| 19                                                  | 15 | 1 | 37 | 34  | -10 | 3 | 9 | 94  | -20  | 11 | 4 | 9 | 37  |
| 20                                                  | 15 | 1 | 37 | 31  | -9  | 3 | 9 | 70  | -20  | -1 | 4 | 9 | 64  |
| 21                                                  | 15 | 1 | 37 | 44  | 8   | 3 | 9 | 21  | -21  | 1  | 4 | 9 | 33  |
| 22                                                  | 15 | 1 | 49 | 53  | 11  | 3 | 9 | 27  | -21  | 3  | 4 | 9 | 20  |
| 23                                                  | 15 | 1 | 42 | 53  | -11 | 4 | 9 | 24  | -21  | 4  | 4 | 9 | 30  |
| 24                                                  | 15 | 1 | 41 | 27  | -11 | 4 | 9 | 25  | -21  | 5  | 4 | 9 | 40  |
| 25                                                  | 15 | 1 | 41 | 61  | -10 | 4 | 9 | 27  | -21  | 6  | 4 | 9 | 35  |
| 26                                                  | 15 | 1 | 38 | 61  | -9  | 4 | 9 | 18  | -21  | 7  | 4 | 9 | 54  |
| 27                                                  | 15 | 1 | 38 | 19  | -7  | 4 | 9 | 21  | -22  | 8  | 4 | 9 | 37  |
| 28                                                  | 15 | 1 | 26 | 76  | -6  | 4 | 9 | 79  | -22  | 9  | 4 | 9 | 38  |
| 29                                                  | 15 | 1 | 17 | 68  | -5  | 4 | 9 | 38  | -21  | 10 | 4 | 9 | 23  |
| 30                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 11 | 4 | 9 | 8   |
| 31                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 12 | 4 | 9 | 8   |
| 32                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 13 | 4 | 9 | 8   |
| 33                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 14 | 4 | 9 | 8   |
| 34                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 15 | 4 | 9 | 8   |
| 35                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 16 | 4 | 9 | 8   |
| 36                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 17 | 4 | 9 | 8   |
| 37                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 18 | 4 | 9 | 8   |
| 38                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 19 | 4 | 9 | 8   |
| 39                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 20 | 4 | 9 | 8   |
| 40                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 21 | 4 | 9 | 8   |
| 41                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 22 | 4 | 9 | 8   |
| 42                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 23 | 4 | 9 | 8   |
| 43                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 24 | 4 | 9 | 8   |
| 44                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 25 | 4 | 9 | 8   |
| 45                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 26 | 4 | 9 | 8   |
| 46                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 27 | 4 | 9 | 8   |
| 47                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 28 | 4 | 9 | 8   |
| 48                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 29 | 4 | 9 | 8   |
| 49                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 30 | 4 | 9 | 8   |
| 50                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 31 | 4 | 9 | 8   |
| 51                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 32 | 4 | 9 | 8   |
| 52                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 33 | 4 | 9 | 8   |
| 53                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 34 | 4 | 9 | 8   |
