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

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A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science.

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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 $\left[CpRu(CO)_2\right]_2$ 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		iv
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 Rhenium	12
	2.4 The $M_2(CO)_{10}$ (M=Mn, Re) Substitution Reactions	19
	2.5 Isomerisation and Scrambling in Manganese and Rhenium Carbonyl Complexes	26
CHAPTER 3	A Kinetic Study of the Substitution Reactions and Isomerisation of $M_2(CO)_{10}$ 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-$Mn_2(CO)_8(Bu^tNC)_2$	58

		PAGE
	3.4.3 Synthesis of $1,1\text{-}Mn_2(CO)_8(Bu^tNC)_2$	58
	3.4.4 Synthesis of $1,2\text{-}Re_2(CO)_8(Bu^tNC)_2$	59
	3.4.5 Synthesis of $1,1\text{-}Re_2(CO)_8(Bu^tNC)_2$	60
	3.4.6 Isomerisation of $M_2(CO)_8(Bu^tNC)_2$ (M=Mn, Re)	61
CHAPTER 4	Carbonyl Substitution Reactions of the Mixed Metal Dimer $MnRe(CO)_{10}$	63
	4.1 Introduction	63
	4.2 Results and Discussion	68
	4.3 X-Ray Crystallography of $MnRe(CO)_9(Bu^tNC)$	76
	4.4 Discussion	78
	4.5 Conclusions	87
	4.6 Experimental	89
	4.6.1 Synthesis of $MnRe(CO)_{10}$	89
	4.6.2 Substitution Reactions of $MnRe(CO)_{10}$	90
	4.6.3 Synthesis of $Mn(CO)_4(Bu^tNC)Re(CO)_5$	90
	4.6.4 Isomerisation of $MnRe(CO)_9(Bu^tNC)$	90
CHAPTER 5	Substitution Reactions of $[CpRu(CO)_2]_2$	91
	5.1 Introduction	91
	5.2 Results	96

		PAGE
5.3	Conclusions	98
5.4	Experimental	101
5.4.1	General	101
5.4.2	Synthesis of $[CpRu(CO)_2]_2$	101
5.4.3	Synthesis of $Cp_2Ru_2(CO)_3(RNC)$	102
CHAPTER 6	Mixed Metal Trimers $M_2Fe(CO)_{14}$	103
6.1	Introduction	103
6.2	Results and Discussion	106
6.3	Conclusions	111
6.4	Experimental	112
6.4.1	Synthesis of $Fe(CO)_4I_2$	112
6.4.2	Synthesis of $Fe(CO)_3(Bu^tNC)I_2$	112
6.4.3	Synthesis of $Re(CO)_5I$	113
6.4.4	Synthesis of $Mn(CO)_5I$	113
6.4.5	Synthesis of $NaRe(CO)_5$	114
6.4.6	Synthesis of $Na_2Fe(CO)_4$	114
6.4.7	Synthesis of $Na_2Fe(CO)_3(Bu^tNC)$	115
6.4.8	Synthesis of $Re_2Fe(CO)_{14}$	115
6.4.9	Synthesis of $Re_2Fe(CO)_{13}(Bu^tNC)$	117

		PAGE
	6.4.10 Synthesis of $Mn_2Fe(CO)_{14}$	118
	6.4.11 Reaction of $Re_2Fe(CO)_{14}$ and Pr^iNC	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	130
Appendix D	List of Publications	160
LIST OF REFERENCES		161

LIST OF TABLES

		PAGE
Table 2.1	Some Examples of Heteronuclear Dimetallic Carbonyl Complexes	10
Table 2.2	Some Examples of Homonuclear Carbonyl Clusters of the Iron Triad	10
Table 2.3	Some Examples of Heteronuclear Trimetallic Carbonyl Complexes	11
Table 2.4	Some Examples of Heteronuclear Polymetallic Carbonyl Complexes ($n > 4$)	11
Table 2.5	Thermodynamic Activation Parameters for Carbonyl Substitution Reactions of $M(CO)_5X$ (M=Mn,Re; X=Cl,Br,I)	14
Table 3.1	Physical and Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M=Mn,Re; n=1-3)	34
Table 3.2	Infrared Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M=Mn,Re; n=1-3)	35
Table 3.3	Physical and Spectral Data for the Complexes $Re(CO)_{5-n}(Bu^tNC)_nI$ (n=0-2)	36

LIST OF TABLES

		PAGE
Table 2.1	Some Examples of Heteronuclear Dimetallic Carbonyl Complexes	10
Table 2.2	Some Examples of Homonuclear Carbonyl Clusters of the Iron Triad	10
Table 2.3	Some Examples of Heteronuclear Trimetallic Carbonyl Complexes	11
Table 2.4	Some Examples of Heteronuclear Polymetallic Carbonyl Complexes (n > 4)	11
Table 2.5	Thermodynamic Activation Parameters for Carbonyl Substitution Reactions of $M(CO)_5X$ (M=Mn,Re; X=Cl,Br,I)	14
Table 3.1	Physical and Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M=Mn,Re; n=1-3)	34
Table 3.2	Infrared Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M=Mn,Re; n=1-3)	35
Table 3.3	Physical and Spectral Data for the Complexes $Re(CO)_{5-n}(^{n}Bu^tNC)_nI$ (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: $Mn_2(CO)_9(Bu^tNC) \longrightarrow Mn_2(CO)_8(Bu^tNC)_2$	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=Mn,Re) with Bu^tNC using PdO Catalyst	48
Table 4.1	Physical and Spectral Data for the Monosubstituted Metal Dimers $MM'(CO)_9(Bu^tNC)$ (M,M'=Mn,Re)	69
Table 4.2	Physical and Spectral Data for the Complexes $MnRe(CO)_9(RNC)$ ($R=Bu^t, Pr^i$, Xy, Cy)	70
Table 4.3	Kinetic Data for Monosubstitution of $MM'(CO)_{10}$(M,M'=Mn,Re) with Bu^tNC using PdO Catalyst at 25°C	74

		PAGE
Table 4.4	Crystallographic and Physical Data for the Complex $Mn(CO)_5Re(CO)_4(Bu^tNC)$	77
Table 4.5	Fractional Coordinates of Atoms in Molecule 1	80
Table 4.6	Fractional Coordinates of Atoms in Molecule 2	81
Table 4.7	Average Bond Angles for the Molecule $Mn(CO)_5Re(CO)_4(Bu^tNC)$	82
Table 4.8	Average Bond Lengths for the Molecule $Mn(CO)_5Re(CO)_4(Bu^tNC)$	83
Table 4.9	A Comparison of Structural Data for Manganese-Rhenium Dimers	84
Table 4.10	Structural Data for the Complexes $MM'(CO)_{10-n}(RNC)_n$ (M,M'=Mn,Re; n=0.4)	86
Table 5.1	Catalysis of $\left[CpRu(CO)_2\right]_2$ Carbonyl Substitution	99
Table 5.2	Spectral Data for the Complexes $Cp_2Ru_2(CO)_3(RNC)$	100
Table 6.1	Physical and Spectral Data for the Complexes $M_2Fe(CO)_{14}$ (M=Mn,Re) and some Derivatives	107

		PAGE
Table C1	Isotropic Temperature Factors for Methyl Group Protons	131
Table C2	Anisotropic Temperature Factors for Molecule 1	132
Table C3	Anisotropic Temperature Factors for Molecule 2	133
Table C4	Observed and Calculated Structure Factors for $MnRe(CO)_9(Bu^tNC)$	134

LIST OF FIGURES

		PAGE
Figure 3.1	Structural Isomers of the Complex $Mn_2(CO)_8(Bu^tNC)_2$	32
Figure 3.2	Typical Infrared Spectra Recorded During the Reactions of $Mn_2(CO)_9(Bu^tNC)$ and Bu^tNC in the Presence of PdO	41
Figure 3.3	Isomerisation Equilibria for $Mn_2(CO)_8(Bu^tNC)_2$	43
Figure 3.4	Typical Infrared Spectra Recorded During the Isomerisation of 1,1-$Mn_2(CO)_8(Bu^tNC)_2$ to an Equilibrium Mixture of the Structural Isomers of $Mn_2(CO)_8(Bu^tNC)_2$	45
Figure 3.5	Thermodynamic Data for the Isomerisation of $Mn_2(CO)_8(Bu^tNC)_2$	46
Figure 4.1	Molecular Structure of $Mn(CO)_5Re(CO)_4(PR_3)$	65
Figure 4.2	Crystal Structure of $MnRe(CO)_9(Bu^tNC)$	79
Figure C1	Unit Cell Molecular Packing Diagram for $MnRe(CO)_9(Bu^tNC)$	131

LIST OF ABBREVIATIONS AND SYMBOLS

M	central (usually metal) atom in a compound
L	ligand
R	alkyl or aryl group
Me	methyl, CH_3
Et	ethyl, C_2H_5
Pr	propyl, C_3H_7
Bu	butyl, C_4H_9
Ph	phenyl, C_6H_5
Cy	cyclohexyl, C_6H_{11}
Xy	xylyl, 2,6-$Me_2C_6H_3$
o-phen	ortho-phenanthroline
DAB	1,4-diazabutadiene
Cp	cyclopentadienyl, $C_5H_5^-$
Mp	pentamethylcyclopentadienyl, $C_5Me_5^-$
thf	tetrahydrofuran
TLC	thin layer chromatography
ir	infrared
uv	ultra-violet
NMR	nuclear magnetic resonance
ms	mass spectrometry
mpt	melting point
n,i,t	normal, iso, tertiary
o,m,p	ortho, meta, para
N.C.R.L.	National Chemical Research Laboratory
N.P.R.L.	National Physical Research Laboratory
C.S.I.R.	Council for Scientific and Industrial Researc

I. 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 homonuclear dimers $M_2(CO)_{10}$ with isonitriles. 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 3) would involve the generation of kinetic data and and the calculations of rate constants for the catalysed and

non-catalysed reactions of $M_2(CO)_{10-n}(RNC)_n$ (M=Mn,Re;n=0-2) with isonitriles. During the course of this work it was observed that the product of the catalysed reaction between $Mn_2(CO)_9(Bu^tNC)$ and Bu^tNC at room temperature was different to that reported earlier. Closer study showed peaks in the infrared spectrum of the new complex to be common with some of the peaks in the infrared spectra of the reported complex. Further the ^1H NMR spectra gave only one resonance which corresponded to one of the two resonances reported for $Mn_2(CO)_8(Bu^tNC)_2$. Thus the data suggested that only one of the two structural isomers of the complex $Mn_2(CO)_8(Bu^tNC)_2$ that are possible had been selectively synthesized. These observations led to the study of the structural isomerisation of the disubstituted manganese complex and an isomerisation mechanism similar to that proposed in the literature for other related complexes (see later) was proposed. Only one of the analogous disubstituted rhenium dimers had been prepared previously and the second was synthesized indirectly to allow a study of the possible isomerisation of the structural isomers of $Re_2(CO)_8(Bu^tNC)_2$.

The logical extension of the study of the homonuclear dimers was a study of the heteronuclear dimer, $MnRe(CO)_{10}$ which had not been considered previously. Results relating to work on this heteronuclear system are presented in Chapter 4. The mixed metal dimer was synthesised by

literature methods and catalysts were used to prepare a series of monosubstituted complexes, $MnRe(CO)_9(RNC)$. The crystal structure of the monosubstituted complex $MnRe(CO)_9(Bu^tNC)$ was determined to confirm the site of substitution (i.e. on manganese or on rhenium) and allow comparisons with the published data for related complexes. The other structural isomer of $MnRe(CO)_9(Bu^tNC)$ was synthesised indirectly and the possible interconversion of these two isomers was studied at elevated temperatures. New complexes of the type $MnRe(CO)_9(RNC)$, for several alkyl and aryl groups R, were synthesised and fully characterised.

The generality of the potential for the catalysed carbonyl substitution reaction in synthetic organometallic chemistry was exploited and new systems for this type of reaction were considered (Chapters 5 and 6). Catalysts were found useful for the carbonyl substitution reactions of $[CoRu(CO)_2]_2$ with isonitrile and a series of monosubstituted dimers of the formula $Co_2Ru_2(CO)_3(RNC)$ were prepared. The requirements for such substitution reactions on the ruthenium dimer made interesting comparisons with the analogous iron complex.

An improved synthesis of $Re_2Fe(CO)_{14}$ from $Re_2(CO)_{10}$ and $Fe(CO)_5$ was developed (Chapter 6) but this method could not be efficiently extended to the synthesis of $Mn_2Fe(CO)_{14}$ as

literature methods and catalysts were used to prepare a series of monosubstituted complexes, $MnRe(CO)_9(RNC)$. The crystal structure of the monosubstituted complex $MnRe(CO)_9(Bu^tNC)$ was determined to confirm the site of substitution (i.e. on manganese or on rhenium) and allow comparisons with the published data for related complexes. The other structural isomer of $MnRe(CO)_9(Bu^tNC)$ was synthesised indirectly and the possible interconversion of these two isomers was studied at elevated temperatures. New complexes of the type $MnRe(CO)_9(RNC)$, for several alkyl and aryl groups R, were synthesised and fully characterised.

The generality of the potential for the catalysed carbonyl substitution reaction in synthetic organometallic chemistry was exploited and new systems for this type of reaction were considered (Chapters 5 and 6). Catalysts were found useful for the carbonyl substitution reactions of $[CpRu(CO)_2]_2$ with isonitrile and a series of monosubstituted dimers of the formula $Cp_2Ru_2(CO)_3(RNC)$ were prepared. The requirements for such substitution reactions on the ruthenium dimer made interesting comparisons with the analogous iron complex.

An improved synthesis of $Re_2Fe(CO)_{14}$ from $Re_2(CO)_{10}$ and $Fe(CO)_5$ was developed (Chapter 6) but this method could not be efficiently extended to the synthesis of $Mn_2Fe(CO)_{14}$ as

the latter product is unstable in most organic solvents. The first substitution reactions of $Re_2Fe(CO)_{14}$ by isonitrile 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 either 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 D.

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 occuring 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.[1-6] 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 of metal atoms i.e. surfaces. This stepwise approach was proposed by Muetterties and co-workers [4] 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.[7] 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 comprising of two or more metals in a bonding interaction,[8] 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[9] 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 [10] since the discovery of nickel tetracarbonyl in 1890 [11] and iron pentacarbonyl one year later.[12,13] Much more recent are studies of binuclear carbonyl complexes which are the simplest transition metal carbonyl clusters. These binuclear carbonyl clusters* 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) $M_2(CO)_{10}$ (M = Mn, Tc, Re),[14,15] $Co_2(CO)_8$** [16-18] and $Fe_2(CO)_9$ [19-21] or 2) $MnRe(CO)_{10}$ etc. (Table 2.1).

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* For the purposes 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: $Fe_2(CO)_9$ was known as early as 1905 [19] but $Os_8(CO)_{23}$ has only recently been reported. [22] $Fe_2(CO)_9$ was the first metal carbonyl to be the subject of a full X-ray crystal structure investigation [20] and as a very useful source of the unstable species $Fe(CO)_4$ 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 $Fe(CO)_5$ to give $Fe_2(CO)_9$,[23] 2) thermal decomposition of $Fe_2(CO)_9$ to give $Fe_3(CO)_{12}$,[24] 3) carbonylation of $RuCl_3$ to give $Ru_3(CO)_{12}$ [25] and 4) pyrolysis of $Os_3(CO)_{12}$ to give mainly $Os_6(CO)_{18}$.[22] There have been many reviews on the subject of metal carbonyl clusters and examples pertinent to this study include reviews on tetranuclear carbonyl clusters [26] and high nuclearity metal carbonyl clusters.[27]

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 [2,4,6,28] 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 $[AgCo(CO)_4]_4$.[29] 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.[30] 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 Dimetallic Carbonyl Complexes

$MM'(CO)_{10}^-$	(M=Cr, Mo, W; M'= Mn, Re)	(31-37)
$MnFe(CO)_9^-$		(32)
$CoM(CO)_9$	(M=Mn, Tc, Re)	(38-47)
$MnM(CO)_{10}$	(M=Tc, Re)	(37, 39, 48-74)

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

$M_2(CO)_9$	(M=Fe, Ru, Os)	(19, 20, 75-77)
$M_3(CO)_{12}$	(M=Fe, Ru, Os)	(78-83)
$Os_5(CO)_{16}$		(22, 84)
$Os_5(CO)_{15}^{2-}$		(22, 85)
$Os_8(CO)_{23}$		(22)
$Os_8(CO)_{22}^{2-}$		(22)

TABLE 2.3 Some Examples of Heteronuclear Trimetallic Carbonyl Complexes

$M_2M'(CO)_{14}$	(M=Mn,Re: M'=Fe,Ru,Os)	(49,59,86-92)
$MnReFe(CO)_{14}$		(71,59,86)
$Mn_2Pt(CO)_{12}$		(93)
$MFe_2(CO)_{12}^-$	(M=Mn,Tc,Re)	(32,91,94-96)
$MOs_2(CO)_{12}^-$	(M=Mn,Re)	(97)
$Mn_2Au(CO)_{10}^-$		(98)

TABLE 2.4 Some Examples of Heteronuclear Polymetallic Carbonyl Clusters (n⩾ 4)

$Co_nRh_m(CO)_{12}$	(n=1,2,3; m=4-n)	(99-102)
$Ru_3Re(CO)_{16}^-$		(97)
$Fe_4M(CO)_{16}^{2-}$	(M=Pd,Pt)	(103,104)
$Rh_5M(CO)_{15}^-$	(M=Ni,Pt)	(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,[10,107-113] and these mechanisms may be easily distinguished when the stoicheometry 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.[114]

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.[115-120]

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.[125,126] When carbonyl exchange reactions were studied using labelled carbon monoxide (^{14}CO) it was seen that the equatorial carbonyls exchanged more rapidly than the axial carbonyl ligands.[125,127]

TABLE 2.5 Thermodynamic Activation Parameters For Carbonyl Substitution Reactions of $M(CO)_5X$ (M=Mn, Re; X=Cl, Br, I)[a]

COMPLEX	$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	$\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$)
$Mn(CO)_5Cl$	115[b]	66[b]
$Re(CO)_5Cl$	114 (128[c])	26 (73[c])
$Mn(CO)_5Br$	118	64
$Re(CO)_5Br$	123 (123[c])	41 (45[c])
$Mn(CO)_5I$	118[d]	46[d]
$Re(CO)_5I$	133 (113[c])	54 (9[c])

[a] Ref. 121 unless otherwise stated*

[b] Ref. 122

[c] Ref. 123

[d] Ref. 124

* Data in ref. 121 is for monosubstitution of $M(CO)_5X$ by PPh_3

The carbonyl substitution reactions of $Re(CO)_5Br$ and its derivatives $Re(CO)_4LBr$ ($L=PPh_3, NC_5H_5, P(OPh)_3$) were the subject of a series of papers by Brown and co-workers.[128-130] 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 $Mn(CO)_4NO$ with phosphines, phosphites and arsines was shown to occur by an associative mechanism,[131] 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 $MeMn(CO)_5$ with a variety of ligands was seen to occur by methyl migration giving the acetyl product [111,132] and a first-order rate dependence on both reactant concentrations was observed.[133] The reactions of acylmanganese pentacarbonyl $RCOMn(CO)_5$ with PPh_3 or I^- were seen to exhibit a first-order dependence on metal carbonyl [134,135] 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 $[Mn(CO)_5]^-$. [136]

The rate of the carbonyl exchange reaction with labelled CO was found to be much more rapid for $HMn(CO)_5$ than for $Mn_2(CO)_{10}$ and the rate determining step was thought to be carbonyl dissociation.[137] The carbonyl substitution reactions of the hydrides $HM(CO)_5$ (M=Mn,Re) by phosphine have been studied and the rhenium complex shown to be far more inert to substitution than the manganese complex.[138,139] The kinetics of some substitution reactions of radical species have been studied; for example the replacement of L by L' in $\cdot Mn(CO)_4L$ where L,L'=phosphine or phosphite.[140] Recent studies have shown that carbonyl substitution in radicals such as $\cdot Re(CO)_5$ is extremely rapid and occurs by an associative mechanism.[141,142]

The carbonyl substitution reactions of $CpM(CO)_3$ (M=Mn,Tc,Re) were seen to be much slower than the analogous reaction with $CpM(CO)_2$ (M=Co,Rh,Ir) which was shown to proceed by a Sn2 mechanism.[137,143] The carbonyl substitution reaction of $CpMn(CO)_3$ using U.V. irradiation proceeded via a mechanism in which ligand dissociation was the rate determining step.[144] A recent study of the kinetics of the substitution reaction of $(\eta\text{-}MeC_5H_4)Mn(CO)_2L$ (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 S_N2 mechanism

is thought to be the pathway of these substitution reactions,[145] 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 $(PPh_3)AuCo(CO)_4$ than for $(PPh_3)AuMn(CO)_5$.[146]

Other mononuclear metal carbonyls whose substitution reactions have been studied for example the hexacarbonyls $M(CO)_6$ (M=Cr,Mo,W),[109,147-150] 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 dimer carbonyls $M_2(CO)_{10}$(M=Mn,Re) by phosphines and phosphites.[151,152] A study of the substitution reactions of $MnRe(CO)_{10}$ by phosphines and phosphites [52] led to a rate equation of the type:

$$k_{obs} = (k_1 + k_2 [PR_3]) [M_2(CO)_{10}]$$

a rate law which had been demonstrated in substitution reactions of other metal carbonyls.[147,151,153] Scrambling reactions between $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been observed at high temperatures [152] but a more recent

suggests the reaction occurs by two possible pathways [154] which gives a complex rate equation of the type:

$$\text{Rate} = k_2 \left[Mn_2(CO)_{10}\right] \left[Re_2(CO)_{10}\right]$$

$$k_2 = p \,/\, \left[1+qp(CO)^3\right]$$

where p is partial pressure of 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 $Mn_2(CO)_{10}$ [155] or $Re_2(CO)_{10}$ [156] led to a very complex rate equation and the mechanism remains poorly understood.

The reaction of $\left[Re(CO)_4X\right]_2$ (X=halide) with PPh_3 or pyridine obeys a 2nd order rate equation with the rate depending on the basicity of the incoming ligand and only <u>cis</u> - $Re(CO)_4LX$ was formed in the reactions.[157] The analogous reaction between $\left[Mn(CO)_4X\right]_2$ and L (L = pyridine, 8 - picoline, 3-chloropyridine) gave a two term rate equation thought to reflect competing associative and dissociative reaction pathways.[158]

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. $Co_4(CO)_9(\mu\text{-}CO)_3$ [115,116] and $Ir_4(CO)_{12}$ [117-120] and their derivatives provide information which may be important for the interpretation of the $M_2(CO)_{10}$(M=Mn,Re) substitution kinetics and will be mentioned where applicable in this work.

2.4 The $M_2(CO)_{10}$ (M=Mn,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 $M_2(CO)_{10}$ (M=Mn,Re) with phosphines (e.g. PPh_3). Interest in this reaction was initiated by the observation that initial substitution of $M_2(CO)_{10}$ by phosphines or phosphites affected the rate of subsequent substitution reactions [151,156,159,160] and that these ligands directed the second substitution exclusively onto the second metal centre.