| 54                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 35 | 4 | 9 | 8   |
| 55                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 36 | 4 | 9 | 8   |
| 56                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 37 | 4 | 9 | 8   |
| 57                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 38 | 4 | 9 | 8   |
| 58                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 39 | 4 | 9 | 8   |
| 59                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 40 | 4 | 9 | 8   |
| 60                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 41 | 4 | 9 | 8   |
| 61                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 42 | 4 | 9 | 8   |
| 62                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 43 | 4 | 9 | 8   |
| 63                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 44 | 4 | 9 | 8   |
| 64                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 45 | 4 | 9 | 8   |
| 65                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 46 | 4 | 9 | 8   |
| 66                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 47 | 4 | 9 | 8   |
| 67                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 48 | 4 | 9 | 8   |
| 68                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 49 | 4 | 9 | 8   |
| 69                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 50 | 4 | 9 | 8   |
| 70                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 51 | 4 | 9 | 8   |
| 71                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 52 | 4 | 9 | 8   |
| 72                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 53 | 4 | 9 | 8   |
| 73                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 54 | 4 | 9 | 8   |
| 74                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 55 | 4 | 9 | 8   |
| 75                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 56 | 4 | 9 | 8   |
| 76                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 57 | 4 | 9 | 8   |
| 77                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 58 | 4 | 9 | 8   |
| 78                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 59 | 4 | 9 | 8   |
| 79                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 60 | 4 | 9 | 8   |
| 80                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 61 | 4 | 9 | 8   |
| 81                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 62 | 4 | 9 | 8   |
| 82                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 63 | 4 | 9 | 8   |
| 83                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 64 | 4 | 9 | 8   |
| 84                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 65 | 4 | 9 | 8   |
| 85                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 66 | 4 | 9 | 8   |
| 86                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 67 | 4 | 9 | 8   |
| 87                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 68 | 4 | 9 | 8   |
| 88                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 69 | 4 | 9 | 8   |
| 89                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 70 | 4 | 9 | 8   |
| 90                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 71 | 4 | 9 | 8   |
| 91                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 72 | 4 | 9 | 8   |
| 92                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 73 | 4 | 9 | 8   |