Complexes of the type $M_2(CO)_{10}$ (M=Mn,Tc,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.[14,15,161,162] 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,[58,148,163,164] the values that have been accepted $\pm$ 154 kJmol^{-1} (Mn-Mn) and $\pm$ 188 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 $\sigma - \sigma^*$ transition of the metal-metal bond[37,48-50,165] in halogenated organic solvents or in hydrocarbons in the presence of free ligands e.g. phosphine, either mononuclear complexes[166] or substituted dimers are formed.[48,167]

It has been generally accepted, until recently,[168] that the major pathway for the photochemical substitution reaction on $M_2(CO)_{10}$ (M=Mn,Re) involves a radical mechanism in which the first step is homolytic fission of the metal-metal bond.[11,14,16,113,114] A recent publication[168] 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 scission. There has been a great deal more disagreement

about the thermal ligand substitution reaction of $Mn_2(CO)_{10}$. 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 [51,53] 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.[56,59,169] 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

$$M_2(CO)_{10} \longrightarrow M_2(CO)_9 + CO \qquad 2.11$$

$$M_2(CO)_9 + L \longrightarrow M_2(CO)_9 L \qquad 2.12$$

$$M_2(CO)_9 L \longrightarrow M_2(CO)_8 L + CO \qquad 2.13$$

$$M_2(CO)_8 L + L \longrightarrow M_2(CO)_8 L_2 \qquad 2.14$$

SCHEME 2.2

$$M_2(CO)_{10} \longrightarrow 2 \cdot M(CO)_5 \qquad 2.21$$

$$\cdot M(CO)_5 + L \longrightarrow \cdot M(CO)_4 L + CO \qquad 2.22$$

$$\cdot M(CO)_4 L + \cdot M(CO)_5 \longrightarrow M_2(CO)_9 L \qquad 2.23$$

$$2 \cdot M(CO)_4 L \longrightarrow M_2(CO)_8 L_2 \qquad 2.24$$

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. Poë 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.[170] Atwood and others, however, maintained that these reactions (decomposition and substitution) were occuring by different mechanisms [171] and so direct comparisons were not meaningful.

One of the strongest arguments in favour of Poë's mechanism was the observation of the synthesis of the bis-phosphine substituted products very early in the reaction of $Mn_2(CO)_{10}$ with PPh_3[155] or $MnRe(CO)_{10}$ with PPh_3.[51] 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,[52] and that the reaction of $Re_2(CO)_{10}$ with PPh_3 is totally suppressed in the presence of a carbon monoxide atmosphere.

If the mixed metal dimer $MnRe(CO)_{10}$ is considered, at no point in its substitution reactions [51,52] or its thermal decomposition under oxygen[53] 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 (step 2.3.4,5). Independent evidence is available to show that the radicals $\cdot M(CO)_5$ recombine at or near diffusion controlled rates [172,173] yet negligible amounts of the mixed metal dimer $MnRe(CO)_{10}$ are formed on heating a solution of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.[152,171]

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 $^{185}Re_2(CO)_{10}$ and $^{187}Re_2(CO)_{10}$ [174] or $Mn_2(^{12}CO)_{10}$ and $Mn_2(^{13}CO)_{10}$ [175] 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

$$MnRe(CO)_{10} \longrightarrow \cdot Mn(CO)_5 + \cdot Re(CO)_5 \qquad 2.3.1$$

$$\cdot Mn(CO)_5 + L \longrightarrow \cdot Mn(CO)_4L + CO \qquad 2.3.2$$

$$\cdot Re(CO)_5 + L \longrightarrow \cdot Re(CO)_4L + CO \qquad 2.3.3$$

$$\cdot Mn(CO)_5 + \cdot Re(CO)_4L \longrightarrow MnRe(CO)_9L \qquad 2.3.4$$

$$\cdot Mn(CO)_4L + \cdot Re(CO)_5 \longrightarrow MnRe(CO)_9L \qquad 2.3.5$$

$$2\cdot Mn(CO)_5 \longrightarrow Mn_2(CO)_{10} \qquad 2.3.6$$

$$2\cdot Re(CO)_5 \longrightarrow Re_2(CO)_{10} \qquad 2.3.7$$

$$\cdot Mn(CO)_5 + \cdot Mn(CO)_4L \longrightarrow Mn_2(CO)_9L \qquad 2.3.8$$

$$\cdot Re(CO)_5 + \cdot Re(CO)_4L \longrightarrow Re_2(CO)_9L \qquad 2.3.9$$

$$2\cdot Mn(CO)_4L \longrightarrow Mn_2(CO)_8L_2 \qquad 2.3.10$$

$$2\cdot Re(CO)_4L \longrightarrow Re_2(CO)_8L_2 \qquad 2.3.11$$

Thus in the thermal ligand substitution reactions of $M_2(CO)_{10}$ (M=Mn, 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 $Mn(CO)_3LL'X$ (L,L'=phosphine, X=halide) which was thought to occur via ligand (L) dissociation.[176] 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 [177] such as transition metal carbonyl complexes. Due to the quadrupole moment of manganese (^{55}Mn, $I=5/2$) the ^{13}C NMR signals tend to be broad and unresolved [178-182] but may be

sharpened in some cases by isotopic enrichment [179] or by thermal decoupling at lower temperatures.[180] The sharp signals for equatorial and axial carbonyl carbon atoms in $PhCH_2Mn(CO)_5$ (-87^oC), $Re_2(CO)_{10}$ (-60^oC) and $Re(CO)_5Br$ (30^oC) [180] shows no scrambling of ligands is occuring at these temperatures. The ^{13}C NMR spectrum of $MeMn(CO)_5$ and $Mn_2(CO)_{10}$ [178,179] gave only a single broad signal at room temperature and it was uncertain if intramolecular ligand exchange was occuring or if the broadening was just a result of ^{55}Mn-^{13}C spin-spin coupling. When ^{17}O NMR spectra of these two complexes were obtained,[183] 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^oC) no ligand scrambling is occuring in $MeMn(CO)_5$ or $Mn_2(CO)_{10}$ Similarly the ^{17}O NMR spectra at ambient temperatures of $Mn_2(CO)_9(PPh_3)$ [184] and $Mn_2(CO)_8(PPh_3)_2$ [185] implied ligand scrambling was not significant.

Using ^1H NMR spectroscopy the isomerisation of $Mn_2(CO)_7(MeNC)_3$ has been observed, the two signals * clearly resolved at 30^oC are seen to coalesce on heating until at 100^oC only one singlet is seen.[186] The best known

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* The low temperature ^1H NMR spectra of $Mn_2(CO)_7(MeNC)_3$ 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 $\left[CpFe(CO)_2\right]_2$ and its derivatives for which the Cotton-Adams mechanism [187] is widely accepted. A similar mechanism is proposed for the isomerisation of $Mn_2(CO)_7(MeNC)_3$ in which two ligands reversibly and simultaneously take up bridging positions and return to equatorial positions on either metal atom.[186] Finally $Cp_2Mn_2(CO)_2(NO)_2$ exists as two isomers in solution [188] and the ^1H NMR data available has been interpreted in terms of the Cotton-Adams mechanism.[187]

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

3.1 Introduction

The synthesis of compounds $M_2(CO)_{10-n}(CNR)_n$ (M=Mn, Re) has been documented since the early 1960's and synthetic strategies were recently reviewed by Yamamoto [189] and Singleton and Oosthuizen. [190] 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, [191] using trimethylamine - N - oxide, [192,193] photochemically, [186,191,194] and by catalytic means. [195-197] Other indirect methods have been utilized to give a variety of isonitrile compounds. [198,199] Generally the upper limit to direct substitution has been n = 4 with only equatorial positions being substituted. However, a series of complexes $Mn_2(CO)_5(CNR)_5$ (R=Me, Ph, p-ClC_6H_4) have been prepared indirectly from $Mn(CO)_5^-$ and $Mn(CNR)_5X$ (X=halide). [200] Substitution into the axial position has been achieved when phosphines rather than isonitriles are used, e.g. ax-$Mn_2(CO)_9(PPh_3)$ [151,155,156,184] ax-$Re_2(CO)_9(PPh_3)$, [156,184,201-203] diax-$Mn_2(CO)_8(PPh_3)_2$, [155,204,205] and diax-$Re_2(CO)_8(PPh_3)_2$. [201-203]

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

known,[186,191,194-197,200] no kinetic data for the reaction of $M_2(CO)_{10}$ or its derivatives with RNC is available. Further, no kinetic evidence for the mechanisms of any of the transition metal catalysed carbonyl substitution reactions[195-197] has been reported. A limited number of kinetic studies have, however, been undertaken on these types of dimers containing a metal-metal bond.[52,206] An extensive kinetic study of the reactions of $M_2(CO)_{10}$(M=Mn,Re) and PR_3 (e.g. R=Ph) was reported and led to some controversy about the mechanism[151,155,206,207] which was only recently resolved by isotopic labelling studies.[174,175] (see Section 2.4)

The strong evidence now available suggests that the substitution of CO on $Mn_2(CO)_{10}$ and $Mn_2(CO)_9L$ by L' (L,L' = PPh_3, $P(OPh)_3$, PBu_3, $AsPh_3$) occurs via a dissociative process[151] with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being 135-160 $kJmol^{-1}$ and 55-97 $JK^{-1}mol^{-1}$ respectively. A similar study on $MnRe(CO)_{10}$[52,171] reacting with L (L=PPh_3, $P(OPh)_3$, PBu_3) showed that the first substitution occurred mainly on the rhenium atom with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being 158-166 $kJmol^{-1}$ and 67-86 $JK^{-1}mol^{-1}$ respectively. Such reactions have been shown to be first-order in metal carbonyl[151] although the order in the incoming ligand is uncertain.[52]

A mixture of the dimers $M_2(CO)_{10}$ (M=Mn,Re) scramble at elevated temperatures by a pathway involving homolytic

fission of the metal-metal bond.[154] There is presently only one report of movement of a non-carbonyl ligand across a Mn-Mn bond.[186] The rearrangement of $Mn_2(CO)_7(CNMe)_3$ 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) $kJmol^{-1}$, $\Delta S^{\ddagger}$ = -74.0 $JK^{-1}mol^{-1}$

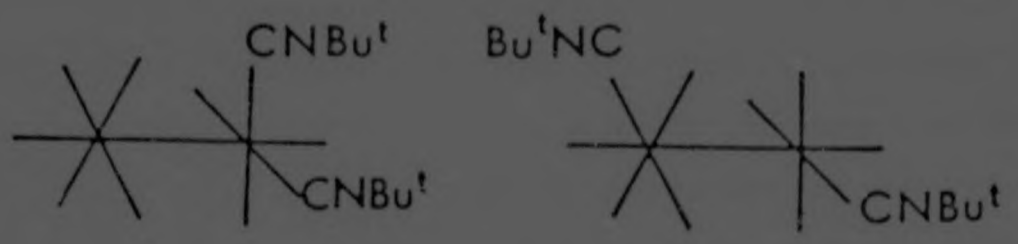
and $\Delta G^{\ddagger}$ = 76.4 (6.1) $kJmol^{-1}$.

A kinetic investigation of the reactions of $M_2(CO)_{10-n}L_n$ (M=Mn, Re; n = 0-2) with L (L=Bu^tNC) (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.

$$M_2(CO)_{10-n}L_n + L \xrightarrow{-CO} M_2(CO)_{9-n}L_{n+1} \qquad (3.11)$$

There are two structural isomers of the complex $Mn_2(CO)_8(Bu^tNC)_2$(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 $Mn_2(CO)_8(Bu^tNC)_2$(eq-eq)



1,1-$Mn_2(CO)_8(Bu^tNC)_2$ 1,2-$Mn_2(CO)_8(Bu^tNC)_2$

3.2 Results

The spectral and physical data for the substituted homonuclear dimers $M_2(CO)_{10-n}(Bu^tNC)_n$ (M=Mn, Re; n=1-3) is given in Tables 3.1 and 3.2 and similar data for the complexes $Re(CO)_{5-n}(Bu^tNC)_nI$ (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 ($t_{\frac{1}{2}}$ < 2 hours) when temperatures in excess of 70°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.

$$Mn_2(CO)_{10} + Bu^tNC \xrightarrow{-CO} Mn_2(CO)_9(Bu^tNC) \qquad (3.21)$$

$$Mn_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow{-CO} Mn_2(CO)_8(Bu^tNC)_2 \qquad (3.22)$$

TABLE 3.1 Physical and Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M = Mn, Re; n = 1 - 3)

Complex	Mpt[a]	Colour	NMR[b]
$Mn_2(CO)_9(Bu^tNC)$	91 - 92	Yellow	0.77
1,1-$Mn_2(CO)_8(Bu^tNC)_2$	99 - 102	Yellow	0.95
1,2-$Mn_2(CO)_8(Bu^tNC)_2$	78 - 80	Yellow	0.91
1,1,2-$Mn_2(CO)_7(Bu^tNC)_3$[c]	109 - 110	Yellow	1.06, 1.00[d]
$Re_2(CO)_9(Bu^tNC)$	104 - 106	White	0.75
1,1-$Re_2(CO)_8(Bu^tNC)_2$	103 - 105	White	0.93
1,2-$Re_2(CO)_8(Bu^tNC)_2$	95 - 96	White	0.87
1,1,2-$Re_2(CO)_7(Bu^tNC)_3$[e]	150 - 152	White	1.02, 0.98[d]

[a] Uncorrected (^oC). [b] Run in C_6D_6 relative to TMS(δ) [c] Ref. 195.
[d] Ratio 1 : 2. [e] Ref. 197.

TABLE 3.2 Infrared Spectral Data for the Complexes $M_2(CO)_{10-n}(Bu^tNC)_n$ (M = Mn, Re; n = 1 - 3)

Complex	Infrared Spectra (cm^{-1})[a]	
	νNC	νCO
$Mn_2(CO)_9(Bu^tNC)$	2170(m)	2092(m)2030(s)1996(vs)1968(m)1958(s)
1,1-$Mn_2(CO)_8(Bu^tNC)_2$	2164(w)2136(w)	2055(m)1999(vs)1977(s)1964(m)1952(m)1934(m)
1,2-$Mn_2(CO)_8(Bu^tNC)_2$	2143(m)	2049(w)2006(s)1977(vs) 1943(m)1939(m)
1,1,2-$Mn_2(CO)_7(Bu^tNC)_3$[b]	2130 2070	2018 1968 1957 1920
$Re_2(CO)_9(Bu^tNC)$	2175(m)	2097(m)2046(s)2015(w)1998(vs)1979(s)1971(m)1953(s)
1,1-$Re_2(CO)_8(Bu^tNC)_2$	2183(m)2157(w)	2065(m)2032(s)1987(vs)1952(m)1935(s)
1,2-$Re_2(CO)_8(Bu^tNC)_2$	2155(m)	2059(w)2024(s)1979(vs) 1935(s)
1,1,2-$Re_2(CO)_7(Bu^tNC)_3$[c]	2154(m)2140(sh)	2030(w)1987(vs)1967(vs)1924(w)1920(s)

[a] Run in hexane. [b] Ref. 195. [c] Ref. 197.

TABLE 3.3 Physical and Spectral Data for the Complexes $Re(CO)_{5-n}(Bu^tNC)_nI$ (n=0-2)

Complex	Colour	Infrared Spectra (cm^{-1})[a]	
		νNC	νCO
$Re(CO)_5I$	White		2146(w)2043(vs)2016(w)1989(s)
$Re(CO)_4(Bu^tNC)I$[b]	Yellow	2192(w)	2102(m)2027(s)2018(vs)1961(s)
$Re(CO)_3(Bu^tNC)_2I$	Yellow	2199(w)2176(m)	2036(vs)1989(s)1935(s)

[a] Recorded in hexane. [b] Synthesised indirectly from $1,2\text{-}Re_2(CO)_8(Bu^tNC)_2$ and I_2.

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.[53,208] The rate constant calculated for this reaction (3.21) was found to be 3.7×10^{-3} s^{-1} ($73^{o}C$) (Table 3.4) which is considerably greater than those calculated for the reaction of $Mn_2(CO)_{10}$ with phosphines[151,155] (see Discussion).

The catalysed reaction of $Mn_2(CO)_{10}$ with Bu^tNC (3.23) occurs rapidly at much lower temperatures. The reaction was followed at room temperature ($18^{o}C$) and at temperatures up to $26^{o}C$, 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

$$Mn_2(CO)_{10} + Bu^tNC \xrightarrow{PdO,\ -CO} Mn_2(CO)_9(Bu^tNC) \qquad (3.23)$$

rate constant for the catalysed reaction was estimated to

TABLE 3.4 Kinetic Data for the Substitution Reactions on $M_2(CO)_{10}$(M=Mn,Re) by Bu^tNC

Reaction	T(^oC)	Catalyst[a]	$M_2(CO)_{10}$[b]	Bu^tNC[b]	k[c]	$t_{\frac{1}{2}}$[d]
3.21	73	-	0.3862	26.60	3.723	11.7(3.5)
3.23	18	PdO	1.0900	34.34	6.505	5.2(8)
3.23	26	PdO	0.9641	22.17	25.050	2.2(10)
3.23	18	PdO	0.9712	12.91	6.621	13.5(4)
3.24	65	Pd/C	0.7991	22.17	2.801	18.7(4.6)
3.24	25	PdO	0.7645	13.79	21.990	3.8(4.5)
3.21[e]	110	-	0.6147	17.05	nr[f]	-

[a] Pd/C is 5% Pd on C.

[b] Initial concentrations in mol l^{-1}($x10^2$).

[c] Pseudo-first-order rate constant in s^{-1}($x10^3$).

[d] Half-life for reaction (min.) and number of half-lives the reaction was followed for in parentheses.

[e] For $Re_2(CO)_{10}$ instead of $Mn_2(CO)_{10}$.

[f] No reaction observed after 6 hours.

be greater than that for the uncatalysed reaction by a factor of approximately 40 at 73°C with a catalyst to dimer ratio of 1:20 (by mass, or 1:7 by moles).

Attempts at substitution on $Re_2(CO)_{10}$ by Bu^tNC without catalyst were not successful (110°C, 5 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 PdO catalyst the reaction occurred at almost the same rate as the equivalent catalysed reaction with $Mn_2(CO)_{10}$ (3.23).

$$Re_2(CO)_{10} + Bu^tNC \xrightarrow{\text{catalyst, } -CO} Re_2(CO)_9(Bu^tNC) \qquad (3.24)$$

The second substitution (3.22) was shown by reactant concentration variation to be independent of isonitrile concentration (when in large excess), see Table 3.5. Figure 3.2 shows examples from a typical set of spectra, in this case corresponding to the reaction of $Mn_2(CO)_9(Bu^tNC)$ with Bu^tNC in the presence of a catalyst (PdO) at 26°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 $\Delta H^{\ddagger}$ = 69.6 (0.8) $kJmol^{-1}$ $\Delta S^{\ddagger}$ = 154.4 (2.3) $JK^{-1}mol^{-1}$ and $\Delta G^{\ddagger}$ = 22.1 (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(^oC)	Catalyst[a]	$M_2(CO)_{10}$[b]	Bu^tNC[b]	k[c]	$t_{\frac{1}{2}}$[d]
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	-	1.3850	20.19	8.060	7.1(6)
3.25	18	PdO	1.0900	23.25	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[e]	110	-	0.4219	23.41	nr[f]	-
3.26	25	PdO	0.7645	13.79	3.260	25.7(4)

[a] Using PdO or no catalyst.

[b] Initial concentrations in mol $l^{-1}(x10^2)$.

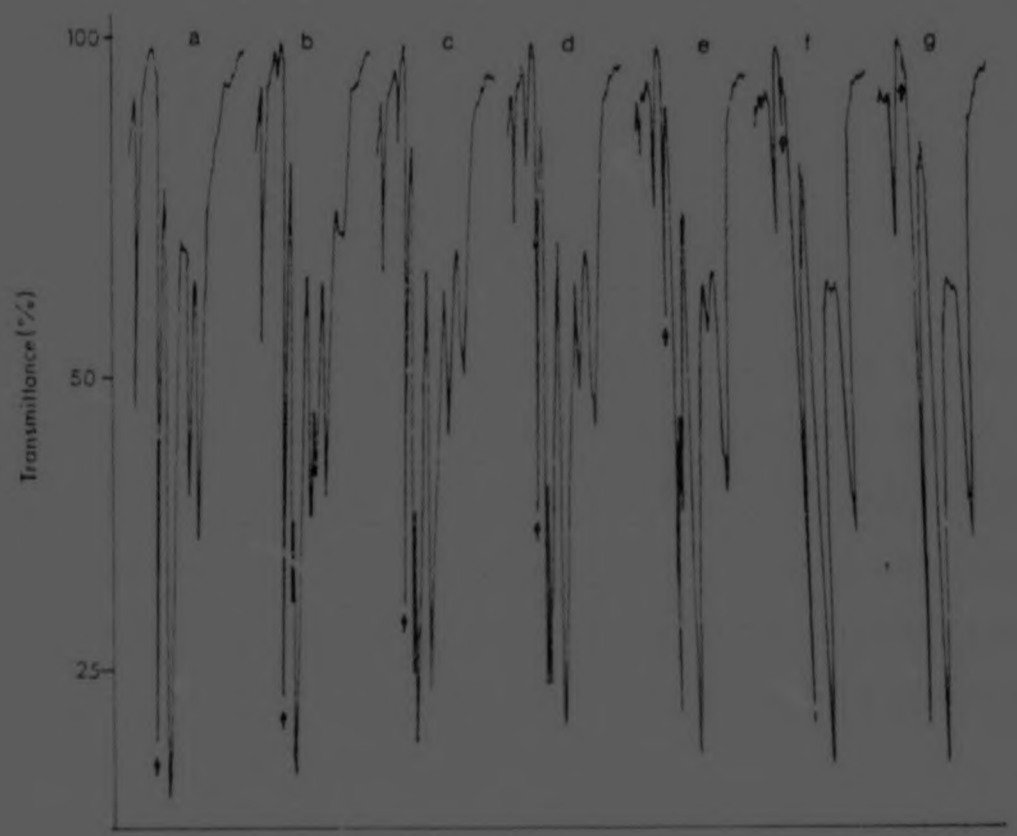
[c] Pseudo-first-order rate constant in $s^{-1}(x10^3)$.

[d] Half-life for reaction (min.) and number of half-lives the reaction was followed for in parentheses.

[e] For $Re_2(CO)_9(Bu^tNC)$ instead of $Mn_2(CO)_9(Bu^tNC)$.

[f] No reaction observed after 6 hours.