| 93                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 74 | 4 | 9 | 8   |
| 94                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 75 | 4 | 9 | 8   |
| 95                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 76 | 4 | 9 | 8   |
| 96                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 77 | 4 | 9 | 8   |
| 97                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 78 | 4 | 9 | 8   |
| 98                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 79 | 4 | 9 | 8   |
| 99                                                  | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 80 | 4 | 9 | 8   |
| 100                                                 | 15 | 1 | 17 | 14  | -5  | 4 | 9 | 38  | -21  | 81 | 4 | 9 | 8   |

## PRESERVED AND CALCULATED STRUCTURE FACTORS FOR DQRI

| PAGE 29 |   |   |    |     |     |   |   |    |     |
|---------|---|---|----|-----|-----|---|---|----|-----|
| H       | K | L | FO | FC  | H   | K | L | FO | FC  |
| 4       | 7 | 9 | 54 | -54 | 4   | 7 | 9 | 27 | -29 |
| 5       | 7 | 9 | 52 | -52 | 5   | 7 | 9 | 21 | -23 |
| 6       | 7 | 9 | 50 | -50 | 6   | 7 | 9 | 21 | -23 |
| 7       | 7 | 9 | 48 | -48 | 7   | 7 | 9 | 21 | -23 |
| 8       | 7 | 9 | 46 | -46 | 8   | 7 | 9 | 21 | -23 |
| 9       | 7 | 9 | 44 | -44 | 9   | 7 | 9 | 21 | -23 |
| 10      | 7 | 9 | 42 | -42 | 10  | 7 | 9 | 21 | -23 |
| 11      | 7 | 9 | 40 | -40 | 11  | 7 | 9 | 21 | -23 |
| 12      | 7 | 9 | 38 | -38 | 12  | 7 | 9 | 21 | -23 |
| 13      | 7 | 9 | 36 | -36 | 13  | 7 | 9 | 21 | -23 |
| 14      | 7 | 9 | 34 | -34 | 14  | 7 | 9 | 21 | -23 |
| 15      | 7 | 9 | 32 | -32 | 15  | 7 | 9 | 21 | -23 |
| 16      | 7 | 9 | 30 | -30 | 16  | 7 | 9 | 21 | -23 |
| 17      | 7 | 9 | 28 | -28 | 17  | 7 | 9 | 21 | -23 |
| 18      | 7 | 9 | 26 | -26 | 18  | 7 | 9 | 21 | -23 |
| 19      | 7 | 9 | 24 | -24 | 19  | 7 | 9 | 21 | -23 |
| 20      | 7 | 9 | 22 | -22 | 20  | 7 | 9 | 21 | -23 |
| 21      | 7 | 9 | 20 | -20 | 21  | 7 | 9 | 21 | -23 |
| 22      | 7 | 9 | 18 | -18 | 22  | 7 | 9 | 21 | -23 |
| 23      | 7 | 9 | 16 | -16 | 23  | 7 | 9 | 21 | -23 |
| 24      | 7 | 9 | 14 | -14 | 24  | 7 | 9 | 21 | -23 |
| 25      | 7 | 9 | 12 | -12 | 25  | 7 | 9 | 21 | -23 |
| 26      | 7 | 9 | 10 | -10 | 26  | 7 | 9 | 21 | -23 |
| 27      | 7 | 9 | 8  | -8  | 27  | 7 | 9 | 21 | -23 |
| 28      | 7 | 9 | 6  | -6  | 28  | 7 | 9 | 21 | -23 |
| 29      | 7 | 9 | 4  | -4  | 29  | 7 | 9 | 21 | -23 |
| 30      | 7 | 9 | 2  | -2  | 30  | 7 | 9 | 21 | -23 |
| 31      | 7 | 9 | 0  | 0   | 31  | 7 | 9 | 21 | -23 |
| 32      | 7 | 9 | 0  | 0   | 32  | 7 | 9 | 21 | -23 |
| 33      | 7 | 9 | 0  | 0   | 33  | 7 | 9 | 21 | -23 |
| 34      | 7 | 9 | 0  | 0   | 34  | 7 | 9 | 21 | -23 |
| 35      | 7 | 9 | 0  | 0   | 35  | 7 | 9 | 21 | -23 |
| 36      | 7 | 9 | 0  | 0   | 36  | 7 | 9 | 21 | -23 |
| 37      | 7 | 9 | 0  | 0   | 37  | 7 | 9 | 21 | -23 |
| 38      | 7 | 9 | 0  | 0   | 38  | 7 | 9 | 21 | -23 |
| 39      | 7 | 9 | 0  | 0   | 39  | 7 | 9 | 21 | -23 |
| 40      | 7 | 9 | 0  | 0   | 40  | 7 | 9 | 21 | -23 |
| 41      | 7 | 9 | 0  | 0   | 41  | 7 | 9 | 21 | -23 |
| 42      | 7 | 9 | 0  | 0   | 42  | 7 | 9 | 21 | -23 |
| 43      | 7 | 9 | 0  | 0   | 43  | 7 | 9 | 21 | -23 |
| 44      | 7 | 9 | 0  | 0   | 44  | 7 | 9 | 21 | -23 |
| 45      | 7 | 9 | 0  | 0   | 45  | 7 | 9 | 21 | -23 |
| 46      | 7 | 9 | 0  | 0   | 46  | 7 | 9 | 21 | -23 |
| 47      | 7 | 9 | 0  | 0   | 47  | 7 | 9 | 21 | -23 |
| 48      | 7 | 9 | 0  | 0   | 48  | 7 | 9 | 21 | -23 |
| 49      | 7 | 9 | 0  | 0   | 49  | 7 | 9 | 21 | -23 |