Figure 3.2 Typical Infrared Spectra Recorded During the Reaction of $Mn_2(CO)_9(Bu^tNC)$ and Bu^tNC in the presence of PdO *



* Infrared spectra recorded between 2100 and 1900cm^{-1} for the reaction of $Mn_2(CO)_9(Bu^tNC)$ with Bu^tNC in the presence of PdO at 25°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 $Mn_2(CO)_{10}$ by Bu^tNC (3.25) over a 7^oC range in temperature gave a similar Arrhenius plot and the activation parameters so obtained are $\Delta H^{\ddagger}$ = 39.2 (0.4) $kJmol^{-1}$, $\Delta S^{\ddagger}$ = 90.0 (1.3) $JK^{-1}mol^{-1}$ and $\Delta G^{\ddagger}$ = 12.2 (0.3) $kJmol^{-1}$.

$$Mn_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow{PdO,\ -CO} Mn_2(CO)_8(Bu^tNC)_2 \quad (3.25)$$

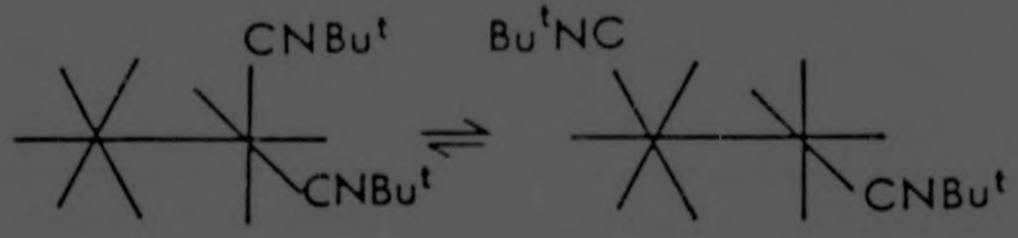
The second substitution on $Re_2(CO)_{10}$ by Bu^tNC could not be followed without a catalyst although prolonged heating of a solution of $Re_2(CO)_9(Bu^tNC)$ and excess Bu^tNC was attempted (110^oC, 6 hours). The catalysed reactions (3.26) proceeds rapidly at low temperatures although it is still considerably slower than the catalysed reactions of $Mn_2(CO)_9(Bu^tNC)$ with Bu^tNC (3.25).

$$Re_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow{PdO,\ -CO} Re_2(CO)_8(Bu^tNC)_2 \quad (3.26)$$

The low temperature catalysed reaction of $Mn_2(CO)_9(Bu^tNC)$ with Bu^tNC (3.25) gave a product with an infrared spectrum different from that previously reported for $Mn_2(CO)_8(Bu^tNC)_2$.[195] 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-$Mn_2(CO)_8(Bu^tNC)_2$ (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 $Mn_2(CO)_8(Bu^tNC)_2$



Pure 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-$Mn_2(CO)_8(Bu^tNC)_2$.[209]

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:

$Mn_2(CO)_9(Bu^tNC) \longrightarrow Mn_2(CO)_8(Bu^tNC)_2$

Reaction	(^oC)	k[a]	$1/T(K^{-1})$	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	-4.8208
3.25	18	4.651	3.4347	-5.3707
3.25	23	6.324	3.3767	-5.0634
3.25	25	6.726	3.3540	-5.0018

[a] Pseudo-first-order rate constants in $s^{-1}(x10^3)$.

TABLE 3.7 Kinetic Data for the Isomerisation of

$Mn_2(CO)_8(Bu^tNC)_2$

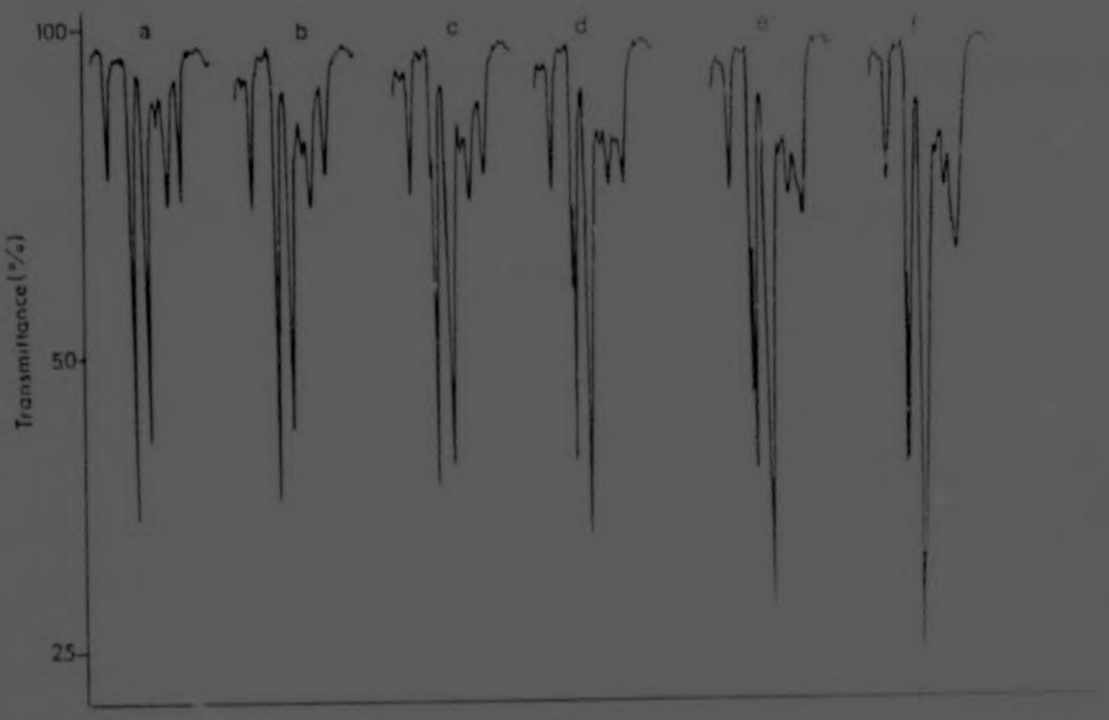
T(^oC)	$Mn_2(CO)_8(Bu^tNC)_2$[a]	k_A[b]	k_B[b]	K_{eq}[c]
52	0.3157	0.6191	0.9410	0.658
52[d]	0.2821	0.5856	0.8783	0.667
71	0.2974	3.2280	4.1740	0.775
73	0.4923	4.2110	5.2705	0.799
84	0.5171	9.8640	11.5660	0.850

[a] Concentration in mol $l^{-1}(x10^2)$.

[b] Rate constant $s^{-1}(x10^4)$. [c] $K_{eq} = k_A/k_B$.

[d] With Bu^tNC present in concentration 0.3325 mol l^{-1}.

Figure 3.4 Typical Infrared Spectra Recorded During the Isomerisation of 1,1-$Mn_2(CO)_8(Bu^tNC)_2$ to an Equilibrium Mixture of the Structural Isomers of $Mn_2(CO)_8(Bu^tNC)_2$*



* Infrared spectra between 2100 and 1900cm^{-1} for the structural isomerisation of $Mn_2(CO)_8(Bu^tNC)_2$ at 52°C recorded at various times

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

1,1-$Mn_2(CO)_8(Bu^tNC)_2$ 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 $Mn_2(CO)_8(Bu^tNC)_2$

1,1-$Mn_2(CO)_8(Bu^tNC)_2$ 1,2-$Mn_2(CO)_8(Bu^tNC)_2$



$\Delta H^{\ddagger}$ = 76.8(1.4)kJmol^{-1} $\Delta H^{\ddagger}$ = 84.5(1.5)kJmol^{-1}

$\Delta S^{\ddagger}$ = 158.7(4.3)JK^{-1}mol^{-1} $\Delta S^{\ddagger}$ = 179.2(4.3)JK^{-1}mol^{-1}

$\Delta G^{\ddagger}_{300}$ = 29.2(1.0)kJmol^{-1} $\Delta G^{\ddagger}_{300}$ = 30.8(1.0)kJmol^{-1}

The complex $Re_2(CO)_8(Bu^tNC)_2$ produced by PdCl catalysed reaction of $Re_2(CO)_9(Bu^tNC)$ and Bu^tNC, had an infrared spectrum which suggested the presence of only the 1,2-isomer. Heating of the complex did not cause any isomerisation to occur as detected by infrared and NMR spectroscopy. The

other isomer, 1,1-$Re_2(CO)_8(Bu^tNC)_2$, was synthesised indirectly from $NaRe(CO)_5$ and $Re(CO)_3(Bu^tNC)_2I$ 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 $M_2(CO)_8(Bu^tNC)_2$ (M = Mn, Re) are presented in Tables 3.1 and 3.2.

The reaction of $Mn_2(CO)_8(Bu^tNC)_2$ with Bu^tNC (3.27) was only observed at elevated temperatures in the presence of a catalyst. When a mixture of the two isomers of $Mn_2(CO)_8(Bu^tNC)_2$ 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 $Re_2(CO)_8(Bu^tNC)_2$ and Bu^tNC reacted (3.28) in the presence of PdO 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 3.9.

$$Mn_2(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow{PdO,\ -CO} Mn_2(CO)_7(Bu^tNC)_3 \quad (3.27)$$

$$Re_2(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow{PdO,\ -CO} Re_2(CO)_7(Bu^tNC)_3 \quad (3.28)$$

TABLE 3.8 Arrhenius Data for the Isomerisation of the Two Isomers of $Mn_2(CO)_8(Bu^tNC)_2$

T(^oC)	k_A [a]	k_B [a]	T^{-1} [b]	ln k_A	ln k_B
52	0.6024	0.9097	3.076	-9.717	-9.305
71	3.2280	4.1740	2.906	-8.038	-7.781
73	4.2110	5.2705	2.889	-7.773	-7.548
84	9.8640	11.5660	2.800	-6.921	-6.762

[a] Rate constants in $s^{-1}(x10^4)$.

[b] $K^{-1}(x10^3)$.

TABLE 3.9 Kinetic Data for the Reactions of $M_2(CO)_8(Bu^tNC)_2$ (M=Mn,Re) with Bu^tNC using PdC Catalyst

Complex	T(^oC)	dimer [a]	Bu^tNC [a]	k [b]
1,1-$Mn_2(CO)_8(Bu^tNC)_2$	73	0.2186	17.73	3.58
1,2-$Mn_2(CO)_8(Bu^tNC)_2$	73	0.2737	17.73	1.43
1,1-$Re_2(CO)_8(Bu^tNC)_2$	80	0.3210	28.67	4.15
1,2-$Re_2(CO)_8(Bu^tNC)_2$	82	0.3576	33.25	2.97

[a] Initial concentrations in mol $l^{-1}(x10^3)$.

[b] Pseudo-first-order rate constant in $s^{-1}(x10^3)$.

TABLE 3.8 Arrhenius Data for the Isomerisation of the Two Isomers of $Mn_2(CO)_8(Bu^tNC)_2$

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[a] Rate constants in $s^{-1}(x10^4)$.

[b] $K^{-1}(x10^3)$.

TABLE 3.9 Kinetic Data for the Reactions of $M_2(CO)_8(Bu^tNC)_2$ (M=Mn,Re) with Bu^tNC using PdCl Catalyst

Complex	T(^oC)	dimer [a]	Bu^tNC [a]	k [b]
1,1-$Mn_2(CO)_8(Bu^tNC)_2$	73	0.2186	17.73	3.58
1,2-$Mn_2(CO)_8(Bu^tNC)_2$	73	0.2737	17.73	1.43
1,1-$Re_2(CO)_8(Bu^tNC)_2$	80	0.3210	28.67	4.15
1,2-$Re_2(CO)_8(Bu^tNC)_2$	82	0.3576	33.25	2.97

[a] Initial concentrations in mol $l^{-1}(x10^3)$.

[b] Pseudo-first-order rate constant in $s^{-1}(x10^3)$.

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 [52,151,153,210]

$$k_{obs} = (k_1 + k_2[L])[M_m(CO)_n]$$

$(k_2 < k_1)$.

e.g reaction 3.31, in which a small ligand

$$M_m(CO)_n + L \xrightarrow{-CO} M_m(CO)_{n-1}L \qquad (3.31)$$

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 $Mn_2(CO)_{10}$ and isonitrile is that the observed rate constant (k_{obs}) is larger than that for the reaction with phosphines [151] or even labelled CO [175] ($3.7\times10^{-3}s^{-1}$ at 73°C for Bu^tNC, $2.6\times10^{-4}s^{-1}$ for PPh_3 at 120°C). Since the

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reaction with PPh_3 and ^{13}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 $k_2[L]$ 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.[52] Extensive kinetic studies by Poë and others [51,155,156,159,163,169,208,211] 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 $M_2(CO)_{10}$ and their derivatives [160,170,212] (see earlier). Poë's mechanism (Scheme 2.2) would be expected to give a mixture of di, mono and unsubstituted dimers from a reaction of $M_2(CO)_{10}$ and 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 $Mn_2(CO)_9(Bu^tNC)$ with Bu^tNC was followed no $Mn_2(CO)_{10}$ was detected during the reaction. Further, Poës' mechanism (Scheme 3.1) would lead to a mixture of radicals $\cdot Mn(CO)_5$ and $\cdot Mn(CO)_4(Bu^tNC)$ and from Brown's work (*cis*-labilization) [128-130] the substitution on $\cdot Mn(CO)_4(Bu^tNC)$ would be

expected to occur more rapidly than that on $\cdot Mn(CO)_5$. 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 [141] showed that reactions upon the radical species $\cdot Re(CO)_5$ proceed by an associative pathway, the CO dissociation being negligible.

An alternative mechanism suggested initially by Basolo and Wawersik [151] and later by Atwood and co-workers [171,206] 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 $M_2(CO)_{10}$ (M=Mn,Re). However, when M_2=MnRe (see later) or the second substitution of CO by L is considered this mechanism also fails to satisfactorily explain the available results. Work by Brown et al [130] has shown cis-labilization to be important in substitution reactions of many metal carbonyls and so $Mn_2(CO)_9(Bu^tNC)$

could be expected to lose a carbonyl most easily from the already substituted metal (Scheme 3.2). To explain how the 1,2-$Mn_2(CO)_8(Bu^tNC)_2$ could be the initial product in reaction 3.32, Atwood and Sonnenberger [52] suggested a transfer of the unsaturation to the second metal via an intermediate (or transition state) that contains a bridging carbonyl. To explain the results it is still necessary for either k_2 to be far greater than k_1 or for the equilibria to strongly favour 2, (Scheme 3.2) but neither of these conditions seems reasonable. Similarly if one considers the data for the reaction of $Re_2(CO)_9(Bu^tNC)$ and Bu^tNC (only data for the catalysed reaction is available) the 1,2-disubstituted product is obtained exclusively and could not be isomerised to the 1,1-disubstituted product even on prolonged heating. Thus Atwood's proposed mechanism may not be involved in the substitution reactions of $M_2(CO)_{10}$ or $M_2(CO)_9(Bu^tNC)$(M=Mn,Re) with Bu^tNC.

Thus an alternative mechanism was sought to explain the results of this study with respect to the results of other studies on the substitution reactions of $M_2(CO)_{10}$ (M=Mn,Re) and their derivatives. Initial substitution to give the 1,1-disubstituted product followed by isomerisation to the 1,2-disubstituted product was the first possibility considered. If the Mn_2 system is considered, the pseudo-first-order rate constant for the substitution of $Mn_2(CO)_9(Bu^tNC)$ by Bu^tNC at 52°C was found to be

Scheme 3.1

$$M_2(CO)_9L \longrightarrow \cdot M(CO)_5 + \cdot M(CO)_4L$$

$$\cdot M(CO)_5 + L \longrightarrow \cdot M(CO)_4L + CO$$

$$\cdot M(CO)_4L + L \dashrightarrow \cdot M(CO)_3L_2 + CO$$

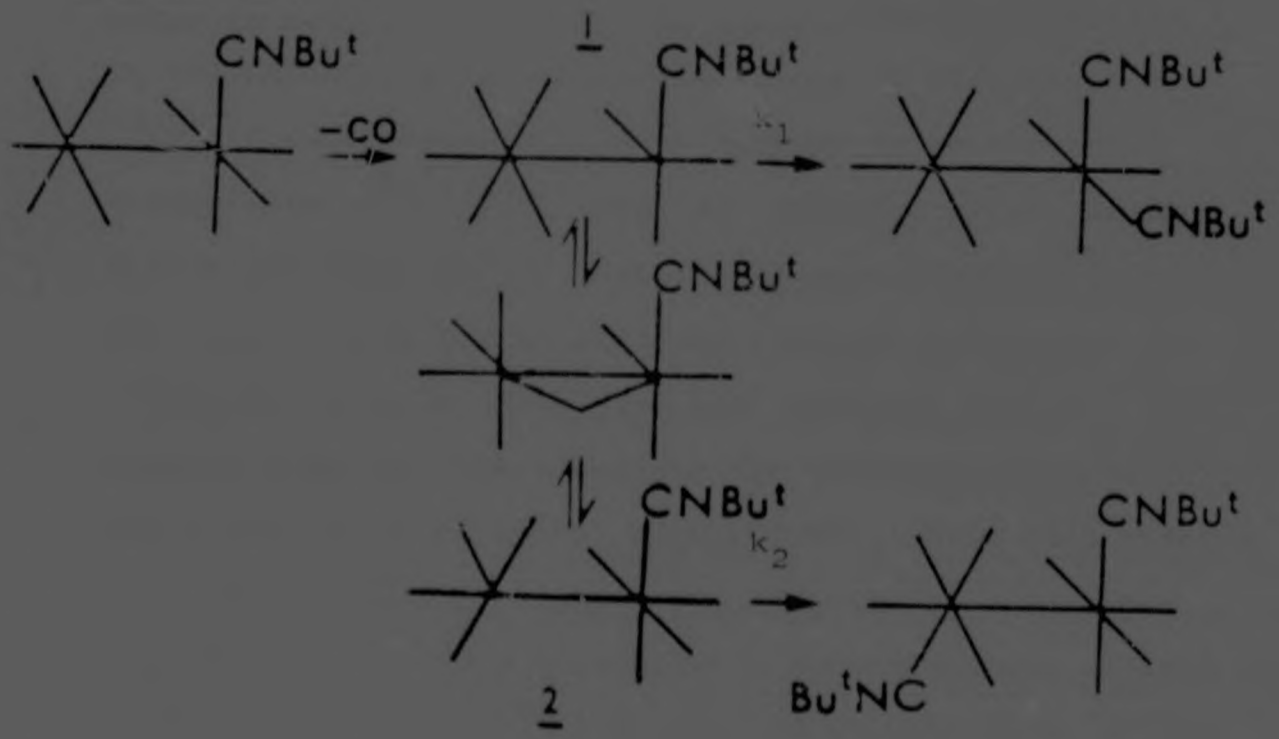
$$\cdot M(CO)_5 + \cdot M(CO)_5 \longrightarrow M_2(CO)_{10}$$

$$\cdot M(CO)_4L + \cdot M(CO)_4L \longrightarrow 1,2\text{-}M_2(CO)_8L_2$$

$$\cdot M(CO)_5 + \cdot M(CO)_3L_2 \longrightarrow 1,1\text{-}M_2(CO)_8L_2$$

$$\cdot M(CO)_4L + \cdot M(CO)_3L_2 \longrightarrow M_2(CO)_7L_3$$

Scheme 3.2



[illegible] whereas the rate constant for the isomerisation of 1,1-$Mn_2(CO)_8(Bu^tNC)_2$ to 1,2-$Mn_2(CO)_8(Bu^tNC)_2$ at the same temperature was found to be only 9.1×10^{-5} s^{-1}. In the Re_2 systems the disubstituted derivative could only be obtained using a catalyst but isomerisation of 1,1-$Re_2(CO)_8(Bu^tNC)_2$ to 1,2-$Re_2(CO)_8(Bu^tNC)_2$ was not achieved even on prolonged heating with or without catalyst present. Thus substitution to give the 1,1 isomer followed by isomerisation was ruled out as a possible pathway.

If one considers the substitution reactions of the mononuclear complexes $M(CO)_5Br$ (M=Mn,Re) they are first order in metal carbonyl concentration.[121,123,128,213] In the carbonyl substitution reactions by phosphines or ^{13}CO the rate determining step appears to be carbonyl dissociation[123,214-217] and the carbonyls cis- to bromine dissociate more rapidly than the trans-carbonyl.[217] The reactions of the substituted carbonyl bromides $M(CO)_4LBr$ (M=Mn,Re) have also been studied, and by ascertaining the rate constants for carbonyl substitution, the ligands L (e.g. L=PPh_3 NC_5H_5, $P(OPh)_3$) have been ordered in terms of their cis-labilizing effects.[129] A possible explanation for the cis-labilizing phenomenon was offered by Atwood and Brown[130] and involved stabilization of the 5-coordinate transition state by ligand L occupying a basal or axial site.

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. $Mn(CO)_5X$ with $X=Mn(CO)_5$ or $Mn(CO)_4(Bu^tNC)$ etc. Thus the initial formation of 1,2-$Mn_2(CO)_8(Bu^tNC)_2$ rather than 1,1-$Mn_2(CO)_8(Bu^tNC)_2$ suggests the group $Mn(CO)_4(Bu^tNC)$ has a greater cis-labilizing effect than the accumulated cis-labilization of $Mn(CO)_5$ and Bu^tNC. Similarly the rate constant for substitution on 1,1-$Mn_2(CO)_8(Bu^tNC)_2$ is greater than that for substitution on 1,2-$Mn_2(CO)_8(Bu^tNC)_2$ and so the cis-labilizing effect of the group $Mn(CO)_3(Bu^tNC)_2$ is greater than the cis-labilizing effect of $Mn(CO)_4(Bu^tNC)$ and Bu^tNC combined. Thus the order in decreasing cis-labilizing effect is $Mn(CO)_3(Bu^tNC)_2 > Mn(CO)_4(Bu^tNC) > Mn(CO)_5$ and other results suggest an analogous series for the rhenium complexes. Unfortunately this work does not allow for the ligands CO and Bu^tNC to be placed in a sequence relative to the metal carbonyls and indeed Atwood suggested that CO and $M(CO)_x$ groups have approximately equal cis-labilizing effects. From electronic considerations alone it is expected that isonitriles, RNC, should have a greater cis-labilizing effect than the carbonyl ligand. Work on carbonyl substitution of $Re(CO)_5I$ by isonitrile 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 carbonyls) in a single ordering scheme.

Of the disubstituted dimers $M_2(CO)_8(Bu^tNC)_2$ only the manganese dimer was seen to undergo isomerisation at under 120°C. The structural isomers could be differentiated by mass spectrometry both giving a molecular ion at 390 but the different metal-metal bond cleavage product allowed identification. Mass spectral analysis was complicated by the fact the isonitrile has a mass of 83 very nearly equivalent to three carbonyl groups (M=84); this problem can be avoided in future work by judicious choice of isonitrile e.g. MeNC (M=41). The various experiments performed showed this isomerisation to be both intramolecular and unimolecular thus the mechanism proposed is consistant with that proposed earlier for the $Mn_2(CO)_7(MeNC)_3$ complex.[186] This involves the synchronous movement of ligands during which two ligands (carbonyls or isonitriles) move into a bridging position and then onto the second metal. The isomerisation mechanism would be critically dependent upon the metal-metal bond length and the increased bond length is thought to be the reason why $Re_2(CO)_8(Bu^tNC)_2$ was not seen to isomerize at temperatures below 120°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 i-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:

$$Mn_2(CO)_{10} + Bu^tNC \xrightarrow{-CO} Mn_2(CO)_9(Bu^tNC) \qquad (3.21)$$

$$Mn_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow{-CO} Mn_2(CO)_8(Bu^tNC)_2 \qquad (3.22)$$

$$Mn_2(CO)_{10} + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Mn_2(CO)_9(Bu^tNC) \qquad (3.23)$$

$$Re_2(CO)_{10} + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Re_2(CO)_9(Bu^tNC) \qquad (3.24)$$

$$Mn_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Mn_2(CO)_8(Bu^tNC)_2 \qquad (3.25)$$

$$Re_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Re_2(CO)_8(Bu^tNC)_2 \qquad (3.26)$$

$$Mn_2(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Mn_2(CO)_7(Bu^tNC)_3 \qquad (3.27)$$

$$Re_2(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow[\text{catalyst}]{-CO} Re_2(CO)_7(Bu^tNC)_3 \qquad (3.28)$$

The uncatalysed substitution of $Re_2(CO)_{10}$ or $Re_2(CO)_9(Bu^tNC)$ with Bu^tNC was not observed even after following each reaction for 6 hours at 110°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-$Mn_2(CO)_8(Bu^tNC)_2$

$Mn_2(CO)_{10}$ (1mmol) and Bu^tNC (2.1mmol) in benzene (30ml) with PdO catalyst (20mg) was stirred at room temperature (20°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 chromagography (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 $Mn_2(CO)_8(Bu^tNC)_2$, alalysis found C=42.94%, H=3.28%, N=5.35%: $C_{18}H_{18}O_8N_2Mn_2$ 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-$Mn_2(CO)_8(Bu^tNC)_2$

Pure 1,2-$Mn_2(CO)_8(Bu^tNC)_2$ (1mmol), synthesized as above was heated to 55°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 ($\pm$ 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 [209] confirmed the isonitrile arrangement. Physical and spectral data are presented in Tables 3.1 and 3.2.

3.4.4 Synthesis of 1,2-$Re_2(CO)_8(Bu^tNC)_2$

$Re_2(CO)_{10}$ (1mmol) and Bu^tNC (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-$Mn_2(CO)_8(Bu^tNC)_2$. 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 ($\pm$ 82%) of the off-white powder were obtained.

3.4.5 Synthesis of 1,1-$Re_2(CO)_8(Bu^tNC)_2$

$Re(CO)_5I$ was synthesized from $Re_2(CO)_{10}$ and I_2 in refluxing benzene (see later), and its purity was judged by its infrared spectrum which showed no $Re_2(CO)_{10}$.[56] Bu^tNC (2.3mmol) was added to a refluxing solution of $Re(CO)_5I$ (1mmol) in benzene (30ml) with $Pd/CaCO_3$ (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%; $C_{13}H_{18}O_3N_2ReI$ required C=27.72%, H=3.20%, N=4.97% and I=22.53%. Other spectral data are given in Table 3.3.

$Re(CO)_3(Bu^tNC)_2I$ (1mmol) was added dropwise as a thf solution (20ml) to a solution of $NaRe(CO)_5$[218] 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 ($\pm$ 82%) of the off-white powder were obtained.

3.4.5 Synthesis of 1,1-$Re_2(CO)_8(Bu^tNC)_2$

$Re(CO)_5I$ was synthesized from $Re_2(CO)_{10}$ and I_2 in refluxing benzene (see later), and its purity was judged by its infrared spectrum which showed no $Re_2(CO)_{10}$.[56] Bu^tNC (2.3mmol) was added to a refluxing solution of $Re(CO)_5I$ (1mmol) in benzene (30ml) with $Pd/CaCO_3$ (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%; $C_{13}H_{18}O_3N_2ReI$ required C=27.72%, H=3.20%, N=4.97% and I=22.53%. Other spectral data are given in Table 3.3.

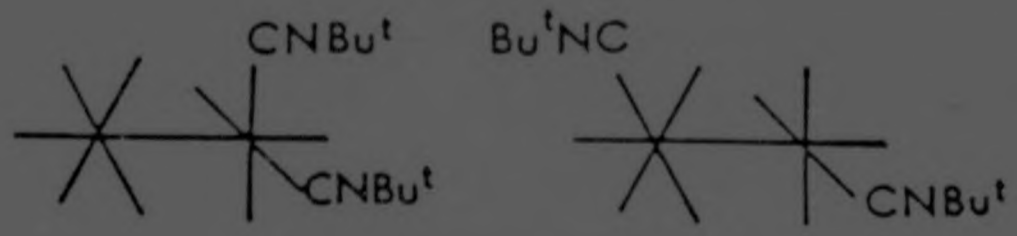
$Re(CO)_3(Bu^tNC)_2I$ (1mmol) was added dropwise as a thf solution (20ml) to a solution of $NaRe(CO)_5$[218] in thf (30ml). The reaction mixture was stirred under an inert atmosphere, at 60°C for 24 hours after which time the solution appeared slightly darker. After filtering and solvent removal the required product was obtained by recrystallization from a refrigerated hexane solution.

Only low product yields ($\pm$ 30%) were obtained and microanalysis found C=28.51%, H=2.52%, N=3.71%; $C_{18}H_{18}O_9N_2Re_2$ requires C=2[illegible].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-$Mn_2(CO)_8(Bu^tNC)_2$ (0.1mmol) 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 $\pm$ 6 hours during which time equilibrium was reached. A similar study of the isomerisation of

1,1-$Mn_2(CO)_8(Bu^tNC)_2$ showed that an identical equilibrium mixture was obtained (at the same temperature) irrespective of the initial choice of isomer.

Solutions of either the 1,1 or 1,2-disubstituted rhenium dimers were heated up to 110°C for ± 6 hours but neither showed any sign of isomerisation under these conditions.

4. CARBONYL SUBSTITUTION REACTIONS OF THE MIXED METAL DIMER $MnRe(CO)_{10}$

4.1 Introduction

The synthesis of $MnRe(CO)_{10}$ from $NaMn(CO)_5$ and $Re(CO)_5Cl$ was first presented by Nesmeyanov *et al* [55] and later repeated by Kaesz *et al*.[56] The infrared spectrum of the heteronuclear dimer was reported by Kaesz,[57] who also showed that the reported infrared spectrum of Nesmeyanov's product [219] was that of a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Kaesz *et al* [57] also showed that the alternative approach to the synthesis of $MnRe(CO)_{10}$, from $Mn(CO)_5Br$ and $NaRe(CO)_5$, only gave a mixture of the homonuclear dimers, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Since this early work a complete infrared spectral assignment of $MnRe(CO)_{10}$ has been reported,[33,57,65,67,220] which included a study of the far-infrared region of the spectrum to obtain the metal-metal stretching frequency.[49]

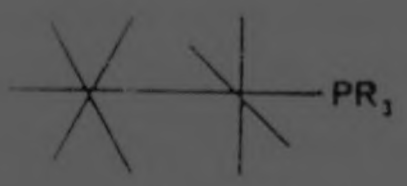
Alternative thermal [220] or photochemical [59,71,72,185] syntheses of the mixed metal carbonyl, $MnRe(CO)_{10}$, have since been reported starting from $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The low yields of $MnRe(CO)_{10}$ obtained by these methods have been improved slightly by varying the initial carbonyl ratio [72] or the mode of irradiation.[185] The synthesis of $MnRe(CO)_{10}$ in moderate yields has also been reported [64] from the reaction of $\left[Mn(CO)_5\right]^-$ with $\left[Re(CO)_6\right]^+$ at -80°C.

The chemistry of $MnRe(CO)_{10}$ has been largely neglected over the years and the few reactions that have been reported are listed below. The direct synthesis of derivatives from $MnRe(CO)_{10}$ have either involved reactions at a carbonyl [221] or substitution of a carbonyl by PR_3 (R=Ph, OPh or Bu^n) to give a carbene or $MnRe(CO)_{10-n}(PR_3)_n$.[51,52,54,62,152,222,223] Indirect methods from $NaMn(CO)_5$ and $(o\text{-phen})Re(CO)_4.Zn_2Cl_6$ or from $Re(CO)_3(DAB)X$ (X=halide) and $Mn(CO)_5^-$ (Na or K salt) have also been used to obtain $MnRe(CO)_{10}$ derivatives [64,224-229] such as $MnRe(CO)_8(o\text{-phen})$ [64] and $MnRe(CO)_8(DAB)$.[228]

The electrochemical reduction of $MnRe(CO)_{10}$ was studied by Gross et al [70] and the reduction potential was found to be intermediate to that of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (as expected) but the metal-metal bond dissociation energy was found to be greater than that for either $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$.[58,70] $MnRe(CO)_{10}$ was seen to undergo a phase transition in the solid state at 70°C [69] very similar to that undergone by $Mn_2(CO)_{10}$ (68°C) [230] and $Re_2(CO)_{10}$ (98°C).[231]

Kinetic studies of the substitution reactions of $MnRe(CO)_{10}$ with phosphines have been reported.[73,152,225,229] 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.[229] (Figure 4.1)

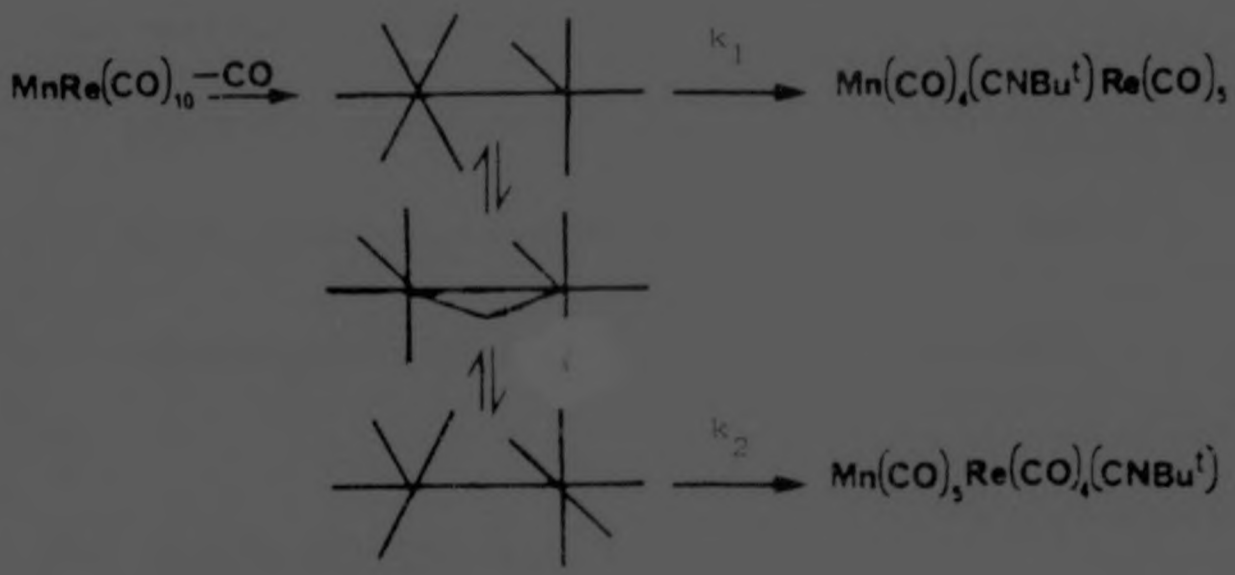
Figure 6.1 Molecular Structure of $Mn(CO)_5Re(CO)_4(PR_3)$



small amounts of the manganese axially substituted isomer, were also obtained [73] but this product could not be converted to the rhenium substituted isomer, thermally.[69,171] The substitution of a second CO by PR_3 into the remaining axial position takes place at a slightly slower rate than for the first CO substitution. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for monosubstitution of $MnRe(CO)_{10}$ by PR_3 (average for R = Ph, OPh or Bu^n) have been calculated by Atwood et al [52] as 161.8 $kJmol^{-1}$ and 77.7 $JK^{-1}mol^{-1}$ respectively and by Poë et al [53] (R = Ph) as 162.8 $kJmol^{-1}$ and 77.4 $JK^{-1}mol^{-1}$ respectively. Although the data is undisputed there is a good deal of controversy over the mechanism of these reactions. The two lines of thought (as with the homonuclear dimers $M_2(CO)_{10}$ (M = Mn or Re)) involve either homolysis of the metal-metal bond with the rate determining step being CO substitution on the radical species and metal-metal bond

reformation,[53,73,225,232] or CO dissociation from the metal dimer as the rate determining step followed by (e.g. L = phosphin addition.[152,207,229] The former mechanism seems unlikely as no homonuclear products such as $Mn_2(CO)_9L$ etc. are detected for the reaction of $MnRe(CO)_{10}$ with $P(C_6H_5)_3$,[152] which is suggested to occur via a mixture of $\cdot Mn(CO)_5$, $\cdot Mn(CO)_4L$, $\cdot Re(CO)_5$ and $\cdot Re(CO)_4L$ radicals. The latter mechanism seems more likely but the product ratio would be dependent on the rate at which CO is lost from either end of the molecule. The metal-carbon bond strengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are 141 $kJmol^{-1}$ and 166 $kJmol^{-1}$ [232] respectively which would suggest that a greater amount of substitution would occur at manganese rather than at rhenium in $MnRe(CO)_{10}$. The mechanism proposed by Atwood et al [207] allows loss of carbonyl at manganese initially, being rapidly followed by transfer of the unsaturation, via a bridging carbonyl to the rhenium atom. (Scheme 4.1) The authors suggested $k_2 > k_1$, but offered no good reason why this should be so. This transfer of unsaturation has also been suggested in a number of metal carbonyl cluster reactions e.g. $Ir_4(CO)_{12}$ with L (L=PPh_3, PBu^n_3, $P(OPh)_3$, $AsPh_3$).[118-120,207] An extremely slow isomerisation of $(PPh_3)(CO)_4MnRe(CO)_5$ to $(CO)_5MnRe(CO)_4(PPh_3)$ was observed by Poë,[160] who suggested a mechanism involving many different radical species, the products of initial homolytic fission of the Mn-Re bond. Poë suggested that the complexity of such an isomerisation was the reason why substantial decomposition was observed.

Scheme 4.1



The following study was undertaken in the hope of clarifying this little understood reaction mechanism. The reaction between $MnRe(CO)_{10}$ and Bu^tNC was studied, the Bu^tNC being chosen as the substituting ligand as it has a small cone angle [233] 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 $MnRe(CO)_9(Bu^tNC)$ 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:

$\underline{cis}$-$Mn(CO)_5.Re(CO)_4C(OCH_3)CH_3$ (ref. 222)

$Cp(CO)_2Mn.Re(CO)_4(\mu\text{-}C(Ph)CO)$ (ref. 54)

$MnRe(CO)_9.(HRe(CO)_5)$ (ref. 234)

4.2 Results and Discussion

The physical and spectral properties of the complexes $MM'(CO)_9(Bu^tNC)$(M,M'=Mn,Re) and the complexes $MnRe(CO)_9(RNC)$(R=Bu^t, Pr^i, Xy, Cy) are given in Tables 4.1 and 4.2 respectively.

$MnRe(CO)_{10}$ was obtained in yields approaching 70%. Although this product did contain some $Mn_2(CO)_{10}$ impurity it could be purified by fractional sublimation, the $Mn_2(CO)_{10}$ subliming at room temperatures with pressures of $\pm 10^{-4}$ atm. Sufficiently pure material was obtained so that the CO substitution reaction could be followed clearly by infrared spectroscopy. Occasionally traces of $Mn_2(CO)_{10}$ were found as an impurity in the heteronuclear dimer; this reacted rapidly and generally, substituted products $MnRe(CO)_9(RNC)$ and $Mn_2(CO)_{10-n}(RNC)_n$(n=1,2) could be separated by column chromatography (silica). The reaction

TABLE 4.1 Physical and Spectral Data for the Monosubstituted Metal Dimers $MM'(CO)_9(Bu^tNC)$ (M,M' = Mn, Re)

Complex	Mpt(^oC)[a]	Infrared Spectra (cm^{-1})[b] ν_{NC}	ν_{CO}			UV[c]	NMR[d]
$Mn_2(CO)_9(Bu^tNC)$	91- 92	2170(m)	2092(m)	2032(s)	1996(vs) 1968(m) 1958(s)	-	0.77
$Re_2(CO)_9(Bu^tNC)$	104-106	2173(m)	2101(m)	2050(s)	2018(sh) 1996(vs) 1979(w) 1970(m) 1952(s)	-	0.75
$Mn(CO)_5Re(CO)_4(Bu^tNC)$	101-102	2182(w)	2090(m)	2041(s)	2024(w) 2002(vs) 1977(m) 1963(s) 1957(s)	322	0.75
$Mn(CO)_4(Bu^tNC)Re(CO)_5$	92- 93	2180(w)	2099(m)	2055(s)	2018(w) 2000(vs) 1979(m) 1971(s) 1954(s)	326	0.76

[a] Uncorrected. [b] Recorded in hexane. [c] Recorded in hexane relative to holmiun standard 361nm .

[d] Recorded in C_6D_6 relative to TMS(δ).

TABLE 4.2 Physical and Spectral Data for the Complexes $MnRe(CO)_9(RNC)$ (R=Bu^t, Pr^i, Xy, Cy)

Complex	Mpt(^oC)[a]	Infrared Spectra (cm^{-1})[b] ν_{NC}	Infrared Spectra (cm^{-1})[b] ν_{CO}	NMR[c]
$MnRe(CO)_9(Bu^tNC)$	101-102	2182(w)	2090(m)2041(s)2024(w)2002(vs)1977(m)1963(s)1957(s)	0.75(s)
$MnRe(CO)_9(Pr^iNC)$	71- 72	2187(w)	2089(m)2040(s)2030(w)2005(vs)1978(m)1963(s)1957(s)	0.54(d)2.99(s)[d]
$MnRe(CO)_9(XyNC)$	109-110	2154(w)	2083(m)2042(s)2026(w)2004(vs)1988(w)1966(s)1960(s)	1.96(s)6.54(m)[e]
$MnRe(CO)_9(CyNC)$	-[f]	2189(w)	2093(m)2047(s)2032(w)2002(vs)1980(m)1964(s)1957(s)	0.75-1.35[g]

[a] Uncorrected. [b] Run in hexane. [c] Recorded in C_6D_6 relative to TMS (δ). [d] Signal Ratio 6:1.
[e] Signal ration 2:1. [f] Oily solid. [g] Complex multiplet.

of $MnRe(CO)_{10}$ with Bu^tNC, (4.1), gave only one monosubstituted product $MnRe(CO)_9(Bu^tNC)$ 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

$$MnRe(CO)_{10} + Bu^tNC \xrightarrow{-CO} MnRe(CO)_9(Bu^tNC) \qquad 4.1$$

repeated on a smaller scale using hexane as a solvent and followed at 25°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 Bu^tNC bonded to the rhenium atom (see later). This rhenium substituted isomer could not be converted thermally to the manganese substituted isomer (95°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°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 $MnRe(CO)_{10}$ by Bu^tNC. Metal-metal bond

cleavage followed by substitution and dimer reformation [51, 54, 222, 223] is also ruled out by the lack of any homonuclear dimers, such as $Mn_2(CO)_{11}$, $Re_2(CO)_9(^tBuNC)$ etc. that would be expected from such a mechanism.

The mechanism proposed by Atwood et al [52] i.e. via a bridged species (Scheme 4.1) would be expected to produce a mixture of both the manganese and rhenium substituted products. To explain the observed substitution anomoly (exclusively at rhenium), it is necessary to make certain assumptions. Either attack at the bridged intermediate occurs exclusively at rhenium or the equilibria are such that the complex with the unsaturated rhenium atom is greatly favoured. No reasons why these assumptions should be true was offered by Atwood and an experiment has been designed to either confirm or refute this mechanism. $Mn_2(^{13}CO)_{10}$ can be prepared from $Mn_2(CO)_{10}$ and ^{13}CO using either thermal or photochemical methods. Using this labelled $Mn_2(CO)_{10}$ the mixed metal dimer $MnRe(CO)_{10}$ can be prepared, in which the carbonyls on the manganese atom are labelled to a known percentage. Neither of the homonuclear dimers $M_2(CO)_{10}$(M=Mn,Re) undergo ligand scrambling at room temperature and so the mixed metal dimer would also be expected to retain the labelling exclusively at manganese. The room temperature, catalysed carbonyl

substitution reaction with Bu^tNC would then be performed in hexane solution in a sealed container under a nitrogen atmosphere. Gas phase 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}CO would confirm the mechanism of Atwood and its absence would strongly suggest a direct substitution mechanism, as suggested earlier.

The rate constant for this substitution (Table 4.3) was found to be $16.0 \times 10^{-3} s^{-1}$. 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 $MnRe(CO)_{10}$ is 1.5 times that for CO dissociation in $Re_2(CO)_{10}$. This suggests that the Re-C bond strength is weaker in $MnRe(CO)_{10}$ than in $Re_2(CO)_{10}$.

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 $MnRe(CO)_{10}$ with Bu^tNC before complete reaction of $MnRe(CO)_{10}$ was observed, it is clear that the rate for the second

TABLE 4.3 Kinetic Data for Monosubstitution of $MM'(CO)_{10}$ (M,M'=Mn,Re) with Bu^tNC using PdO catalyst at 25°C

Complex	$MM'(CO)_{10}$ [a]	Bu^tNC [a]	k [b]	$t_{½}$ [c]	k' [b,d]
$Mn_2(CO)_{10}$	0.4385	8.868	20.89	6.2(4.8)	2.61
$Re_2(CO)_{10}$	0.7645	13.790	21.99	3.8(4.5)	2.75
$MnRe(CO)_{10}$	0.3645	8.868	16.01	11.7(3.6)	4.00

[a] Initial concentrations in mol $l^{-1}(x10^2)$.

[b] Pseudo-first-order rate constant in $s^{-1}(x10^3)$.

[c] Half-life for reaction (min.) and number of half-lives the reaction was followed for in parentheses.

[d] Rate constant per equatorial carbonyl.

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

$$Mn(CO)_5 \gtrsim Re(CO)_4(Bu^tNC) > Re(CO)_5$$

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

$$Mn(CO)_3(Bu^tNC)_2 > Mn(CO)_4(Bu^tNC) > Mn(CO)_5 \gtrsim Re(CO)_4(Bu^tNC) > Re(CO)_5.$$

Unlike the cis-labilization data presented for the complexes $M(CO)_4LBr(M=Mn,Re;L=CO,NC_5H_5,PPh_3,P(OPh)_3)$ [128,129] steric factors are negligible and the series is a result of only (or predominantly) electronic effects.

Subsequent work in this laboratory [235] has produced a mixture of disubstituted products from the reaction of $(CO)_5MnRe(CO)_4(Bu^tNC)$ and Bu^tNC, but with a dominance of $(CO)_5MnRe(CO)_3(Bu^tNC)_2$ and a lesser amount of $(CO)_4(Bu^tNC)MnRe(CO)_4(Bu^tNC)$. This confirms the ordering presented above with $Mn(CO)_5$ having a greater cis-labilizing effect than $Re(CO)_4(Bu^tNC)$. Study of the reaction of the disubstituted complexes with isonitrile (RNC) is in progress and a comparison, using the reactions:

$$2,2\text{-}MnRe(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow{-CO} 1,2,2\text{-}MnRe(CO)_7(Bu^tNC)_3$$

$$1,2\text{-}MnRe(CO)_8(Bu^tNC)_2 + Bu^tNC \xrightarrow{-CO} 1,2,2\text{-}MnRe(CO)_7(Bu^tNC)_3 + 1,1,2\text{-}MnRe(CO)_7(Bu^tNC)_3$$

of rate constants and product ratios will lead to being able to place $Re(CO)_3(Bu^tNC)_2$ in the above order.