| 50      | 7 | 9 | 0  | 0   | 50  | 7 | 9 | 21 | -23 |
| 51      | 7 | 9 | 0  | 0   | 51  | 7 | 9 | 21 | -23 |
| 52      | 7 | 9 | 0  | 0   | 52  | 7 | 9 | 21 | -23 |
| 53      | 7 | 9 | 0  | 0   | 53  | 7 | 9 | 21 | -23 |
| 54      | 7 | 9 | 0  | 0   | 54  | 7 | 9 | 21 | -23 |
| 55      | 7 | 9 | 0  | 0   | 55  | 7 | 9 | 21 | -23 |
| 56      | 7 | 9 | 0  | 0   | 56  | 7 | 9 | 21 | -23 |
| 57      | 7 | 9 | 0  | 0   | 57  | 7 | 9 | 21 | -23 |
| 58      | 7 | 9 | 0  | 0   | 58  | 7 | 9 | 21 | -23 |
| 59      | 7 | 9 | 0  | 0   | 59  | 7 | 9 | 21 | -23 |
| 60      | 7 | 9 | 0  | 0   | 60  | 7 | 9 | 21 | -23 |
| 61      | 7 | 9 | 0  | 0   | 61  | 7 | 9 | 21 | -23 |
| 62      | 7 | 9 | 0  | 0   | 62  | 7 | 9 | 21 | -23 |
| 63      | 7 | 9 | 0  | 0   | 63  | 7 | 9 | 21 | -23 |
| 64      | 7 | 9 | 0  | 0   | 64  | 7 | 9 | 21 | -23 |
| 65      | 7 | 9 | 0  | 0   | 65  | 7 | 9 | 21 | -23 |
| 66      | 7 | 9 | 0  | 0   | 66  | 7 | 9 | 21 | -23 |
| 67      | 7 | 9 | 0  | 0   | 67  | 7 | 9 | 21 | -23 |
| 68      | 7 | 9 | 0  | 0   | 68  | 7 | 9 | 21 | -23 |
| 69      | 7 | 9 | 0  | 0   | 69  | 7 | 9 | 21 | -23 |
| 70      | 7 | 9 | 0  | 0   | 70  | 7 | 9 | 21 | -23 |
| 71      | 7 | 9 | 0  | 0   | 71  | 7 | 9 | 21 | -23 |
| 72      | 7 | 9 | 0  | 0   | 72  | 7 | 9 | 21 | -23 |
| 73      | 7 | 9 | 0  | 0   | 73  | 7 | 9 | 21 | -23 |
| 74      | 7 | 9 | 0  | 0   | 74  | 7 | 9 | 21 | -23 |
| 75      | 7 | 9 | 0  | 0   | 75  | 7 | 9 | 21 | -23 |
| 76      | 7 | 9 | 0  | 0   | 76  | 7 | 9 | 21 | -23 |
| 77      | 7 | 9 | 0  | 0   | 77  | 7 | 9 | 21 | -23 |
| 78      | 7 | 9 | 0  | 0   | 78  | 7 | 9 | 21 | -23 |
| 79      | 7 | 9 | 0  | 0   | 79  | 7 | 9 | 21 | -23 |
| 80      | 7 | 9 | 0  | 0   | 80  | 7 | 9 | 21 | -23 |
| 81      | 7 | 9 | 0  | 0   | 81  | 7 | 9 | 21 | -23 |
| 82      | 7 | 9 | 0  | 0   | 82  | 7 | 9 | 21 | -23 |
| 83      | 7 | 9 | 0  | 0   | 83  | 7 | 9 | 21 | -23 |
| 84      | 7 | 9 | 0  | 0   | 84  | 7 | 9 | 21 | -23 |
| 85      | 7 | 9 | 0  | 0   | 85  | 7 | 9 | 21 | -23 |
| 86      | 7 | 9 | 0  | 0   | 86  | 7 | 9 | 21 | -23 |
| 87      | 7 | 9 | 0  | 0   | 87  | 7 | 9 | 21 | -23 |
| 88      | 7 | 9 | 0  | 0   | 88  | 7 | 9 | 21 | -23 |
| 89      | 7 | 9 | 0  | 0   | 89  | 7 | 9 | 21 | -23 |
| 90      | 7 | 9 | 0  | 0   | 90  | 7 | 9 | 21 | -23 |
| 91      | 7 | 9 | 0  | 0   | 91  | 7 | 9 | 21 | -23 |
| 92      | 7 | 9 | 0  | 0   | 92  | 7 | 9 | 21 | -23 |
| 93      | 7 | 9 | 0  | 0   | 93  | 7 | 9 | 21 | -23 |
| 94      | 7 | 9 | 0  | 0   | 94  | 7 | 9 | 21 | -23 |
| 95      | 7 | 9 | 0  | 0   | 95  | 7 | 9 | 21 | -23 |
| 96      | 7 | 9 | 0  | 0   | 96  | 7 | 9 | 21 | -23 |
| 97      | 7 | 9 | 0  | 0   | 97  | 7 | 9 | 21 | -23 |
| 98      | 7 | 9 | 0  | 0   | 98  | 7 | 9 | 21 | -23 |
| 99      | 7 | 9 | 0  | 0   | 99  | 7 | 9 | 21 | -23 |
| 100     | 7 | 9 | 0  | 0   | 100 | 7 | 9 | 21 | -23 |

| COPYING AND CALCULATED STRUCTURE FACTORS FOR DUNE |   |   |    |    |    |   |   |    |    | PAGE 24 |   |   |    |    |     |   |   |    |    |
|---------------------------------------------------|---|---|----|----|----|---|---|----|----|---------|---|---|----|----|-----|---|---|----|----|
| H                                                 | K | L | FO | FC | H  | K | L | FO | FC | H       | K | L | FO | FC | H   | K | L | FO | FC |
| 0                                                 | 0 | 0 | 27 | 29 | 1  | 5 | 0 | 33 | 39 | 1       | 5 | 0 | 33 | 39 | 1   | 5 | 0 | 33 | 39 |
| 1                                                 | 0 | 0 | 27 | 24 | 2  | 5 | 0 | 33 | 29 | 2       | 5 | 0 | 33 | 24 | 3   | 5 | 0 | 33 | 29 |