4.3. X-ray Crystallography of $MnRe(CO)_9(Bu^tNC)$

Single orange plate shaped crystals were obtained after a period of 48 hours from a refrigerated hexane solution of $MnRe(CO)_9(Bu^tNC)$. Using oscillation and Weissenberg photographs, recorded with Cu-K_α 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 Cu-K_α 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 $Mn(CO)_5Re(CO)_4(Bu^tNC)$

Crystal Data	
Formula	$C_{14}H_9NO_9MnRe$
Molecular Weight	576.36
Melting Point	103°C
Crystallisation Solvent	hexane
Crystal System	Monoclinic
Space Group	$P2_1/n$
a/Å	15.262(3)
b/Å	20.856(5)
c/Å	12.051(3)
β/°	91.54(6)
V/Å^3	3839.45
Z	8
Dc/gcm^{-3}	1.994
Dm (by floatation)/gcm^{-3}	1.90
μ(Cu-Kα)	166.09
F(000)	2175.55
Data Collection	
Crystal Dimensions/mm^3	0.15x0.015x0.30mm^3
Scan Mode	$\omega - 2\theta$
Scan Speed/°θs^{-1}	0.048
Scan Width/°θ	1.20
Range Scanned/°θ	5 - 60
Number of Reflections Collected	8174
Number of Observed Reflections	5705
Significance Test	$F_o > \sigma(F_c)$
Stability of Standard Reflections	98.4%

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.[236]

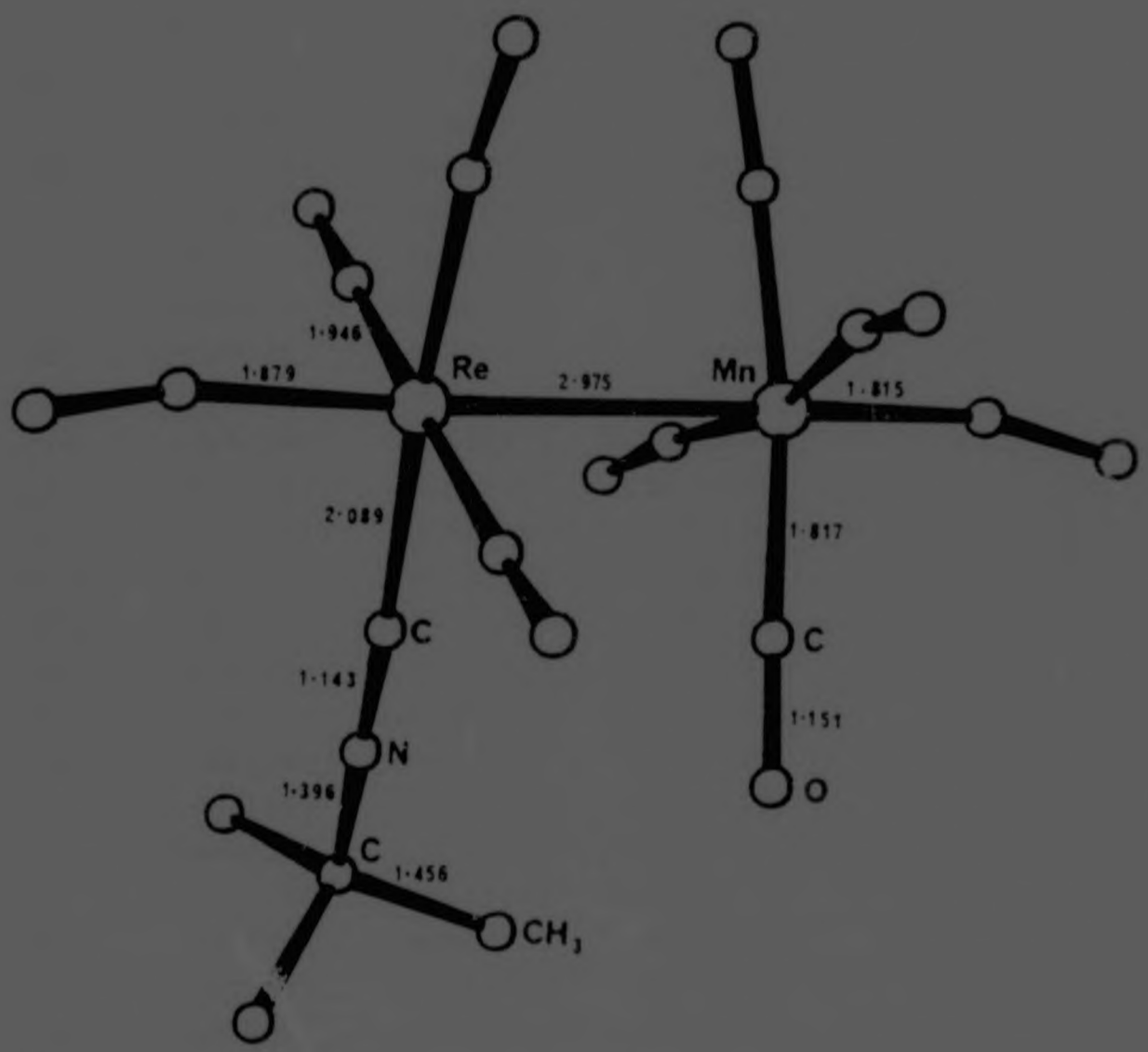
The structure was refined using a unit weighting scheme and only isotropic temperature factors to R_f = 13.24%. Inclusion of absorption corrections reduced this to R_f = 9.89% (R_w = 8.76%). The final coordinates of all the non-hydrogen atoms in the asymmetric unit are given in Tables 4.5 and 4.6. An Ortep diagram[237] 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 C.

4.4 Discussion

The crystal structure of $MnRe(CO)_9(Bu^tNC)$ 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 $M_2(CO)_{10-n}(RNC)_n$ (M=Mn, Re; n=0-4).

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 0.06Å longer than the average Mn-Re bond previously reported and both the manganese-

Figure 4.2 Crystal Structure of $MnRe(CO)_9(Bu^tNC)$*



* 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)	.4643(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(10)	.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(10)	.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)	.2597(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 $Mn(CO)_5Re(CO)_4(Bu^tNC)$ [a]

Re-Mn-C1	178.4 (16)
Re-Mn-C_{eq} [b]	84.5 (11)
Mn-Re-C_{eq} [c]	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_{eq} [b]-O	173.9 (6)
Re-C_{eq} [c]-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 [d]	110.1 (6)
C-C11-C [d]	108.7 (6)

[a] Measured in degrees, e.s.d. in parentheses.

[b] Average for equatorial carbonyls.

[c] Average for C6 and C8.

[d] Average for C12, C13 and C14.

TABLE 4.8 Average Bond Lengths for the Molecule $Mn(CO)_5Re(CO)_4(Bu^tNC)$[a]

Mn-Re	2.975 (4)
Mn-C1	1.815 (9)
Mn-C_{eq}[b]	1.817 (5)
Re-C_{eq}[c]	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[d]	1.456 (5)
C-O	1.151 (3)

[a] Measured in Å with e.s.d. in parentheses.

[b] Average for C2-C5.

[c] Average fo. C6-C8.

[d] Average for C12-C14.

TABLE 4.9 A Comparison of Structural Data for Manganese - Rhenium Dimers[a]

Complex	Bond Lengths[b]			Bond Angles[c]	
	Re-Mn	Re-C	Mn-C	Re-Mn-C	Mn-Re-C
$Mn(CO)_5Re(CO)_4(Bu^tNC)$[d]	2.975(7)	1.929(7)	1.817(7)	84.5(11)	88.7(12)
cis-$Mn(CO)_5Re(CO)_4C(OCH_3)CH_3$[e]	2.972(1)	1.988(26)	1.843(20)	87.3(4)	84.3(7)
$(\eta\text{-}C_5H_5)(CO)_2MnRe(CO)_4(\mu\text{-}C(Ph)CO)$[f]	2.817(3)	1.96 (5)	1.84 (6)	-	-
$MnRe(CO)_9$ $HRe(CO)_5$[g]	2.960(3)	1.953(30)	1.823(30)	87.2(11)	85.3(14)

[a] Bond lengths in Å and bond angles in degrees, e.s.d. in parentheses

[b] Average for carbonyls.

[c] Average for equatorial carbonyls.

[d] Structure presented in this chapter.

[e] Ref. 222.

[f] Ref. 54.

[g] 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 metals (ligand-metal-ligand bond angles in the range 84.5^{o} - 95.5^{o}).

More interesting comparisons are made between the structure of $MnRe(CO)_9(Bu^tNC)$ and other substituted dimers of the formula $M_2(CO)_{10-n}(RNC)_n$ (M=Mn,Re; n=0-4) and relevant structural data is listed in Table 4.10. The structure showed the isonitrile to occupy an equatorial site on the rhenium atom. The structure was found to be staggered with dihedral angles between 43.1^{o} and 46.9^{o}. This feature of staggered equatorial ligands has been found in all the structures reported for complexes of the general formula $M_2(CO)_{10-n}(RNC)_n$ (M=Mn,Re; n=0-4). The metal-metal bond length in the mixed metal dimer 2.975Å is within one estimated standard deviation of that which might have been predicted by averaging the metal-metal bond lengths for the complexes $Mn_2(CO)_{10}$ and $Re_2(CO)_9(Bu^tNC)$.

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 $Re_2(CO)_6(XyNC)_4$, which may be due to the fact that in $Re_2(CO)_6(XyNC)_4$ all the equatorial carbonyls are trans- to an isonitrile. As expected the rhenium-carbonyl bond lengths are consistently longer than the manganese-carbonyl bond

TABLE 4.10 Structural Data for the Complexes $MM'(CO)_{10-n}(RNC)_n$ (M, M'=Mn, Re; n=0-4)[a]

Complex	M-M'	M-C_{ax}	M-C_{eq}	M-C_{iso}	M-M-C_{ax}	M-M-C_{eq}	M-M-C_{iso}	M-C-O	M-C-N	C-N-C
$Mn_2(CO)_{10}$[b]	2.904(1)	1.811(3)	1.856(2)	-	177.0(1)	86.4(1)	-	178.9(3)	-	-
$Re_2(CO)_{10}$[b]	3.041(1)	1 929(7)	1.987(6)	-	176.3(2)	86.4(2)	-	178.8(8)	-	-
$Re_2(CO)_9(Bu^tNC)$[c]	3.048(1)	1.902(19)	1.955(22)	2.068(15)	177.0(6)	86.8(5)	87.5(4)	176.1(18)	175.5(13)	175.7(18)
$Mn_2(CO)_8(Bu^tNC)_2$[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)
$Re_2(CO)_8(XyNC)_2$[c]	3.047(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)
$Re_2(CO)_7(MeNC)_3$[c]	3.049(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)
$Mn_2(CO)_6(XyNC)_4$[c]	2.946(6)	1.720(20)	1.810(20)	1.900(20)	173.0(10)	83.0(10)	90.0(10)	176.0(25)	176.0(20)	176.0(20)
$Re_2(CO)_6(XyNC)_4$[c]	3.081(2)	1.968(20)	1.952(20)	2.029(20)	178.5(8)	85.1(8)	87.9(8)	174.2(22)	176.2(18)	176.8(21)
$MnRe(CO)_9(Bu^tNC)$	2.975(4)	1.815(10)[e] 1.879(10)[f]	1.817(5)[e] 1.946(6)[f]	2.089(9)	178.4(2)[e] 177.6(9)[f]	84.5(11)[e] 89.3(12)[f]	86.7(8)	174.6(35)[e] 173.9(40)[f]	177.4(28)	175.7(31)

[a] Bond lengths in Å and angles in degrees, e.s.d. in parentheses.

[b] Ref. 15. [c] Ref. 197. [d] Ref. 209.

[e] M=Mn. [f] M=Re.

lengths. The rhenium-isonitrile bond length was found to be 0.02Å longer than the rhenium-isonitrile bond length in $Re_2(CO)_9(Bu^tNC)$.

The equatorial ligands were all found to be bending inwards towards the centre of the metal-metal bond with the deviation from the perfectly octahedral geometry (i.e. 90^o angles) being more pronounced on the manganese atom. The isonitrile ligand was bent inwards 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 $MnRe(CO)_{10}$ allowed a study of the carbonyl substitution reactions of this heteronuclear dimer to be undertaken. The reactivity of $MnRe(CO)_{10}$ is analogous to that of the homonuclear dimers (see earlier) and thus to obtain substituted derivatives in fair to good yields fairly rapidly, a catalyst must be used. No attempt to optimize catalyst or conditions was made here but generally good yields (50-70%) of monosubstituted complexes could be obtained rapidly, using the experimental conditions employed (see later).

The rate of the PdO catalysed substitution reaction of $MnRe(CO)_{10}$ with Bu^tNC 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($X=Mn(CO)_5$) causes a labilization of the cis-carbonyls in $XRe(CO)_5$ relative to $Re_2(CO)_{10}$($X=Re(CO)_5$).

The structure of the monosubstituted heteronuclear dimer $MnRe(CO)_9(Bu^tNC)$ was completely solved by X-ray crystallographic methods. This showed conclusively that the catalysed carbonyl substitution reaction of $MnRe(CO)_{10}$ 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 $M_2(CO)_{10-n}(RNC)_n$ ($n=0-4$; $M=Mn, Re$; $R=Me, Bu^t, 2,6-Me_2C_6H_3$).

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* No isomerisation of $MnRe(CO)_9(Bu^tNC)$ was observed when either the manganese or the rhenium substituted dimer was heated in i – octane solution to 90^oC for 8 hours.

4.6 Experimental

4.6.1 Synthesis of $MnRe(CO)_{10}$

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. $Mn_2(CO)_{10}$ (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 $NaMn(CO)_5$ was used *in situ* and yields were assumed to be 70%*. An appropriate amount of $Re(CO)_5Br$ (1.4mmol) was then added to the $NaMn(CO)_5$ as a thf solution (30ml). 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 mpt and infrared spectrum with the literature data.[220]

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* Yields of $NaMn(CO)_5$ were probably greater than 70% but an excess $NaMn(CO)_5$ was preferable to an excess of $Re(CO)_5Br$ in the subsequent reaction.

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

In the presence of the catalyst PdO, a solution of $MnRe(CO)_{10}$ (1mmol) and isonitrile (1.1mmol), in hexane (50ml) 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 $-5^{o}C$. Yields were between 65-75%.

The complexes were all shades of yellow. Other physical and spectral data for the complexes with R=Bu^{t}, Pr^{i}, 2,6-$Me_2C_6H_3$ and C_6H_{11} are given in Table 4.2.

4.6.3 Synthesis of $Mn_2(CO)_4(Bu^{t}NC)Re(CO)_5$(eq)

1,2-$Mn_2(CO)_8(Bu^{t}NC)_2$ was prepared from $Mn_2(CO)_{10}$ and 2.2 equivalents of $Bu^{t}NC$ using PdO catalyst as described earlier (Section 3.4.2). The required product was then synthesized in the same manner as $MnRe(CO)_{10}$(Section 4.6.1) using 1,2-$Mn_2(CO)_8(Bu^{t}NC)_2$ in place of $Mn_2(CO)_{10}$. 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 $MnRe(CO)_9(Bu^{t}NC)$

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

5. SUBSTITUTION REACTIONS OF $[CpRu(CO)_2]_2$

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.[137] Indeed, modifying the cyclopentadienyl ring can have dramatic effects on both the rate and mechanism of the carbonyl substitution reactions.[238-241]

Studied in this chapter are the substitution reactions of $[CpRu(CO)_2]_2$ with isonitriles. This metal dimer first reported in 1962, has been largely neglected when compared to the analogous iron compound $[CpFe(CO)_2]_2$.* 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 $FeRu(CO)_4Cp_2$ has been synthesised [243] and a crystal structure showed two carbonyls to be bridging.[244]

The iron dimer has been prepared by several methods [245, 246], which generally involve the reaction of an iron carbonyl with cyclopentadiene or one of its derivatives such as methylcyclopentadiene [245] or pentamethylcyclopentadiene.[246] The ruthenium dimer however, was first synthesised from $[Ru(CO)_2I_2]_n$ and NaCp.[242] Since then other ruthenium carbonyl halides and sodium cyclopentadienides have also been used.[247-249] Quantitative yields of the ruthenium dimer have been reported when synthesised from $H_4Ru_4(CO)_{12}$ and cyclopentadiene [250] in the presence of air, whereas analogous reactions using other ruthenium carbonyls give lower yields.[251,252]

The organic chemistry of the diruthenium centre stabilized by cyclopentadienyl and carbonyl ligands has only recently been reported,[253] 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 $[CpRu(CO)_2]_2$.

The monosubstituted complexes $Cp_2Fe_2(CO)_3(RNC)$ (R=Me,Et,Pr^i,Bu^t,Ph) have been prepared by direct substitution on the dimer.[254,255] The phenyl isonitrile complex has also been reported from the reduction of $CpFe(CO)(PhNC)I$.[256] Using more forcing conditions the

more highly substituted complexes $Cp_2Fe_2(CO)_2(RNC)_2$ (e.g. R=Me,Et,Bu,Ph) and $Cp_2Fe_2(CO)(RNC)_3$ (R=Me,Et,Pr^i) have been prepared but only with lower or unreported yields. The synthesis of the completely substituted dimers $Cp_2Fe_2(RNC)_4$ has been reported [257] and recently a crystal structure determination and variable temperature ^1H NMR study on complexes of this type has been performed.[258] Fewer isonitrile substituted derivatives of the ruthenium dimer have been prepared. Unspecified yields of the monosubstituted complexes $Cp_2Ru_2(CO)_3(RNC)$ (R=Me,Et,Pr^i,Bu^t) were obtained by prolonged refluxing in xylene of $\left[CpRu(CO)_2\right]_2$ and isonitrile.[255] Only with isopropyl isonitrile has the disubstituted ruthenium dimer been obtained [259], and then only in low yields from a reaction involving prolonged heating. Other reactions of the dimer carbonyls $\left[CpM(CO)_2\right]_2$ which are relevant to this work include the reaction with halogenated hydrocarbons CX_4(X=Cl,Br) to give the carbonyl halides $CpM(CO)_2X$ (M=Fe,[260] Ru [261,262]). The same carbonyl halides are produced by the thermal metal-metal bond cleavage of the dimers in the presence of the halogens X_2 (M=Fe,[263,264] Ru[252,265]).

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

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

$$Cp(CO)_2Fe(\mu\text{-}CO)Fe(CO)(PR_3)Cp \ .$$

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, $P(OR)_3$, gives a mixture of products $CpRu(CO)_2R$ and $CpRu\left(P(OR)_3\right)_2\left(P(O)(OR)_2\right)$.[268] Under vigorous conditions (140°C, 48 hours) a mixture of $Cp_2Ru_2(CO)_3(PR_3)$ and $CpRu(CO)(PR_3)H$ was obtained from $\left[CpRu(CO)_2\right]_2$ and phosphine PR_3 (R_3=Pr^n_3, Me_2Ph) and when excess PMe_2Ph was used $CpRu(PMe_2Ph)_2H$ was prepared.[268] 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.[241]

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

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}H and ^{13}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 $Cp_2Fe_2(CO)_{4-n}(RNC)_n$ (n=1,2) have been shown to exist in solution as a mixture of rapidly interconverting structural isomers.[187,274]

In this chapter the catalysed carbonyl substitution reactions,[275] as developed for other systems e.g. $Mn_2(CO)_{10}$,[195] $Re_2(CO)_{10}$,[197] $Fe(CO)_5$[276] 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 $\left[CpRu(CO)_2\right]_2$ system, and will be elaborated on in future work.[235] The ultimate objectives of this work include the catalysed synthesis of the complexes in the series $Cp_2Ru_2(CO)_{4-n}(RNC)_n$(n=1-4) and a study of both the chemistry of these substituted dimers

(e.g. reaction with electrophiles [277]) and their possible role as catalysts especially in those reactions in which $\left[CpRu(CO)_2\right]_2$ has already found a use.[272,273]

5.2 Results

The catalysed reactions of the dimer $\left[CpRu(CO)_2\right]_2$ 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. Bu^tNC 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 $\left[MpFe(CO)_2\right]_2$ ($Mp=C_5Me_5$) or PtO_2 as catalyst, yields > 50% of crude product $Cp_2Ru_2(CO)_3(RNC)$ were obtained, after only 6 hours stirring in refluxing toluene. Of the catalysts considered in this study the best was found to be PdO which for Bu^tNC 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. $C_6H_{11}NC$, 80% yield after 1 hour and $2,6\text{-}Me_2C_6H_3NC$, 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 derivates 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 $Cp_2Ru_2(CO)_3(Bu^tNC)$. 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.[255] 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 $Cp_2Ru_2(CO)_3(RNC)$ (R=Me,Et,Pr^i) using variable temperature ^1H NMR but only terminal isomers for the tertiary butyl derivative were observed.[255]

The disubstituted complex $Cp_2Ru_2(CO)_2(Bu^tNC)_2$ was observed when excess Bu^tNC was reacted with $[CpRu(CO)_2]_2$ in the presence of PdO and after prolonged heating (110°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 $Cp_2Ru_2(CO)_2(Pr^iNC)_2$.[259]

5.3 Conclusions

This work indicates that the use of catalysts to synthesize the monosubstituted derivatives $Cp_2Ru_2(CO)_3(RNC)$ 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 hightly substituted derivatives was made here but the complex $Cp_2Ru_2(CO)_2(Bu^tNC)_2$

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

TABLE 5.1 Catalysis of $[CpRu(CO)_2]_2$ Carbonyl Substitution [a]

Isonitrile	Catalyst	Time(hours)	Yield(%) [b]
Bu^tNC	NONE	24	30
Bu^tNC	$[MpFe(CO)_2]_2$	6	50
Bu^tNC	PtO_2	6	55
Bu^tNC	PdO	2	80
MeNC	"	4	65
Pr^iNC	"	1	45
$C_6H_{11}NC$	"	1	80
$2,6\text{-}Me_2C_6H_3NC$	"	5	90

[a] All reactions done in refluxing toluene using a mole ratio of reactants $[CpRu(CO)_2]_2$: RNC of approximately 1:1.1 .

[b] Estimated by infrared spectroscopy .

TABLE 5.2 Spectral Data for the Complexes $Cp_2Ru_2(CO)_3(RNC)$

R	Infrared (cm^{-1})[a]							NMR[b,c]		
								Cp		
Me	2160(w)	2060(w)	2000(vs)	1960(s)	1800(m)	1755(m)	1730(s)	4.74	-	3.05
Pr^i	2150(sh)	2130(m)	2005(vs)	1960(vs)	1800(m)	1775(s)	1710(m)	4.83	3.42[d]	1.10[e]
Bu^t	2125(m)	2090(sh)	1995(sh)	1950(s)	-	1765(vs)	-	4.89	-	0.90
Cy[f]	2130(w)	2100(sh)	1990(vs)	1945(s)	1795(w)	1760(m)	1705(w)	4.92/4.75	-	0.98-0.74[d]
Xy[g]	2140(m)	2100(sh)	1990(vs)	1955(sh)	1805(w)	1789(m)	1775(m)	4.80	6.68[d]	2.17

[a] Recorded in CH_2Cl_2 (cm^{-1}).

[b] Recorded in C_6D_6 relative to TMS(δ).

[c] $\left[CpRu(CO)_2\right]_2$ gives a singlet, δ = 4.76 ppm.

[d] Broad.

[e] Doublet J = 3.5 Hz.

[f] Cy = C_6H_{11}.

[g] Xy = 2,6-$Me_2C_6H_3$.

was observed when a solution of $\left[CpRu(CO)_2\right]_2$ and 2 mole equivalents of Bu^tNC 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 ($\left[MpFe(CO)_2\right]_2$[246]) or obtained from chemical suppliers (see Appendix A).

5.4.2 Synthesis of $\left[CpRu(CO)_2\right]_2$

The crude product, was synthesized by the literature method[252] 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 $-5^{o}C$) for several weeks before noticable decomposition occurred. The product was identified by infrared and ^{1}H NMR spectroscopy and microanalysis found C=37.90%, H=2.41%; $C_{14}H_{10}O_4Ru_2$ requires C=37.83%, H=2.27%.

5.4.3 Synthesis of $Cp_2Ru_2(CO)_3(RNC)$

$$\left[CpRu(CO)_2\right]_2 + RNC \longrightarrow Cp_2Ru_2(CO)_3(RNC) \quad . \qquad 5.4.1$$

Catalyst (20mg) and RNC (0.22 mmol) was added to a solution of $\left[CpRu(CO)_2\right]_2$ 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 $-5^{o}C$.