| 2                                                 | 0 | 0 | 17 | 14 | 3  | 5 | 0 | 26 | 19 | 4       | 5 | 0 | 26 | 14 | 5   | 5 | 0 | 26 | 19 |
| 3                                                 | 0 | 0 | 12 | 11 | 5  | 5 | 0 | 19 | 12 | 7       | 5 | 0 | 19 | 11 | 7   | 5 | 0 | 19 | 12 |
| 4                                                 | 0 | 0 | 8  | 8  | 8  | 5 | 0 | 12 | 8  | 9       | 5 | 0 | 12 | 8  | 10  | 5 | 0 | 12 | 8  |
| 5                                                 | 0 | 0 | 4  | 4  | 10 | 5 | 0 | 8  | 4  | 11      | 5 | 0 | 8  | 4  | 12  | 5 | 0 | 8  | 4  |
| 6                                                 | 0 | 0 | 4  | 4  | 11 | 5 | 0 | 8  | 4  | 13      | 5 | 0 | 8  | 4  | 14  | 5 | 0 | 8  | 4  |
| 7                                                 | 0 | 0 | 4  | 4  | 12 | 5 | 0 | 8  | 4  | 15      | 5 | 0 | 8  | 4  | 16  | 5 | 0 | 8  | 4  |
| 8                                                 | 0 | 0 | 4  | 4  | 13 | 5 | 0 | 8  | 4  | 17      | 5 | 0 | 8  | 4  | 18  | 5 | 0 | 8  | 4  |
| 9                                                 | 0 | 0 | 4  | 4  | 14 | 5 | 0 | 8  | 4  | 19      | 5 | 0 | 8  | 4  | 20  | 5 | 0 | 8  | 4  |
| 10                                                | 0 | 0 | 4  | 4  | 15 | 5 | 0 | 8  | 4  | 21      | 5 | 0 | 8  | 4  | 22  | 5 | 0 | 8  | 4  |
| 11                                                | 0 | 0 | 4  | 4  | 16 | 5 | 0 | 8  | 4  | 23      | 5 | 0 | 8  | 4  | 24  | 5 | 0 | 8  | 4  |
| 12                                                | 0 | 0 | 4  | 4  | 17 | 5 | 0 | 8  | 4  | 25      | 5 | 0 | 8  | 4  | 26  | 5 | 0 | 8  | 4  |
| 13                                                | 0 | 0 | 4  | 4  | 18 | 5 | 0 | 8  | 4  | 27      | 5 | 0 | 8  | 4  | 28  | 5 | 0 | 8  | 4  |
| 14                                                | 0 | 0 | 4  | 4  | 19 | 5 | 0 | 8  | 4  | 29      | 5 | 0 | 8  | 4  | 30  | 5 | 0 | 8  | 4  |
| 15                                                | 0 | 0 | 4  | 4  | 20 | 5 | 0 | 8  | 4  | 31      | 5 | 0 | 8  | 4  | 32  | 5 | 0 | 8  | 4  |
| 16                                                | 0 | 0 | 4  | 4  | 21 | 5 | 0 | 8  | 4  | 33      | 5 | 0 | 8  | 4  | 34  | 5 | 0 | 8  | 4  |
| 17                                                | 0 | 0 | 4  | 4  | 22 | 5 | 0 | 8  | 4  | 35      | 5 | 0 | 8  | 4  | 36  | 5 | 0 | 8  | 4  |
| 18                                                | 0 | 0 | 4  | 4  | 23 | 5 | 0 | 8  | 4  | 37      | 5 | 0 | 8  | 4  | 38  | 5 | 0 | 8  | 4  |
| 19                                                | 0 | 0 | 4  | 4  | 24 | 5 | 0 | 8  | 4  | 39      | 5 | 0 | 8  | 4  | 40  | 5 | 0 | 8  | 4  |
| 20                                                | 0 | 0 | 4  | 4  | 25 | 5 | 0 | 8  | 4  | 41      | 5 | 0 | 8  | 4  | 42  | 5 | 0 | 8  | 4  |
| 21                                                | 0 | 0 | 4  | 4  | 26 | 5 | 0 | 8  | 4  | 43      | 5 | 0 | 8  | 4  | 44  | 5 | 0 | 8  | 4  |
| 22                                                | 0 | 0 | 4  | 4  | 27 | 5 | 0 | 8  | 4  | 45      | 5 | 0 | 8  | 4  | 46  | 5 | 0 | 8  | 4  |
| 23                                                | 0 | 0 | 4  | 4  | 28 | 5 | 0 | 8  | 4  | 47      | 5 | 0 | 8  | 4  | 48  | 5 | 0 | 8  | 4  |
| 24                                                | 0 | 0 | 4  | 4  | 29 | 5 | 0 | 8  | 4  | 49      | 5 | 0 | 8  | 4  | 50  | 5 | 0 | 8  | 4  |
| 25                                                | 0 | 0 | 4  | 4  | 30 | 5 | 0 | 8  | 4  | 51      | 5 | 0 | 8  | 4  | 52  | 5 | 0 | 8  | 4  |
| 26                                                | 0 | 0 | 4  | 4  | 31 | 5 | 0 | 8  | 4  | 53      | 5 | 0 | 8  | 4  | 54  | 5 | 0 | 8  | 4  |