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 Schubert and Sheline [86] 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 $\left[(C_7H_7)Fe(CO)_3\right]$ and $\left[Mn(CO)_4Br\right]_2$.[87]

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

was obtained from the reaction between $Mn(CO)_5^-$ and $Fe(CO)_5$ and its structure was proposed to be that of a trigonal cluster analogous to $\left[HFe_3(CO)_{11}\right]^-$ with which it is isoelectronic.[94]

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

The infrared spectrum of the complexes $M_2Fe(CO)_{14}$ (M_2=Mn_2, Re_2, MnRe) were recorded in hexane solution and show 3, 4 and 5 terminal carbonyl bonds respectively.[71,86,87,220*] 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.[220] An added problem related to product characterisation is the decomposition of these complexes in organic solvents.[220]

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 $Mn_2Fe(CO)_{14}$ by an X-ray crystallographic structure determination,[90,278] from which a mean Mn-Fe distance of 2.815Å was reported. Levy et al [92] have also refined crystallographic data for $Re_2Fe(CO)_{14}$ in which the Re-Fe distances of

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* No absorptions in the bridging carbonyl region were observed.

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2.876Å and 2.849Å were found. Few other details of this structure were however reported.

An investigation of the metal-metal stretching frequencies of the compounds $MM'Fe(CO)_{14}$ ($MM'=Mn_2$, MnRe) established force constants for the metal-metal bonds.[49] The electronic structure of these trinuclear carbonyls was investigated by Gray et al [88] and compared to those of other trinuclear carbonyls such as $M_3(CO)_{12}$ (M=Ru, Os, Fe). The lowest electronic excitation was predicted to be a $\sigma \rightarrow \sigma^*$ 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 $MM'Fe(CO)_{14}$ ($MM'=Mn_2, Re_2$, MnRe) respectively. With the structural[90,92,278] and spectral [49,71,220] data for these linear trinuclear carbonyls available a quantum-mechanical study was undertaken [89] to develop potential models and calculate atomic and average molecular polarizabilities.

There are no reported reactions of the linear trimers $MM'Fe(CO)_{14}$ (M,M'=Mn,Re) either resulting in cleavage of a metal-metal bond or involving carbonyl ligand substitution, other than the reported decomposition in organic solvents.[220] 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:

$$2NaM(CO)_5 + Fe(CO)_4X_2 \longrightarrow M_2Fe(CO)_{14} + 2NaX \qquad 6.1$$

$$2M(CO)_5X + Na_2Fe(CO)_4 \longrightarrow M_2Fe(CO)_{14} + 2NaX \qquad 6.2$$

(M=Mn,Re; X=halide).

Thus the situation is similar to that for the synthesis of $MnRe(CO)_{10}$ (see Chapter 4) and as with the $MnRe(CO)_{10}$ only one of the two possible routes was found to give the required product.[57] 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[a]	Infrared Spectra[b]
$Re_2Fe(CO)_{14}$[c]	white	163-165	2097(m)2020(s)1983(m)
$Mn_2Fe(CO)_{14}$	red	115-117	2068(m)2020(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)1939(s)

[a] Uncorrected values in ^oC.

[b] Recorded in hexane (cm^{-1}).

[c] Mass spectrometry gave a molecular ion of 822($Re_2Fe(CO)_{14}$ requires M=821.99, based on ^{187}Re).

[d] Mass spectrometry gave a molecular ion or 877($Re_2Fe(CO)_{13}(Bu^tNC)$ requires M=877.11, based on ^{187}Re).

[e] ^1H NMR gives a singlet at 0.86 ppm in C_6D_6.

[f] ^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 $Mn_2Fe(CO)_{14}$ 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 analagous rhenium trimer, $Re_2Fe(CO)_{14}$. The reaction of $NaRe(CO)_5$ and $Fe(CO)_4I_2$, (6.1), (M=Re; X=I) gave the desired product $Re_2Fe(CO)_{14}$ in moderate yields (20-40% based on $Re_2(CO)_{10}$). The alternative approach, (6.2), (M=Re, X=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 $M_2Fe(CO)_{14}$ (M=Mn, Re) is presented in Table 6.1.

Having devised a route to the trimer $Re_2Fe(CO)_{14}$ an attempt was then made to investigate the chemistry of the linear trimer. In particular the reaction with isonitrile

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* $Na_2Fe(CO)_4$ was synthesized by a modification of the literature method[279] 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 $Re_2Fe(CO)_{13}(RNC)$. The reaction of the trimer with isonitrile in the presence of a catalyst was expected to give a substituted trimer, $M_2Fe(CO)_{13}(RNC)$ and from a knowledge of the catalysed substitution reactions of $Fe(CO)_5$ [276] and $Re_2(CO)_{10}$,[197] the substitution might be expected to occur at the iron atom.

The reaction with Bu^tNC 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 $Re(CO)_5I$ and $Na_2Fe(CO)_3(Bu^tNC)$ (synthesized by a modified literature procedure [270]). 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 ($Re_2Fe(CO)_{13}(Bu^tNC)$ requires 877.11). Other important fragments that were observed are 168. ($Fe(CO)_4$, M=167.89) and 382 ($Re(CO)_4(Bu^tNC)$, 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)Å 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, $Re_2Fe(CO)_{14}$, 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 $NaFe(CO)_3(Bu^tNC).Re(CO)_5$. Thus the substitution reaction of the unsubstituted trimer with Bu^tNC 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 [197] to be $Re_2(CO)_8(Pr^iNC)_2$. 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 "$\cdot Re(CO)_4(Pr^iNC)$" and "$\cdot Fe(CO)_4$" and 3) rapid decomposition or reformation of metal-metal bonds giving 1,2-$Re_2(CO)_8(Pr^iNC)_2$ and other unidentified metal compounds.

Clearly further work is required to establish the viability of the catalysed substitution reaction on the trimer $Re_2Fe(CO)_{14}$ 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 $Re_2Fe(CO)_{14}$. The heterotrimetallic carbonyl $MnReFe(CO)_{14}$ 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 $Fe(CO)_4I_2$ [280]

$Fe(CO)_5$ (5mmol) was stirred in a two necked flask under an inert atmosphere in a cold bath ($\pm$ 0°C). I_2 (5.2mmol) was then added dropwise as a cooled chloroform solution (50ml) over a period of 10 mins. Stirring at 0°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 [281] and analysis found C=11.41%, I=57.65%; $C_4O_4FeI_2$ requires C=11.39%, I=56.19. Before use. $Fe(CO)_4I_2$ was stored in the dark, under nitrogen and at -5°C.

6.4.2 Synthesis of $Fe(CO)_3(Bu^tNC)I_2$

This was synthesized as above but replacing $Fe(CO)_5$ by $Fe(CO)_4(Bu^tNC)$, which was prepared by the catalytic method [276] from $Fe(CO)_5$ and Bu^tNC. The product, a black solid, was obtained in 45% yield based on $Fe(CO)_5$, and was

identified by comparison of mpt (72-74°C, decomp.) and infrared spectra (γNC,2200(vs)cm^{-1}: γCO,2100(s), 2065(m), 2045(m)cm^{-1}, $CHCl_3$) with those in the literature.[281]

6.4.3 Synthesis of $Re(CO)_5I$

See Chapter 4.

6.4.4 Synthesis of $Mn(CO)_5I$

A solution of $Mn_2(CO)_{10}$ (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 $\pm$5 min stirring at room temperature (20°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 $NaMn(CO)_5$.[218] A tetrahydrofuran solution of I_2 (10.5mmol, 25ml) was then added dropwise to the $NaMn(CO)_5$. 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 I_2 and after drying the solution with anhydrous sodium sulphate, solvent removal

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

6.4.5 Synthesis of $NaRe(CO)_5$ [218]

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°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 $Na_2Fe(CO)_4$ [279]

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. $Na_2Fe(CO)_4$ was used *in situ* and the synthesis was assumed to be quantitative based on $Fe(CO)_5$.

6.4.7 Synthesis of $Na_2Fe(CO)_3(Bu^tNC)$

$Fe(CO)_4(Bu^tNC)$ was synthesized from $Fe(CO)_5$ and Bu^tNC,[276] this was then used as a tetrahydrofuran solution in the same manner as $Fe(CO)_5$ in the previously described synthesis of $Na_2Fe(CO)_4$. Being even more air-sensitive than $Na_2Fe(CO)_4$, the product $Na_2Fe(CO)_3(Bu^tNC)$ 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 $Re_2Fe(CO)_{14}$

a) Reaction of $NaRe(CO)_5$ + $Fe(CO)_4I_2$

$Fe(CO)_4I_2$ (1.5mmol) in tetrahydrofuran (30ml) was added dropwise to a solution of $NaRe(CO)_5$ (2.8mmol) in tetrahydrofuran (25ml) maintaining an inert atmosphere. The reaction was stirred for a further two hours at room temperature (20^oC). 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 $\pm 60^{\circ}C$ the solvent was removed and on cooling to room temperature microcrystals formed. Cooling the solution in a dichloromethane slush ($-77^{\circ}C$) a pale yellow powder was collected by decanting off the solvent at low temperature. This pale yellow powder was identified by infrared spectroscopy [220] and melting point 163-165°C (uncorrected; lit. 163°C [91]). The yield was estimated to be 24% based on $NaRe(CO)_5$.

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, $Re_2Fe(CO)_{14}$, is presented in Table 6.1.

b) Reaction of $Na_2Fe(CO)_4$ and $Re(CO)_5I$

$Re(CO)_5I$ (2mmol) in tetrahydrofuran (30ml) was added to $Na_2Fe(CO)_4$ (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 $Re_2Fe(CO)_{13}(Bu^tNC)$

a) Reaction of $Re_2Fe(CO)_{14}$ with Bu^tNC

Bu^tNC (0.1mmol) was added to $Re_2Fe(CO)_{14}$ (0.09mmol) in tetrahydrofuran (50ml) with 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 $Re_2Fe(CO)_{13}(Bu^tNC)$ by both methods (a) and (b) were found to be 25 - 30%.

b) Reaction of $NaRe(CO)_5$ with $Fe(CO)_3(Bu^tNC)I_2$

A solution of $Fe(CO)_3(Bu^tNC)I_2$ (2.5mmol) in tetrahydrofuran was added dropwise to a $NaRe(CO)_5$ (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 $Re_2Fe(CO)_{14}$ and Bu^tNC (6.4.9a), and are presented in Table 6.1.

6.4.10 Synthesis of $Mn_2Fe(CO)_{14}$

$Mn(CO)_5I$ (2mmol) was added dropwise as a tetrahydrofuran solution to a solution of $Na_2Fe(CO)_4$ (1mmol, estimated). After 2½ 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 $Mn_2(CO)_{10}$. Use of a continuous Soxhlet extraction on the brown powder (hexane at $\pm$ 60°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°C (Lit. 112°C, [86]) and infrared spectroscopy (Table 6.1), (yield 15-20%).

6.4.11 Reaction of $Re_2Fe(CO)_{14}$ and Pr^iNC

The reaction described earlier (6.4.9a) was repeated using isopropyl isonitrile in place of Bu^tNC.

The tetrahydrofuran solution containing both reactants and PdO 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 $Re_2(CO)_{10}$[197] the product was identified as 1,2-$Re_2(CO)_8(Pr^iNC)_2$ and was isolated in 40% yield.

7. 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 $M_2(CO)_{10-n}(RNC)_n$ (M=Mn, Re; n=0-2) with isonitriles, resulted in a comprehensive set of rate constants for both the catalysed and uncatalysed (when $t_{\frac{1}{2}} < 4$ hours, at 120°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 $M_2(CO)_{10-n}(RNC)_n$ (M=Mn, Re; n=1-4) which proceed rapidly at ambient temperatures, whereas the uncatalysed reactions recuired prolonged heating. The Arrhenius plots for the reaction:

$$Mn_2(CO)_9(Bu^tNC) + Bu^tNC \xrightarrow{-CO} Mn_2(CO)_8(Bu^tNC)_2$$

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 $Mn_2(CO)_8(Bu^tNC)_2$ 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 $M_2(CO)_9(Bu^tNC)$ 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 ($X=M(CO)_m(Bu^tNC)_n$) was determined. The results presented earlier suggest orders of increasing cis-labilization are:

$$M(CO)_5 < M(CO)_4(Bu^tNC) < M(CO)_3(Bu^tNC)_2 \quad (M=Mn,Re)$$

and

$$Re(CO)_5 < Mn(CO)_5.$$

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

$Mn_2(CO)_{10-n}L_n$ (L=phosphine; n=1,2) are consistent with axial phosphine substitution,[151] whereas the di-rhenium analogues are known with both axial and equatorially substituted phosphines.[159,284] Such observations are consistent with the proposed importance of steric factors, as the metal-metal bond length is approximately 0.2Å longer in the rhenium dimers.

The movement of ligands (RNC,CO) between metal atoms was observed for the complex $Mn_2(CO)_8(Bu^tNC)_2$ but not for the rhenium analogue or for the mixed metal dimer $MnRe(CO)_9(Bu^tNC)$. 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 $Mn_2(CO)_8(Bu^tNC)_2$ was found to be intramolecular and unimolecular and a mechanism involving two bridging ligands, analogous to that widely accepted for $[CpFe(CO)_2]_2$[187], was proposed.

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

determination. Indeed the molecule $MnRe(CO)_9(Bu^tNC)$ 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. $d_{Mn-Re} = 2.975\text{Å}$, $d_{Mn-CO} = 1.816\text{Å}$, $d_{Re-CO} = 1.896\text{Å}$ etc. A bending of the equatorial ligands was observed with an average metal-metal-equatorial carbonyl angle of 86.4°, similar to data reported for the analogous homonuclear dimers. The manganese substituted complex $MnRe(CO)_9(Bu^tNC)$ was synthesised indirectly and an X-ray crystal structure determination on this dimer is to be performed in the near future.

The reactions of $\left[CpRu(CO)_2\right]_2$ with a variety of isonitriles to give $Cp_2Ru_2(CO)_3(RNC)$ 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 $Re_2Fe(CO)_{14}$ was prepared from $Re_2(CO)_{10}$ and $Fe(CO)_5$ via $NaRe(CO)_5$ and $Fe(CO)_4I_2$ 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 $Re_2Fe(CO)_{14}$ 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 A

THE 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,

Pd/C (5%)

(b) B. Owen Jones,

Na (metal).

(c) Fluka A. G. Chemicals,

Bu^tNC, Pr^iNC, $C_6H_{11}NC$, $2,6\text{-}Me_2C_6H_3NC$.

(d) Johnson Matthey Chemicals Limited,

PdO, PtO_2, $CoCl_2.6H_2O$.

(e) Merck Chemicals,

$Pd/CaCO_3$ (10%), molecular sieve (type 4Å), KI, benzophenone, silica gel and alumina.

(f) Protea Laboratory Services,

I_2, sodium thiosulphate.

(g) SAAR Chem. Pty. Ltd.,

Br_2.

(h) Strem Chemicals Incorporated,

$Fe(CO)_5$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$.

Appendix B

GENERAL 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 ($\pm 0.5^{o}C$) 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°C, either from hexane or a mixture of hexane and other organic solvents.

(d) Instrumentation

Infrared spectra were recorded using NaCl cells of either 0.1 or 0.05 mm pathlength on either a Jasco IRA-1, a Pye Unicam SP 300 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.L., C.S.I.R., Pretoria, under the instruction of Dr. M. O. Albers.

All nuclear magnetic resonance spectra were recorded using a Varian EM360A NMR spectrophotometer or a Bruker WP 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. P. Boshoff using a Varian Mat CH7 mass spectrometer or by Dr. L. Fourie at Potchefstroom University.*

Microanalysis were performed by Microanalytical Division of N.C.R.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-Debyeflex 1001 fully stabalized X-ray generator. The intensity data was collected by Mr. J. Albain at the N.P.R.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 C

X-RAY CRYSTAL STRUCTURE DATA

Tables for the final atomic coordinates of the atoms in the molecule $MnRe(CO)_9(Bu^tNC)$ 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 CH_3 groups and only an isotropic temperature factor was determined.

TABLE C1 Isotropic Temperature Factors for Methyl Group Protons

Methyl Group Carbon Atom	Isotropic Temperature Factor	
	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 $MnRe(CO)_9(Bu^tNC)$

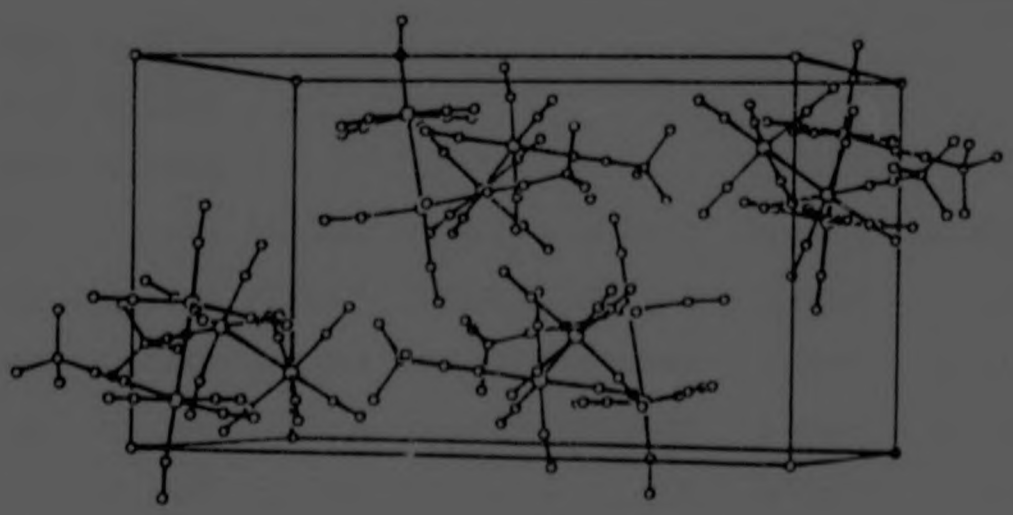


TABLE C2 Anisotropic Temperature Factors for Molecule 1

	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	0.0087	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					
01	0.2477	0.0304	0.0794	0.0082	0.0035	0.0149
02	0.0566	0.0695	0.0583	0.0042	0.0055	0.0242
03	0.0379	0.0943	0.1258	0.0195	0.0117	0.0047
04	0.1093	0.0916	0.0918	0.0010	-0.0187	-0.0358
05	0.0590	0.1096	0.0854	0.0071	0.0228	0.0048
06	0.0557	0.0979	0.0886	0.0050	0.0024	-0.0259
07	0.0513	0.1419	0.0880	-0.0244	0.0092	-0.0327
08	0.1145	0.0628	0.0999	0.0163	0.0170	0.0167
09	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

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC
2	0	0	634	-632
4	0	0	72	78
6	0	0	77	66
8	0	0	81	87
10	0	0	75	58
14	0	0	78	-74
16	0	0	124	134
2	1	0	138	-227
3	1	0	158	-234
4	1	0	159	203
5	1	0	211	255
6	1	0	90	-102
7	1	0	135	-153
9	1	0	21	14
10	1	0	26	27
11	1	0	46	42
12	1	0	80	-82
13	1	0	24	-22
14	1	0	71	81
15	1	0	44	-45
17	1	0	20	-7
1	2	0	47	-72
2	2	0	65	-104
3	2	0	32	28
4	2	0	47	62
5	2	0	62	98
6	2	0	54	-84
7	2	0	211	-307
8	2	0	45	65
9	2	0	243	344
10	2	0	43	-73
11	2	0	133	-185
12	2	0	50	66
13	2	0	47	65
14	2	0	39	-58
2	3	0	36	-47
3	3	0	103	132
4	3	0	132	165
5	3	0	230	-312
6	3	0	103	-128
7	3	0	125	174
8	3	0	21	-8
10	3	0	37	40
11	3	0	74	-102
12	3	0	78	-105
13	3	0	39	49
14	3	0	54	84
15	3	0	33	-38
16	3	0	37	-82
0	4	0	418	-528
1	4	0	174	220
2	4	0	172	219
3	4	0	179	-223
4	4	0	110	-130
5	4	0	147	183
6	4	0	42	-41
7	4	0	71	-93
8	4	0	151	169
9	4	0	59	77
10	4	0	112	-128
11	4	0	75	-95
12	4	0	29	36
13	4	0	60	82
14	4	0	23	29
15	4	0	37	-52
16	4	0	55	-67
1	5	0	44	-57
2	5	0	212	232
3	5	0	136	153
4	5	0	245	-271
5	5	0	158	-183
6	5	0	140	161
7	5	0	125	142
8	5	0	103	-118
9	5	0	28	-23
10	5	0	33	47
11	5	0	25	-30
12	5	0	29	24
13	5	0	42	51
14	5	0	53	-57
0	6	0	222	-247
1	6	0	303	347
2	6	0	94	116
3	6	0	189	-182
4	6	0	243	-243
5	6	0	50	51
6	6	0	154	170
7	6	0	99	84
8	6	0	133	-143
9	6	0	144	-139
10	6	0	107	114
11	6	0	58	50
12	6	0	110	-115
14	6	0	67	72
15	6	0	30	-28
16	6	0	31	-33
1	7	0	104	107
2	7	0	150	159
3	7	0	114	-116
4	7	0	199	-208
5	7	0	144	148
6	7	0	90	98
7	7	0	43	-45
9	7	0	29	-20
10	7	0	43	-47
11	7	0	106	97
12	7	0	72	64
13	7	0	99	-83
14	7	0	57	-49
15	7	0	71	68
16	7	0	24	23
0	8	0	59	64
1	8	0	144	-136
2	8	0	25	-13
3	8	0	161	160
4	8	0	133	-138
5	8	0	148	-150
6	8	0	200	203
7	8	0	63	57
8	8	0	277	-269
10	8	0	189	180
11	8	0	45	38
12	8	0	101	-92
14	8	0	30	32
15	8	0	26	20
1	9	0	37	44
2	9	0	191	-178
3	9	0	130	-124
4	9	0	155	150
6	9	0	57	-65
8	9	0	90	87
11	9	0	36	24
13	9	0	77	-74
14	9	0	48	44
15	9	0	47	43
0	10	0	22	-21
1	10	0	354	-336
2	10	0	41	31
3	10	0	240	224
4	10	0	58	49
5	10	0	120	-105
7	10	0	61	55
9	10	0	22	-1
12	10	0	26	18
13	10	0	44	-32
14	10	0	27	-5
15	10	0	67	60
3	11	0	131	123
4	11	0	100	90
5	11	0	186	-175
6	11	0	129	-125
7	11	0	100	90
8	11	0	51	48
9	11	0	43	45
11	11	0	56	-65
13	11	0	46	44
15	11	0	33	-30
0	12	0	52	32
1	12	0	116	-103
3	12	0	74	62
4	12	0	110	85
5	12	0	57	-50
6	12	0	153	-137
7	12	0	89	74
8	12	0	211	189
9	12	0	69	-50
10	12	0	124	-109
11	12	0	37	25
12	12	0	95	74
13	12	0	42	-28

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
14	12	0	42	-31	2	16	0	121	-91	4	20	0	120	-77	-8	1	1	121	-91	-3	2	1	224	-179
1	13	0	62	-53	3	16	0	101	-80	6	20	0	56	37	-7	1	1	139	-108	-2	2	1	373	-313
2	13	0	34	28	4	16	0	108	93	1	21	0	27	-22	-6	1	1	98	79	-1	2	1	174	152
3	13	0	84	77	5	16	0	80	54	2	21	0	24	-2	-5	1	1	204	167	0	2	1	631	590
4	13	0	86	-81	7	16	0	79	-57	3	21	0	64	42	-4	1	1	128	-106	1	2	1	129	-120
6	13	0	80	75	8	16	0	62	-55	5	21	0	60	-33	-3	1	1	202	-173	2	2	1	518	-501
7	13	0	41	-33	9	16	0	73	54	7	21	0	49	22	-2	1	1	252	-209	3	2	1	152	149
10	13	0	31	-39	10	16	0	30	30	0	22	0	99	-71	-1	1	1	104	100	4	2	1	264	254
11	13	0	54	-40	11	16	0	62	-49	2	22	0	78	49	1	1	1	77	-77	5	2	1	23	-33
12	13	0	30	40	1	17	0	39	24	3	22	0	39	26	2	1	1	284	238	6	2	1	70	-66
13	13	0	70	53	2	17	0	40	30	4	22	0	-2	-17	3	1	1	39	31	7	2	1	80	74
14	13	0	39	-33	3	17	0	67	-42	5	22	0	73	-49	4	1	1	150	-128	8	2	1	104	92
0	14	0	170	146	5	17	0	36	28	2	23	0	38	27	5	1	1	160	140	9	2	1	68	-63
1	14	0	149	128	6	17	0	25	-33	-13	0	1	29	22	6	1	1	133	118	11	2	1	81	72
2	14	0	143	-119	7	17	0	28	-18	-11	0	1	180	-122	7	1	1	173	-156	13	2	1	63	-58
3	14	0	62	-47	10	17	0	34	35	-9	0	1	262	215	8	1	1	98	-74	14	2	1	31	-20
4	14	0	108	84	0	18	0	56	-53	-7	0	1	405	-348	9	1	1	23	24	15	2	1	52	49
6	14	0	129	-100	2	18	0	52	45	-5	0	1	373	336	10	1	1	48	38	16	2	1	71	77
8	14	0	132	101	3	18	0	72	-62	-3	0	1	181	-164	11	1	1	78	75	-14	3	1	45	-43
10	14	0	83	-60	4	18	0	69	-47	3	0	1	71	-87	13	1	1	44	-40	-12	3	1	55	52
11	14	0	38	30	5	18	0	120	95	5	0	1	115	106	14	1	1	79	-61	-9	3	1	60	-52
12	14	0	42	30	6	18	0	83	44	7	0	1	241	210	15	1	1	36	28	-8	3	1	78	-62
1	15	0	32	22	7	18	0	98	-73	9	0	1	386	-343	16	1	1	54	51	-7	3	1	75	-76
3	15	0	82	-59	8	18	0	62	-40	11	0	1	297	256	17	1	1	20	-27	-6	3	1	164	139
4	15	0	75	-74	9	18	0	91	58	13	0	1	121	-93	-16	2	1	102	95	-5	3	1	214	205
5	15	0	75	56	10	18	0	41	28	15	0	1	104	84	-14	2	1	107	-85	-4	3	1	181	-168
6	15	0	92	83	1	19	0	33	-31	17	0	1	25	-21	-13	2	1	48	47	-3	3	1	278	-265
7	15	0	60	-52	2	19	0	49	-22	-16	1	1	55	-41	-11	2	1	64	-53	-2	3	1	259	233
8	15	0	35	-34	3	19	0	52	47	-14	1	1	129	100	-10	2	1	24	44	-1	3	1	255	244
9	15	0	41	41	4	19	0	32	24	-13	1	1	29	17	-9	2	1	35	27	0	3	1	116	-116
10	15	0	28	-29	10	19	0	22	25	-12	1	1	159	-135	-7	2	1	106	-85	1	3	1	145	-148
12	15	0	26	17	0	20	0	114	-78	-11	1	1	47	37	-6	2	1	45	52	2	3	1	174	-146
0	16	0	50	34	2	20	0	129	89	-10	1	1	149	116	-5	2	1	219	174	3	3	1	46	46
1	16	0	124	116	1	20	0	25	20	-9	1	1	36	-29	-4	2	1	113	105	4	3	1	22	14

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	3	1	158	147	11	4	1	136	-141	-16	6	1	31	-38	-6	7	1	105	-116	5	8	1	155	187
6	3	1	108	-118	12	4	1	107	125	-14	6	1	38	35	-4	7	1	179	231	6	8	1	108	107
7	3	1	147	-138	13	4	1	45	41	-12	6	1	25	32	-3	7	1	161	210	7	8	1	81	-85
8	3	1	73	75	14	4	1	61	-87	-11	6	1	62	85	-2	7	1	204	-267	8	8	1	95	-102
9	3	1	60	55	-15	5	1	37	-48	-10	6	1	73	-94	-1	7	1	209	-269	10	8	1	60	68
10	3	1	45	-47	-14	5	1	41	-72	-9	6	1	25	-32	0	7	1	23	58	12	8	1	37	-52
12	3	1	28	-26	-13	5	1	55	65	-8	6	1	108	144	1	7	1	204	263	14	8	1	25	28
13	3	1	28	-22	-12	5	1	101	139	-7	6	1	81	76	2	7	1	120	153	15	8	1	22	-26
14	3	1	56	53	-11	5	1	103	-125	-6	6	1	125	-168	3	7	1	24	-21	-15	9	1	58	46
15	3	1	42	41	-10	5	1	110	-128	-5	6	1	193	-218	4	7	1	68	-72	-13	9	1	77	-76
16	3	1	38	-33	-9	5	1	67	83	-4	6	1	106	132	5	7	1	57	-74	-12	9	1	41	-36
-14	4	1	50	-59	-8	5	1	83	91	-3	6	1	308	371	7	7	1	105	129	-11	9	1	110	106
-12	4	1	108	96	-7	5	1	28	1	-1	6	1	97	-124	9	7	1	66	-77	-10	9	1	97	88
-11	4	1	47	35	-6	5	1	28	-34	1	6	1	69	100	11	7	1	26	26	-9	9	1	94	-90
-10	4	1	108	-95	-5	5	1	48	-38	2	6	1	40	48	12	7	1	32	37	-8	9	1	71	-51
-9	4	1	164	-170	-4	5	1	85	78	3	6	1	101	-138	14	7	1	43	-54	-7	9	1	27	30
-8	4	1	60	38	-3	5	1	27	-21	4	6	1	32	-48	15	7	1	39	-55	-5	9	1	123	-124
-7	4	1	243	252	-2	5	1	211	230	5	6	1	102	148	-15	8	1	62	63	-5	9	1	52	63
-6	4	1	88	-95	0	5	1	43	-54	6	6	1	30	-27	-14	8	1	56	48	-4	9	1	195	210
-5	4	1	199	-209	1	5	1	66	-62	7	6	1	54	-85	-13	8	1	62	-60	-3	9	1	74	-82
-4	4	1	182	187	2	5	1	26	-33	8	6	1	77	100	-12	8	1	74	-58	-2	9	1	182	-193
-3	4	1	43	-14	3	5	1	100	110	9	6	1	59	79	-10	8	1	68	57	0	9	1	100	112
-2	4	1	250	-255	4	5	1	142	154	10	6	1	114	-156	-9	8	1	42	-41	1	9	1	85	76
0	4	1	38	67	5	5	1	166	-179	11	6	1	82	-100	-7	8	1	30	-38	2	9	1	96	-96
1	4	1	164	-170	6	5	1	152	-160	12	6	1	82	114	-6	8	1	25	38	3	9	1	103	-103
2	4	1	196	-196	7	5	1	135	152	13	6	1	52	70	-4	8	1	57	-81	4	9	1	24	23
3	4	1	113	114	8	5	1	131	135	14	6	1	24	-46	-3	8	1	107	115	5	9	1	101	107
4	4	1	320	318	9	5	1	33	-52	15	6	1	37	-50	-2	8	1	46	64	6	9	1	145	139
5	4	1	52	-63	10	5	1	49	-47	-16	7	1	32	31	-1	8	1	231	-263	7	9	1	112	-125
6	4	1	226	-217	11	5	1	55	-43	-13	7	1	48	58	0	8	1	41	-67	8	9	1	104	-92
7	4	1	152	-158	13	5	1	40	33	-11	7	1	66	-84	1	8	1	308	365	10	9	1	28	3
8	4	1	126	133	14	5	1	45	62	-10	7	1	70	-79	2	8	1	70	84	11	9	1	52	56
9	4	1	196	203	15	5	1	32	-36	-9	7	1	83	89	3	8	1	298	-355	13	9	1	41	-42
10	4	1	90	-103	16	5	1	26	-49	-8	7	1	112	123	4	8	1	167	-183	15	9	1	23	16

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-15	10	1	27	27	-2	11	1	114	110	9	12	1	29	-35	-6	14	1	133	-117	4	15	1	59	-43
-12	10	1	31	-28	-1	11	1	108	109	10	12	1	71	58	-5	14	1	29	18	5	15	1	48	-35
-10	10	1	109	92	0	11	1	105	-90	12	12	1	56	-40	-4	14	1	104	83	6	15	1	87	73
-9	10	1	23	-9	1	11	1	42	-32	14	12	1	46	39	-3	14	1	42	-29	7	15	1	53	43
-8	10	1	242	-227	2	11	1	52	-51	-14	13	1	38	38	-2	14	1	28	-14	8	15	1	56	-52
-6	10	1	286	263	3	11	1	72	-73	-13	13	1	27	29	-1	14	1	86	78	9	15	1	83	-76
-5	10	1	170	149	4	11	1	106	96	-11	13	1	39	-25	0	14	1	33	-25	11	15	1	41	49
-4	10	1	218	-208	5	11	1	90	77	-10	13	1	35	-28	1	14	1	172	-149	-11	16	1	24	-14
-3	10	1	159	-150	6	11	1	53	-59	-8	13	1	29	10	2	14	1	95	79	-10	16	1	55	-44
-2	10	1	119	115	7	11	1	106	-82	-7	13	1	52	43	3	14	1	153	152	-9	16	1	50	36
0	10	1	77	-69	8	11	1	30	30	-6	13	1	110	94	4	14	1	73	-69	-8	16	1	106	83
1	10	1	75	62	9	11	1	82	72	-5	13	1	108	-98	5	14	1	142	-115	-7	16	1	93	-70
3	10	1	32	-21	11	11	1	31	-23	-4	13	1	173	-162	6	14	1	37	46	-6	16	1	122	-95
5	10	1	33	22	13	11	1	26	-24	-3	13	1	136	122	7	14	1	104	83	-5	16	1	137	118
6	10	1	97	103	14	11	1	51	44	-2	13	1	187	173	8	14	1	76	65	-4	16	1	130	106
7	10	1	82	-70	15	11	1	37	37	-1	13	1	67	-70	9	14	1	83	-69	-3	16	1	112	-101
8	10	1	195	-197	-13	12	1	68	59	0	13	1	185	-169	10	14	1	88	-71	-2	16	1	147	-115
9	10	1	58	60	-11	12	1	40	-32	1	13	1	43	-30	11	14	1	57	48	0	16	1	140	120
10	10	1	173	166	-10	12	1	37	27	2	13	1	164	151	12	14	1	84	81	1	16	1	85	71
11	10	1	32	24	-8	12	1	83	-78	3	13	1	91	84	13	14	1	28	-25	2	16	1	110	-92
12	10	1	138	-128	-7	12	1	40	35	4	13	1	54	-47	-13	15	1	81	73	3	16	1	85	-66
13	10	1	24	-27	-6	12	1	133	120	5	13	1	70	-62	-12	15	1	74	-59	4	16	1	63	54
14	10	1	88	84	-5	12	1	73	-63	6	13	1	108	-95	-11	15	1	100	-80	6	16	1	72	-59
15	10	1	20	7	-4	12	1	118	-111	7	13	1	42	43	-10	15	1	97	80	8	16	1	68	60
-15	11	1	44	30	-2	12	1	130	121	8	13	1	87	83	-9	15	1	86	45	9	16	1	71	-51
-13	11	1	78	-72	-1	12	1	182	171	9	13	1	36	-42	-8	15	1	66	-55	10	16	1	70	-60
-11	11	1	116	93	0	12	1	128	-123	10	13	1	28	-14	-7	15	1	103	-87	11	16	1	85	73
-9	11	1	122	-94	1	12	1	305	-275	13	13	1	25	25	-6	15	1	68	57	12	16	1	70	50
-8	11	1	49	-33	2	12	1	72	60	-13	14	1	68	57	-4	15	1	48	40	-10	17	1	92	75
-7	11	1	165	138	3	12	1	306	270	-11	14	1	70	-53	-3	15	1	85	74	-9	17	1	29	29
-6	11	1	53	48	4	12	1	52	48	-10	14	1	55	-45	-1	15	1	140	-123	-8	17	1	64	-47
-5	11	1	101	-91	5	12	1	148	-136	-9	14	1	70	54	0	15	1	27	5	-7	17	1	41	-28
-4	11	1	127	-124	7	12	1	87	84	-8	14	1	134	121	1	15	1	37	27	-6	17	1	25	-16
-3	11	1	114	-106	8	12	1	58	-54	-7	14	1	73	-58	3	15	1	55	49	-5	17	1	61	42

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	17	1	91	76	-3	19	1	99	-73	0	22	1	77	-50	-7	1	2	59	50	4	2	2	285	-250
-3	17	1	84	-64	-2	19	1	24	-18	1	22	1	23	25	-6	1	2	123	84	5	2	2	58	61
-2	17	1	70	-54	-1	19	1	103	79	2	22	1	106	68	-5	1	2	124	-114	6	2	2	98	102
-1	17	1	104	83	1	19	1	59	-46	4	22	1	113	-77	-3	1	2	225	211	7	2	2	36	37
0	17	1	89	71	4	19	1	45	44	-3	23	1	73	44	-2	1	2	20	18	8	2	2	82	-86
1	17	1	72	-61	5	19	1	41	17	-2	23	1	34	-28	-1	1	2	217	-202	9	2	2	149	-140
2	17	1	68	-59	6	19	1	55	-48	-1	23	1	69	-49	0	1	2	80	73	10	2	2	78	66
4	17	1	26	-19	7	19	1	56	-32	0	23	1	36	28	1	1	2	312	292	11	2	2	142	101
5	17	1	38	29	8	19	1	39	22	1	23	1	70	55	2	1	2	20	-14	12	2	2	80	-72
6	17	1	104	83	9	19	1	56	40	2	23	1	35	-24	3	1	2	144	-125	13	2	2	96	-87
8	17	1	68	-53	-7	20	1	117	82	-16	0	2	53	-59	4	1	2	74	49	14	2	2	47	45
10	17	1	24	15	-5	20	1	165	-131	-14	0	2	108	95	5	1	2	27	26	15	2	2	90	86
-10	18	1	28	-13	-4	20	1	37	-32	-12	0	2	60	-46	6	1	2	18	30	16	2	2	26	-24
-9	18	1	34	-21	-3	20	1	140	110	-10	0	2	77	58	8	1	2	88	-83	-15	3	2	30	-12
-8	18	1	38	-37	-1	20	1	32	-12	-8	0	2	127	-78	10	1	2	118	100	-14	3	2	63	57
-7	18	1	38	15	0	20	1	38	18	-6	0	2	66	39	11	1	2	28	-27	-12	3	2	167	-133
-6	18	1	43	34	1	20	1	31	-32	-4	0	2	181	166	12	1	2	45	-38	-11	3	2	59	56
-5	18	1	27	-13	5	20	1	53	49	-2	0	2	130	-114	13	1	2	24	30	-10	3	2	176	158
-4	18	1	28	19	6	20	1	24	-22	0	0	2	468	-400	15	1	2	38	-32	-9	3	2	155	-136
-2	18	1	78	-60	7	20	1	50	-34	2	0	2	306	282	-13	2	2	35	-27	-8	3	2	255	-234
-1	18	1	32	-28	-7	21	1	21	-19	4	0	2	231	-231	-11	2	2	80	68	-7	3	2	125	122
0	18	1	96	84	-6	21	1	35	-41	6	0	2	218	192	-10	2	2	37	18	-5	3	2	228	202
1	18	1	67	48	-4	21	1	23	-7	8	0	2	248	-159	-9	2	2	86	80	-5	3	2	93	70
2	18	1	182	-118	-3	21	1	42	39	10	0	2	139	117	-7	2	2	219	-211	-4	3	2	538	-433
3	18	1	89	-68	-2	21	1	42	27	16	0	2	44	-50	-6	2	2	67	51	-3	3	2	18	-22
4	18	1	212	166	-1	21	1	65	-47	-17	1	2	59	-48	-5	2	2	333	301	-2	3	2	190	169
5	18	1	90	70	0	21	1	35	-20	-15	1	2	103	87	-4	2	2	162	-134	-1	3	2	55	-36
6	18	1	148	-117	1	21	1	28	14	-14	1	2	46	37	-3	2	2	180	-168	0	3	2	31	-26
7	18	1	62	-45	4	21	1	40	20	-13	1	2	98	-88	-2	2	2	80	70	1	3	2	57	-53
8	18	1	34	27	5	21	1	51	-22	-12	1	2	66	-52	-1	2	2	174	154	2	3	2	111	-101
9	18	1	24	19	-5	22	1	32	-24	-11	1	2	63	43	0	2	2	121	-114	3	3	2	114	98
-9	19	1	29	-11	-3	22	1	35	29	-10	1	2	81	72	1	2	2	225	-193	4	3	2	347	-308
-8	19	1	60	42	-2	22	1	34	28	-9	1	2	24	-12	2	2	2	118	109	6	3	2	202	192
-5	19	1	54	40	-1	22	1	37	-31	-8	1	2	135	-106	3	2	2	58	38	7	3	2	124	-124

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
8	3	2	129	-131	-14	5	2	35	7	-6	6	2	54	-54	4	7	2	38	-37	15	8	2	31	-40
9	3	2	65	52	-12	5	2	36	-37	-5	6	2	81	-58	5	7	2	110	-125	-14	9	2	39	-39
10	3	2	112	105	-10	5	2	88	89	-4	6	2	180	167	6	7	2	47	-51	-13	9	2	46	53
12	3	2	81	-83	-9	5	2	23	-43	-2	6	2	279	-269	7	7	2	156	162	-12	9	2	45	54
-16	4	2	39	30	-8	5	2	85	-87	0	6	2	104	108	8	7	2	121	142	-11	9	2	90	-97
-14	4	2	64	-56	-7	5	2	23	25	1	6	2	19	-37	9	7	2	71	-77	-10	9	2	45	-68
-12	4	2	54	44	-5	5	2	133	126	2	6	2	102	81	10	7	2	81	-94	-9	9	2	92	111
-11	4	2	58	-40	-4	5	2	77	-76	3	6	2	108	125	-15	8	2	30	-22	-8	9	2	79	97
-10	4	2	32	-29	-3	5	2	377	-338	4	6	2	190	187	-14	8	2	27	44	-7	9	2	132	-169
-9	4	2	32	24	-2	5	2	209	191	5	6	2	160	-160	-13	8	2	24	-3	-6	9	2	36	-48
-8	4	2	41	34	-1	5	2	277	259	6	6	2	217	-228	-12	8	2	41	-48	-5	9	2	68	101
-7	4	2	78	-80	0	5	2	236	-235	7	6	2	92	90	-11	8	2	28	41	-4	9	2	85	111
-6	4	2	246	229	1	5	2	221	-227	8	6	2	111	116	-9	8	2	37	-53	-3	9	2	30	22
-4	4	2	118	-124	2	5	2	68	73	10	6	2	57	-58	-8	8	2	82	89	-2	9	2	106	-140
-3	4	2	254	-220	3	5	2	126	131	12	6	2	69	82	-7	8	2	42	53	-1	9	2	103	-124
-2	4	2	168	150	4	5	2	102	-100	14	6	2	41	-53	-6	8	2	123	-147	0	9	2	134	102
-1	4	2	98	80	6	5	2	100	-93	15	6	2	25	-14	-5	8	2	82	-108	1	9	2	75	98
0	4	2	139	123	8	5	2	91	88	16	6	2	27	27	-4	8	2	190	236	2	9	2	42	-56
1	4	2	111	-109	7	5	2	40	-49	-15	7	2	28	-42	-3	8	2	132	158	4	9	2	58	86
2	4	2	142	-133	8	5	2	21	-13	-13	7	2	66	43	-2	8	2	144	-176	5	9	2	48	-69
3	4	2	188	167	9	5	2	84	88	-12	7	2	58	50	-1	8	2	33	-37	6	9	2	33	-48
4	4	2	262	255	10	5	2	24	-31	-11	7	2	72	-90	0	8	2	93	106	7	9	2	56	75
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6	4	2	159	-152	14	5	2	23	35	-9	7	2	151	162	3	8	2	19	-3	9	9	2	76	-103
7	4	2	109	98	15	5	2	29	38	-8	7	2	118	139	4	8	2	23	-23	11	9	2	74	84
8	4	2	82	68	16	5	2	16	-23	-7	7	2	177	-187	5	8	2	67	71	13	9	2	27	-12
9	4	2	98	-89	-14	6	2	25	-23	-6	7	2	55	-59	7	8	2	29	-37	15	9	2	21	-42
11	4	2	79	77	-13	6	2	58	72	-5	7	2	75	81	8	8	2	61	86	-15	10	2	42	51
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13	4	2	85	-85	-11	6	2	67	-70	-2	7	2	128	130	10	8	2	76	-108	-12	10	2	35	-35
14	4	2	30	30	-10	6	2	74	-64	-1	7	2	55	49	11	8	2	31	-46	-11	10	2	57	46
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-16	5	2	53	-53	-8	6	2	22	23	2	7	2	139	139	13	8	2	52	73	-8	10	2	42	37
-15	5	2	68	-73	-7	6	2	53	60	3	7	2	46	53	14	8	2	66	-93	-6	10	2	37	-44

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJP1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-13	11	2	63	55	-12	11	2	109	104	-5	14	2	104	-120	-8	15	2	30	-41	9	16	2	36	-48
-12	10	2	85	89	-11	10	2	46	-37	-6	14	2	143	-120	-7	15	2	91	46	11	16	2	23	22
-11	9	2	27	27	-10	9	2	81	-74	-7	14	2	117	-111	-6	15	2	43	-32	12	16	2	25	22
-10	8	2	24	-24	-9	8	2	98	-95	-8	14	2	150	141	-5	15	2	53	-52	13	16	2	29	-23
-9	7	2	67	-94	-8	7	2	91	-79	-9	14	2	111	-111	-4	15	2	81	-98	14	16	2	71	-70
-8	6	2	74	-84	-7	6	2	96	-79	-10	14	2	129	111	-3	15	2	91	75	15	16	2	105	88
-7	5	2	31	29	-6	5	2	193	178	-11	14	2	132	-116	-2	15	2	164	-140	0	17	2	80	60
-6	4	2	122	-77	-5	4	2	143	-142	-12	14	2	140	-121	-1	15	2	130	-113	1	17	2	112	-83
-5	3	2	232	-250	-4	3	2	122	-117	-13	14	2	197	-187	0	15	2	201	-177	2	17	2	59	43
-4	2	2	164	-175	-3	2	2	74	65	-14	14	2	151	128	1	15	2	111	98	3	17	2	53	-43
-3	1	2	29	25	-2	1	2	31	-28	-15	14	2	115	-94	2	15	2	23	-12	4	17	2	91	34
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-7	3	2	66	64	2	3	2	60	73	-13	13	2	74	-65	6	15	2	99	-68	8	17	2	34	21
-8	4	2	74	-84	3	4	2	60	-39	-12	13	2	71	-27	7	15	2	124	-108	9	17	2	36	28
-9	5	2	44	-77	4	5	2	42	-23	-11	13	2	42	-39	8	15	2	122	-104	10	17	2	70	-55
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-11	7	2	27	27	6	7	2	65	-54	-9	13	2	91	77	10	15	2	104	77	12	17	2	156	-128
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR OJR1