| 27                                                | 0 | 0 | 4  | 4  | 32 | 5 | 0 | 8  | 4  | 55      | 5 | 0 | 8  | 4  | 56  | 5 | 0 | 8  | 4  |
| 28                                                | 0 | 0 | 4  | 4  | 33 | 5 | 0 | 8  | 4  | 57      | 5 | 0 | 8  | 4  | 58  | 5 | 0 | 8  | 4  |
| 29                                                | 0 | 0 | 4  | 4  | 34 | 5 | 0 | 8  | 4  | 59      | 5 | 0 | 8  | 4  | 60  | 5 | 0 | 8  | 4  |
| 30                                                | 0 | 0 | 4  | 4  | 35 | 5 | 0 | 8  | 4  | 61      | 5 | 0 | 8  | 4  | 62  | 5 | 0 | 8  | 4  |
| 31                                                | 0 | 0 | 4  | 4  | 36 | 5 | 0 | 8  | 4  | 63      | 5 | 0 | 8  | 4  | 64  | 5 | 0 | 8  | 4  |
| 32                                                | 0 | 0 | 4  | 4  | 37 | 5 | 0 | 8  | 4  | 65      | 5 | 0 | 8  | 4  | 66  | 5 | 0 | 8  | 4  |
| 33                                                | 0 | 0 | 4  | 4  | 38 | 5 | 0 | 8  | 4  | 67      | 5 | 0 | 8  | 4  | 68  | 5 | 0 | 8  | 4  |
| 34                                                | 0 | 0 | 4  | 4  | 39 | 5 | 0 | 8  | 4  | 69      | 5 | 0 | 8  | 4  | 70  | 5 | 0 | 8  | 4  |
| 35                                                | 0 | 0 | 4  | 4  | 40 | 5 | 0 | 8  | 4  | 71      | 5 | 0 | 8  | 4  | 72  | 5 | 0 | 8  | 4  |
| 36                                                | 0 | 0 | 4  | 4  | 41 | 5 | 0 | 8  | 4  | 73      | 5 | 0 | 8  | 4  | 74  | 5 | 0 | 8  | 4  |
| 37                                                | 0 | 0 | 4  | 4  | 42 | 5 | 0 | 8  | 4  | 75      | 5 | 0 | 8  | 4  | 76  | 5 | 0 | 8  | 4  |
| 38                                                | 0 | 0 | 4  | 4  | 43 | 5 | 0 | 8  | 4  | 77      | 5 | 0 | 8  | 4  | 78  | 5 | 0 | 8  | 4  |
| 39                                                | 0 | 0 | 4  | 4  | 44 | 5 | 0 | 8  | 4  | 79      | 5 | 0 | 8  | 4  | 80  | 5 | 0 | 8  | 4  |
| 40                                                | 0 | 0 | 4  | 4  | 45 | 5 | 0 | 8  | 4  | 81      | 5 | 0 | 8  | 4  | 82  | 5 | 0 | 8  | 4  |
| 41                                                | 0 | 0 | 4  | 4  | 46 | 5 | 0 | 8  | 4  | 83      | 5 | 0 | 8  | 4  | 84  | 5 | 0 | 8  | 4  |
| 42                                                | 0 | 0 | 4  | 4  | 47 | 5 | 0 | 8  | 4  | 85      | 5 | 0 | 8  | 4  | 86  | 5 | 0 | 8  | 4  |
| 43                                                | 0 | 0 | 4  | 4  | 48 | 5 | 0 | 8  | 4  | 87      | 5 | 0 | 8  | 4  | 88  | 5 | 0 | 8  | 4  |
| 44                                                | 0 | 0 | 4  | 4  | 49 | 5 | 0 | 8  | 4  | 89      | 5 | 0 | 8  | 4  | 90  | 5 | 0 | 8  | 4  |
| 45                                                | 0 | 0 | 4  | 4  | 50 | 5 | 0 | 8  | 4  | 91      | 5 | 0 | 8  | 4  | 92  | 5 | 0 | 8  | 4  |
| 46                                                | 0 | 0 | 4  | 4  | 51 | 5 | 0 | 8  | 4  | 93      | 5 | 0 | 8  | 4  | 94  | 5 | 0 | 8  | 4  |
| 47                                                | 0 | 0 | 4  | 4  | 52 | 5 | 0 | 8  | 4  | 95      | 5 | 0 | 8  | 4  | 96  | 5 | 0 | 8  | 4  |
| 48                                                | 0 | 0 | 4  | 4  | 53 | 5 | 0 | 8  | 4  | 97      | 5 | 0 | 8  | 4  | 98  | 5 | 0 | 8  | 4  |
| 49                                                | 0 | 0 | 4  | 4  | 54 | 5 | 0 | 8  | 4  | 99      | 5 | 0 | 8  | 4  | 100 | 5 | 0 | 8  | 4  |
| 50                                                | 0 | 0 | 4  | 4  | 55 | 5 | 0 | 8  | 4  | 101     | 5 | 0 | 8  | 4  | 102 | 5 | 0 | 8  | 4  |
| 51                                                | 0 | 0 | 4  | 4  | 56 | 5 | 0 | 8  | 4  | 103     | 5 | 0 | 8  | 4  | 104 | 5 | 0 | 8  | 4  |
| 52                                                | 0 | 0 | 4  | 4  | 57 | 5 | 0 | 8  | 4  | 105     | 5 | 0 | 8  | 4  | 106 | 5 | 0 | 8  | 4  |
| 53                                                | 0 | 0 | 4  | 4  | 58 | 5 | 0 | 8  | 4  | 107     | 5 | 0 | 8  | 4  | 108 | 5 | 0 | 8  | 4  |
| 54                                                | 0 | 0 | 4  | 4  | 59 | 5 | 0 | 8  | 4  | 109     | 5 | 0 | 8  | 4  | 110 | 5 | 0 | 8  | 4  |
| 55                                                | 0 | 0 | 4  | 4  | 60 | 5 | 0 | 8  | 4  | 111     | 5 | 0 | 8  | 4  | 112 | 5 | 0 | 8  | 4  |
| 56                                                | 0 | 0 | 4  | 4  | 61 | 5 | 0 | 8  | 4  | 113     | 5 | 0 | 8  | 4  | 114 | 5 | 0 | 8  | 4  |
| 57                                                | 0 | 0 | 4  | 4  | 62 | 5 | 0 | 8  | 4  | 115     | 5 | 0 | 8  | 4  | 116 | 5 | 0 | 8  | 4  |
| 58                                                | 0 | 0 | 4  | 4  | 63 | 5 | 0 | 8  | 4  | 117     | 5 | 0 | 8  | 4  | 118 | 5 | 0 | 8  | 4  |
| 59                                                | 0 | 0 | 4  | 4  | 64 | 5 | 0 | 8  | 4  | 119     | 5 | 0 | 8  | 4  | 120 | 5 | 0 | 8  | 4  |
| 60                                                | 0 | 0 | 4  | 4  | 65 | 5 | 0 | 8  | 4  | 121     | 5 | 0 | 8  | 4  | 122 | 5 | 0 | 8  | 4  |
| 61                                                | 0 | 0 | 4  | 4  | 66 | 5 | 0 | 8  | 4  | 123     | 5 | 0 | 8  | 4  | 124 | 5 | 0 | 8  | 4  |
| 62                                                | 0 | 0 | 4  | 4  | 67 | 5 | 0 | 8  | 4  | 125     | 5 | 0 | 8  | 4  | 126 | 5 | 0 | 8  | 4  |
| 63                                                | 0 | 0 | 4  | 4  | 68 | 5 | 0 | 8  | 4  | 127     | 5 | 0 | 8  | 4  | 128 | 5 | 0 | 8  | 4  |
| 64                                                | 0 | 0 | 4  | 4  | 69 | 5 | 0 | 8  | 4  | 129     | 5 | 0 | 8  | 4  | 130 | 5 | 0 | 8  | 4  |
| 65                                                | 0 | 0 | 4  | 4  | 70 | 5 | 0 | 8  | 4  | 131     | 5 | 0 | 8  | 4  | 132 | 5 | 0 | 8  | 4  |
| 66                                                | 0 | 0 | 4  | 4  | 71 | 5 | 0 | 8  | 4  | 133     | 5 | 0 | 8  | 4  | 134 | 5 | 0 | 8  | 4  |
| 67                                                | 0 | 0 | 4  | 4  | 72 | 5 | 0 | 8  | 4  | 135     | 5 | 0 | 8  | 4  | 136 | 5 | 0 | 8  | 4  |
| 68                                                | 0 | 0 | 4  | 4  | 73 | 5 | 0 | 8  | 4  | 137     | 5 | 0 | 8  | 4  | 138 | 5 | 0 | 8  | 4  |
| 69                                                | 0 | 0 | 4  | 4  | 74 | 5 | 0 | 8  | 4  | 139     | 5 | 0 | 8  | 4  | 140 | 5 | 0 | 8  | 4  |
| 70                                                | 0 | 0 | 4  | 4  | 75 | 5 | 0 | 8  | 4  | 141     | 5 | 0 | 8  | 4  | 142 | 5 | 0 | 8  | 4  |
| 71                                                | 0 | 0 | 4  | 4  | 76 | 5 | 0 | 8  | 4  | 143     | 5 | 0 | 8  | 4  | 144 | 5 | 0 | 8  | 4  |
| 72                                                | 0 | 0 | 4  | 4  | 77 | 5 | 0 | 8  | 4  | 145     | 5 | 0 | 8  | 4  | 146 | 5 | 0 | 8  | 4  |
| 73                                                | 0 | 0 | 4  | 4  | 78 | 5 | 0 | 8  | 4  | 147     | 5 | 0 | 8  | 4  | 148 | 5 | 0 | 8  | 4  |
| 74                                                | 0 | 0 | 4  | 4  | 79 | 5 | 0 | 8  | 4  | 149     | 5 | 0 | 8  | 4  | 150 | 5 | 0 | 8  | 4  |
| 75                                                | 0 | 0 | 4  | 4  | 80 | 5 | 0 | 8  | 4  | 151     | 5 | 0 | 8  | 4  | 152 | 5 | 0 | 8  | 4  |
| 76                                                | 0 | 0 | 4  | 4  | 81 | 5 | 0 | 8  | 4  | 153     | 5 | 0 | 8  | 4  | 154 | 5 | 0 | 8  | 4  |
| 77                                                | 0 | 0 | 4  | 4  | 82 | 5 | 0 | 8  | 4  | 155     | 5 | 0 | 8  | 4  | 156 | 5 | 0 | 8  | 4  |
| 78                                                | 0 | 0 | 4  | 4  | 83 | 5 | 0 | 8  | 4  | 157     | 5 | 0 | 8  | 4  | 158 | 5 | 0 | 8  | 4  |
| 79                                                | 0 | 0 | 4  | 4  | 84 | 5 | 0 | 8  | 4  | 159     | 5 | 0 | 8  | 4  | 160 | 5 | 0 | 8  | 4  |
| 80                                                | 0 | 0 | 4  | 4  | 85 | 5 | 0 | 8  | 4  | 161     | 5 | 0 | 8  | 4  | 162 | 5 | 0 | 8  | 4  |
| 81                                                | 0 | 0 | 4  | 4  | 86 | 5 | 0 | 8  | 4  | 163     | 5 | 0 | 8  | 4  | 164 | 5 | 0 | 8  | 4  |
| 82                                                | 0 | 0 | 4  | 4  | 87 | 5 | 0 | 8  | 4  | 165     | 5 | 0 | 8  | 4  | 166 | 5 | 0 | 8  | 4  |
| 83                                                | 0 | 0 | 4  | 4  | 88 | 5 | 0 | 8  | 4  | 167     | 5 | 0 | 8  | 4  | 168 | 5 | 0 | 8  | 4  |
| 84                                                | 0 | 0 | 4  | 4  | 89 | 5 | 0 | 8  | 4  | 169     | 5 | 0 | 8  | 4  | 170 | 5 | 0 | 8  | 4  |
| 85                                                | 0 | 0 | 4  | 4  | 90 | 5 | 0 | 8  | 4  | 171     | 5 | 0 | 8  | 4  | 172 | 5 | 0 | 8  | 4  |
| 86                                                | 0 | 0 | 4  | 4  | 91 | 5 | 0 | 8  | 4  | 173     | 5 | 0 | 8  | 4  | 174 | 5 | 0 | 8  | 4  |
| 87                                                | 0 | 0 | 4  | 4  | 92 | 5 | 0 | 8  | 4  | 175     | 5 | 0 | 8  | 4  | 176 | 5 | 0 | 8  | 4  |
| 88                                                | 0 | 0 | 4  | 4  | 93 | 5 | 0 | 8  | 4  | 177     | 5 | 0 | 8  | 4  | 178 | 5 | 0 | 8  | 4  |
| 89                                                | 0 | 0 | 4  | 4  | 94 | 5 | 0 | 8  | 4  | 179     | 5 | 0 | 8  | 4  | 180 | 5 | 0 | 8  | 4  |
| 90                                                | 0 | 0 | 4  | 4  | 95 | 5 | 0 | 8  | 4  | 181     | 5 | 0 | 8  | 4  | 182 | 5 | 0 | 8  | 4  |
| 91                                                | 0 | 0 | 4  | 4  | 96 | 5 | 0 | 8  | 4  | 183     | 5 | 0 | 8  | 4  | 184 | 5 | 0 | 8  | 4  |
| 92                                                | 0 | 0 | 4  | 4  | 97 | 5 | 0 | 8  | 4  | 185     | 5 | 0 | 8  | 4  | 186 | 5 | 0 | 8  | 4  |
| 93                                                | 0 | 0 | 4  | 4  | 98 | 5 | 0 | 8  | 4  | 187     | 5 | 0 | 8  | 4  | 188 | 5 | 0 | 8  | 4  |
| 94                                                | 0 | 0 | 4  | 4  | 99 | 5 | 0 | 8  | 4  | 189     | 5 | 0 | 8  | 4  | 1   |   |   |    |    |







Appendix DLIST OF PUBLICATIONS

The following is a list of publications that have arisen from the work carried out in this dissertation.

(a) D. J. Robinson, G. W. Harris, J. C. A. Boeyens, and N. J. Coville, "A structural and Kinetic Investigation of the Isomers of  $M_2(CO)_8(Bu^+NC)_2$  ( $M=Ir, Re$ )", J. Chem. Soc., Chem. Commun., in press.

(b) E. A. Darling, D. J. Robinson and N. J. Coville, "The Palladium Catalysed Reactions of  $MnRe(CO)_5$  and Isonitriles and the Crystal and Molecular Structure of  $Mn(CO)_5Re(CO)_4(Bu^+NC)_2$ ", manuscript in preparation.

(c) I. O. Albers, N. J. Coville, D. J. Robinson and E. Singleton, "Substitution Chemistry of  $[CoRu(CO)_2]$  Reactions with Isonitriles", manuscript in preparation.

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