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11	1	1	74	74

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
15	4	3	50	41	-10	6	3	120	-126	-7	7	3	93	92	6	8	3	73	-72	-7	10	3	27	-23
16	4	3	29	-22	-9	6	3	46	52	-5	7	3	57	-54	7	8	3	186	195	-6	10	3	41	-61
-13	5	3	26	13	-8	6	3	103	107	-3	7	3	47	-41	8	8	3	45	45	-5	10	3	35	-45
-12	5	3	42	-44	-7	6	3	33	-32	-2	7	3	135	139	9	8	3	116	-126	-4	10	3	116	152
-11	5	3	54	56	-5	6	3	122	118	-1	7	3	148	147	11	8	3	54	72	-3	10	3	31	53
-10	5	3	142	127	-4	6	3	168	-150	0	7	3	303	-302	12	8	3	30	23	-2	10	3	166	-209
-9	5	3	202	-196	-3	6	3	132	-124	1	7	3	159	-159	-14	9	3	47	65	0	10	3	118	151
-8	5	3	226	-215	-2	6	3	192	182	2	7	3	187	195	-11	9	3	32	-46	1	10	3	59	-77
-7	5	3	210	201	-1	6	3	72	74	3	7	3	148	152	-9	9	3	85	110	2	10	3	80	-97
-6	5	3	269	264	0	6	3	34	-38	4	7	3	175	-183	-8	9	3	60	59	3	10	3	53	69
-5	5	3	178	-173	1	6	3	51	-53	5	7	3	56	-57	-7	9	3	180	-200	6	10	3	45	52
-4	5	3	308	-293	2	6	3	54	42	6	7	3	175	171	-5	9	3	153	173	9	10	3	24	-38
-3	5	3	209	197	3	6	3	43	42	7	7	3	21	24	-4	9	3	45	-48	10	10	3	26	-30
-2	5	3	74	66	4	6	3	45	39	8	7	3	164	-172	-3	9	3	159	-190	12	10	3	47	65
-1	5	3	309	-281	5	6	3	108	-111	9	7	3	52	53	-2	9	3	110	128	13	10	3	40	41
1	5	3	18	-12	6	6	3	53	-52	10	7	3	28	34	-1	9	3	141	163	14	10	3	56	-69
2	5	3	175	-148	7	6	3	101	101	11	7	3	66	-66	0	9	3	126	-141	-14	11	3	51	-53
3	5	3	45	36	8	6	3	89	92	13	7	3	37	48	1	9	3	66	-68	-13	11	3	52	59
4	5	3	42	-37	9	6	3	74	-68	15	7	3	21	22	2	9	3	194	218	-12	11	3	44	58
5	5	3	24	-13	10	6	3	30	-21	-13	8	3	44	47	4	9	3	140	-157	-11	11	3	80	-97
6	5	3	124	125	11	6	3	85	80	-11	8	3	56	-59	5	9	3	24	28	-10	11	3	32	-39
7	5	3	89	-88	12	6	3	33	-41	-9	8	3	89	102	7	9	3	79	91	-9	11	3	98	117
8	5	3	147	-148	13	6	3	70	-70	-8	8	3	47	-48	8	9	3	27	38	-7	11	3	137	-169
9	5	3	78	72	14	6	3	52	59	-7	8	3	36	-41	9	9	3	85	-106	-5	11	3	162	207
10	5	3	115	113	15	6	3	39	46	-6	8	3	49	46	10	9	3	23	-26	-3	11	3	90	-123
11	5	3	73	-66	16	6	3	29	-44	-5	8	3	67	-58	11	9	3	53	69	-1	11	3	22	29
12	5	3	112	-116	-16	7	3	61	-85	-3	8	3	116	118	12	9	3	26	28	0	11	3	89	107
13	5	3	69	58	-15	7	3	36	-49	-2	8	3	91	-89	13	9	3	39	-58	2	11	3	96	-115
14	5	3	43	47	-14	7	3	72	75	-1	8	3	124	-134	15	9	3	29	44	4	11	3	87	111
15	5	3	41	-45	-12	7	3	80	-83	1	8	3	42	37	-15	10	3	25	-30	5	11	3	37	-51
-15	6	3	24	31	-11	7	3	24	22	2	8	3	66	-69	-14	10	3	23	37	6	11	3	65	-79
-14	6	3	37	-37	-10	7	3	122	121	3	8	3	71	84	-12	10	3	60	-72	7	11	3	71	92
-12	6	3	63	67	-9	7	3	48	-50	4	8	3	94	95	-10	10	3	55	77	8	11	3	41	38
-11	6	3	39	-52	-8	7	3	122	-122	5	8	3	149	-157	-8	10	3	31	-36	9	11	3	91	-107

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
11	11	3	88	105	-1	13	3	24	32	-9	15	3	72	-64	9	16	3	25	-15	10	18	3	24	23
13	11	3	54	-51	0	13	3	168	184	-8	15	3	102	101	10	16	3	38	31	-8	19	3	82	-60
14	11	3	23	-6	1	13	3	79	-86	-7	15	3	114	111	11	16	3	23	-28	-7	19	3	27	1
-13	12	3	55	-54	2	13	3	227	-244	-6	15	3	103	-98	-11	17	3	50	40	-6	19	3	73	67
-12	12	3	25	-27	3	13	3	108	111	-5	15	3	142	-128	-10	17	3	37	-40	-4	19	3	79	-73
-11	12	3	82	50	4	13	3	199	211	-4	15	3	76	78	-9	17	3	61	-59	-3	19	3	28	30
-9	12	3	49	-53	5	13	3	78	-76	-3	15	3	77	81	-8	17	3	71	82	-2	19	3	68	54
-8	12	3	78	-83	6	13	3	32	-34	-2	15	3	91	-89	-7	17	3	47	40	-1	19	3	72	-58
-5	12	3	23	18	7	13	3	41	40	0	15	3	57	52	-6	17	3	45	-33	0	19	3	37	-25
-4	12	3	73	79	11	13	3	25	-30	1	15	3	36	-35	-3	17	3	83	49	1	19	3	101	80
-3	12	3	106	-117	12	13	3	23	22	3	15	3	29	-26	-2	17	3	34	39	3	19	3	93	-74
-2	12	3	51	-59	-12	14	3	61	57	5	15	3	44	41	-1	17	3	140	-120	4	19	3	31	-25
-1	12	3	73	81	-10	14	3	39	-40	6	15	3	30	-21	0	17	3	91	-72	5	19	3	58	46
0	12	3	50	53	-9	14	3	29	-11	7	15	3	55	-48	1	17	3	141	119	6	19	3	63	47
1	12	3	38	34	-6	14	3	75	88	8	15	3	70	69	2	17	3	110	96	8	19	3	72	-51
2	12	3	20	-30	-5	14	3	24	28	9	15	3	84	71	3	17	3	85	-71	9	19	3	35	-30
3	12	3	115	-134	-4	14	3	93	-93	10	15	3	66	-55	4	17	3	80	-81	-8	20	3	20	-2
4	12	3	34	-44	-2	14	3	115	113	11	15	3	105	-95	5	17	3	68	52	-7	20	3	24	-8
5	12	3	121	135	-1	14	3	24	-29	12	15	3	35	32	6	17	3	26	-1	-5	20	3	81	58
7	12	3	121	-120	0	14	3	90	-94	-11	16	3	42	-46	7	17	3	68	-59	-4	20	3	41	28
8	12	3	33	20	1	14	3	108	109	-9	16	3	39	39	8	17	3	35	32	-3	20	3	125	-104
9	12	3	98	87	2	14	3	53	48	-8	16	3	33	-23	10	17	3	47	-39	-2	20	3	36	-19
10	12	3	45	-47	3	14	3	107	-113	-5	16	3	73	-57	-10	18	3	45	38	-1	20	3	87	73
11	12	3	49	-42	4	14	3	75	73	-4	16	3	43	-32	-7	18	3	24	19	5	20	3	22	5
12	12	3	43	41	5	14	3	66	68	-3	16	3	162	138	-6	18	3	44	-39	7	20	3	30	-10
-13	13	3	29	21	6	14	3	88	-90	-2	16	3	36	17	-4	18	3	66	43	-6	21	3	95	72
-12	13	3	82	85	7	14	3	64	-56	-1	16	3	110	-94	-2	18	3	32	-18	-4	21	3	74	-48
-10	13	3	32	-23	8	14	3	33	23	0	16	3	39	-12	2	18	3	28	12	-3	21	3	39	-27
-7	13	3	49	49	9	14	3	63	59	3	16	3	48	49	3	18	3	54	40	-2	21	3	29	18
-6	13	3	23	-20	11	14	3	39	-38	4	16	3	23	-1	4	18	3	115	-95	-1	21	3	77	54
-5	13	3	49	-52	12	14	3	24	-16	5	16	3	68	-56	5	18	3	59	-61	1	21	3	64	-44
-4	13	3	139	144	-12	15	3	26	30	6	16	3	37	18	6	18	3	145	132	3	21	3	33	19
-3	13	3	42	43	-11	15	3	75	68	7	16	3	54	46	7	18	3	49	40	4	21	3	23	-27
-2	13	3	148	-158	-10	15	3	73	-75	8	16	3	40	-26	8	18	3	82	-69	5	21	3	28	-22

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	21	3	49	47	0	1	4	248	222	15	2	4	37	-40	-8	4	4	170	-153	0	5	4	255	241
-4	22	3	42	-27	1	1	4	425	-386	-15	3	4	39	35	-7	4	4	30	-19	1	5	4	217	216
-3	22	3	24	-20	3	1	4	380	337	-13	3	4	71	-68	-6	4	4	131	122	2	5	4	223	-211
-2	22	3	29	9	4	1	4	46	-38	-11	3	4	60	58	-4	4	4	107	99	3	5	4	210	-195
-1	22	3	32	19	5	1	4	300	-272	-10	3	4	99	-96	-3	4	4	28	21	4	5	4	244	232
1	22	3	40	-22	6	1	4	97	87	-9	3	4	97	88	-2	4	4	254	-237	5	5	4	241	234
2	22	3	25	-15	7	1	4	165	146	-8	3	4	220	191	-1	4	4	30	-24	6	5	4	265	-253
4	22	3	72	59	9	1	4	81	-78	-7	3	4	192	-183	0	4	4	251	231	7	5	4	193	-186
-16	0	4	57	-55	10	1	4	88	-79	-6	3	4	318	-267	2	4	4	39	-44	8	5	4	222	216
-14	0	4	32	1	11	1	4	45	41	-5	3	4	157	150	4	4	4	23	13	9	5	4	82	58
-10	0	4	108	-95	12	1	4	108	94	-4	3	4	378	313	5	4	4	52	49	10	5	4	36	-41
-8	0	4	133	116	14	1	4	85	-59	-3	3	4	137	-122	6	4	4	60	56	12	5	4	34	-33
-6	0	4	123	-115	16	1	4	39	28	-2	3	4	206	-195	7	4	4	59	-62	-15	6	4	38	-44
-4	0	4	211	-186	-14	2	4	38	37	-1	3	4	186	157	8	4	4	177	-154	-14	6	4	44	-60
-2	0	4	362	326	-13	2	4	31	27	0	3	4	113	107	9	4	4	49	48	-11	6	4	70	64
0	0	4	643	-554	-12	2	4	48	-30	2	3	4	88	-62	10	4	4	164	149	-9	6	4	146	-131
2	0	4	172	153	-11	2	4	194	-180	3	3	4	187	-170	12	4	4	25	-27	-8	6	4	91	82
6	0	4	151	-134	-9	2	4	242	210	4	3	4	69	70	13	4	4	38	39	-7	6	4	101	93
8	0	4	209	173	-7	2	4	173	-147	5	3	4	217	196	15	4	4	32	-26	-6	6	4	97	-94
10	0	4	230	-214	-6	2	4	38	31	6	3	4	40	-43	-16	5	4	63	72	-3	6	4	89	-92
12	0	4	75	90	-3	2	4	31	34	7	3	4	39	-33	-15	5	4	78	82	-2	6	4	108	98
-16	1	4	23	-29	-2	2	4	60	-49	8	3	4	77	75	-14	5	4	76	-75	-1	6	4	221	213
-15	1	4	94	-79	-1	2	4	356	-312	9	3	4	35	-28	-13	5	4	105	-98	1	6	4	244	-238
-13	1	4	139	120	0	2	4	98	86	10	3	4	137	-128	-12	5	4	101	79	2	6	4	56	-54
-11	1	4	176	-157	1	2	4	410	361	11	3	4	60	43	-11	5	4	99	98	3	6	4	71	73
-10	1	4	24	-27	2	2	4	39	31	12	3	4	142	127	-10	5	4	107	-89	4	6	4	63	-58
-9	1	4	145	136	3	2	4	211	-182	13	3	4	51	-36	-9	5	4	97	-101	5	6	4	63	61
-8	1	4	148	132	5	2	4	39	-37	14	3	4	101	-88	-8	5	4	98	95	6	6	4	104	92
-7	1	4	39	-39	6	2	4	32	-31	15	3	4	55	54	-7	5	4	25	-21	7	6	4	159	-155
-6	1	4	251	-209	7	2	4	144	130	-16	4	4	46	44	-6	5	4	64	50	9	6	4	139	134
-5	1	4	33	-25	8	2	4	23	16	-15	4	4	29	-30	-5	5	4	36	30	11	6	4	83	-82
-4	1	4	331	277	9	2	4	100	-94	-14	4	4	31	4	-4	5	4	133	-113	13	6	4	37	37
-2	1	4	251	-218	11	2	4	46	42	-12	4	4	63	-64	-3	5	4	20	33	14	6	4	31	26
-1	1	4	107	98	14	2	4	23	-23	-10	4	4	144	133	-1	5	4	92	-86	-14	7	4	38	-36

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-12	7	4	41	44	-3	8	4	41	-34	9	9	4	46	51	-4	11	4	90	-113	-8	13	4	39	-40
-9	7	4	145	-160	-2	8	4	117	120	10	9	4	34	50	-3	11	4	134	-167	-7	13	4	87	-104
-8	7	4	94	-81	-1	8	4	63	53	11	9	4	57	-71	-2	11	4	89	86	-6	13	4	75	90
-7	7	4	271	275	0	8	4	157	-162	12	9	4	25	11	-1	11	4	85	82	-5	13	4	143	167
-6	7	4	88	79	1	8	4	87	88	13	9	4	44	54	0	11	4	48	-70	-4	13	4	79	-87
-5	7	4	242	-243	2	8	4	139	148	-14	10	4	22	-3	2	11	4	125	166	-3	13	4	165	-187
-4	7	4	149	-143	3	8	4	47	-44	-11	10	4	26	-18	3	11	4	55	-75	-2	13	4	44	56
-3	7	4	280	287	4	8	4	28	-29	-9	10	4	54	67	4	11	4	158	-200	-1	13	4	81	90
-2	7	4	98	96	5	8	4	36	-29	-8	10	4	35	-44	6	11	4	88	128	0	13	4	24	-33
-1	7	4	292	-283	6	8	4	44	-45	-7	10	4	56	-85	8	11	4	38	-55	1	13	4	30	-42
0	7	4	56	-50	7	8	4	60	53	-6	10	4	47	39	9	11	4	24	-33	3	13	4	71	74
1	7	4	139	141	8	8	4	91	88	-5	10	4	23	8	10	11	4	30	41	4	13	4	64	73
2	7	4	118	-113	9	8	4	22	-9	-3	10	4	84	100	11	11	4	41	50	5	13	4	82	-91
3	7	4	98	98	10	8	4	58	-62	-2	10	4	59	-65	12	11	4	25	-35	6	13	4	48	-62
4	7	4	92	93	13	8	4	35	-48	-1	10	4	143	-164	13	11	4	39	-58	7	13	4	46	57
6	7	4	44	-50	14	8	4	25	36	1	10	4	86	104	-13	12	4	25	-22	9	13	4	47	-45
7	7	4	110	-104	-14	9	4	61	84	2	10	4	22	18	-12	12	4	51	-52	10	13	4	28	33
8	7	4	28	-24	-12	9	4	78	-87	3	10	4	20	-25	-11	12	4	33	29	11	13	4	82	80
9	7	4	116	114	-10	9	4	88	104	4	10	4	21	14	-10	12	4	74	91	12	13	4	30	-37
10	7	4	54	53	-9	9	4	26	-21	5	10	4	40	-44	-8	12	4	81	-90	13	13	4	73	-70
11	7	4	96	-91	-8	9	4	77	-88	6	10	4	30	-26	-3	12	4	32	43	-12	14	4	26	-8
12	7	4	62	-59	-7	9	4	119	123	7	10	4	80	85	-2	12	4	53	-77	-10	14	4	29	38
13	7	4	82	78	-6	9	4	36	28	9	10	4	85	-107	0	12	4	68	81	-9	14	4	56	-59
14	7	4	39	47	-5	9	4	161	-166	10	10	4	23	15	1	12	4	25	-45	-7	14	4	56	58
15	7	4	56	-62	-4	9	4	22	19	11	10	4	47	77	2	12	4	69	-96	-3	14	4	87	-90
-14	8	4	23	-25	-3	9	4	151	160	13	10	4	29	-46	4	12	4	23	11	-1	14	4	88	78
-13	8	4	24	3	-2	9	4	46	57	14	10	4	20	9	6	12	4	33	42	1	14	4	29	-27
-12	8	4	66	74	-1	9	4	37	-40	-14	11	4	55	63	8	12	4	55	-64	2	14	4	24	-21
-10	8	4	117	-121	0	9	4	161	-172	-12	11	4	91	-115	10	12	4	22	17	7	14	4	42	-44
-9	8	4	39	50	1	9	4	22	-11	-10	11	4	40	63	11	12	4	30	32	9	14	4	62	53
-8	8	4	132	130	2	9	4	200	217	-9	11	4	40	66	-13	13	4	32	32	10	14	4	27	-27
-7	8	4	69	71	4	9	4	211	-230	-7	11	4	77	-112	-12	13	4	34	22	11	14	4	22	-14
-6	8	4	63	-70	6	9	4	147	160	-6	11	4	30	41	-11	13	4	34	-43	12	14	4	23	28
-5	8	4	66	-63	8	9	4	132	-140	-5	11	4	110	143	-9	13	4	55	53	-12	15	4	62	61

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-11	15	4	52	-46	-7	17	4	28	9	5	19	4	65	47	-15	1	5	35	-21	-2	2	5	232	196
-10	15	4	47	-45	-6	17	4	107	-92	7	19	4	61	-59	-13	1	5	91	83	-1	2	5	66	55
-9	15	4	40	32	-5	17	4	53	-37	-4	20	4	25	7	-11	1	5	137	-119	0	2	5	396	-350
-5	15	4	24	-10	-4	17	4	106	88	0	20	4	50	33	-10	1	5	46	38	1	2	5	47	43
-4	15	4	23	18	-3	17	4	65	50	1	20	4	30	32	-9	1	5	45	38	2	2	5	188	181
-3	15	4	20	-28	-2	17	4	98	-94	2	20	4	42	-35	-8	1	5	54	-41	3	2	5	111	-105
-2	15	4	32	-41	-1	17	4	25	-20	6	20	4	51	42	-7	1	5	47	32	4	2	5	118	-113
-1	15	4	82	81	0	17	4	103	101	-4	21	4	35	-13	-6	1	5	199	174	5	2	5	26	-21
0	15	4	68	72	2	17	4	67	-61	-3	21	4	27	15	-4	1	5	282	-256	6	2	5	31	24
1	15	4	84	-85	3	17	4	30	16	-2	21	4	38	26	-2	1	5	285	253	7	2	5	50	52
2	15	4	104	-111	4	17	4	27	18	-1	21	4	45	-40	-1	1	5	79	-73	8	2	5	67	63
3	15	4	111	107	5	17	4	51	-41	0	21	4	34	-32	0	1	5	190	-167	9	2	5	26	-17
4	15	4	127	127	8	17	4	65	60	1	21	4	75	58	1	1	5	50	-44	10	2	5	139	-132
5	15	4	105	-95	10	17	4	49	-38	3	21	4	87	-85	2	1	5	123	111	12	2	5	56	58
6	15	4	77	-78	-9	18	4	49	32	5	21	4	79	82	3	1	5	183	186	-15	3	5	47	-43
7	15	4	65	64	-7	18	4	48	-48	-3	22	4	35	-37	4	1	5	109	-101	-14	3	5	45	41
8	15	4	57	45	-5	18	4	40	23	-2	22	4	37	-42	5	1	5	232	-208	-13	3	5	128	125
9	15	4	43	-38	-2	18	4	23	-20	-1	22	4	52	49	7	1	5	113	98	-12	3	5	46	-42
-11	16	4	21	-18	-1	18	4	68	-52	0	22	4	25	19	8	1	5	27	-33	-11	3	5	158	-143
-10	16	4	35	-43	1	18	4	38	24	1	22	4	32	-17	9	1	5	56	-55	-10	3	5	54	44
-7	16	4	25	2	2	18	4	29	16	-13	0	5	40	-39	10	1	5	85	74	-9	3	5	179	154
-6	16	4	25	-9	4	18	4	27	-13	-11	0	5	183	150	12	1	5	108	-92	-7	3	5	78	-68
-2	16	4	34	20	7	18	4	27	10	-9	0	5	262	-232	13	1	5	25	5	-6	3	5	96	-79
0	16	4	66	-51	-8	19	4	50	36	-7	0	5	229	219	14	1	5	82	60	-5	3	5	79	82
2	16	4	65	62	-7	19	4	62	57	-5	0	5	144	-120	-14	2	5	60	47	-4	3	5	178	157
3	16	4	24	-28	-6	19	4	49	-41	-3	0	5	106	88	-13	2	5	43	-40	-2	3	5	130	-119
5	16	4	38	30	-4	19	4	60	38	-1	0	5	224	196	-12	2	5	36	-30	-1	3	5	109	108
6	16	4	52	-50	-3	19	4	49	35	1	0	5	224	-203	-11	2	5	34	29	0	3	5	27	21
7	16	4	34	-34	-2	19	4	48	-33	3	0	5	100	96	-9	2	5	64	46	1	3	5	144	-131
8	16	4	60	40	-1	19	4	93	-80	7	0	5	81	-72	-7	2	5	85	78	2	3	5	105	97
9	16	4	24	23	0	19	4	39	24	9	0	5	109	97	-6	2	5	172	-151	3	3	5	269	256
10	16	4	37	-28	1	19	4	80	68	11	0	5	100	-81	-5	2	5	139	-121	4	3	5	75	-70
-10	17	4	44	-30	3	19	4	68	-37	13	0	5	41	30	-4	2	5	24	-26	5	3	5	291	-269
-8	17	4	81	73	4	19	4	31	-23	15	0	5	23	3	-3	2	5	40	46	6	3	5	156	148

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	3	5	259	243	-9	5	5	70	71	3	6	5	43	33	-12	8	5	40	41	2	9	5	43	-44
8	3	5	113	-108	-8	5	5	39	28	4	6	5	89	83	-9	8	5	45	-47	3	9	5	26	-20
9	3	5	158	-147	-7	5	5	168	-146	5	6	5	34	27	-8	8	5	53	56	4	9	5	125	132
11	3	5	77	75	-6	5	5	123	-113	7	6	5	39	-33	-7	8	5	71	64	6	9	5	122	-132
12	3	5	32	38	-5	5	5	189	178	8	6	5	92	-80	-6	8	5	71	-71	7	9	5	24	-25
13	3	5	25	-15	-4	5	5	168	162	10	6	5	84	84	-4	8	5	23	-28	8	9	5	93	96
-14	4	5	38	39	-3	5	5	199	-184	12	6	5	46	-36	-3	8	5	52	-44	9	9	5	71	74
-14	4	5	74	77	-2	5	5	268	-247	14	6	5	23	14	-2	8	5	94	89	10	9	5	47	-50
-12	4	5	78	-74	-1	5	5	214	198	-15	7	5	32	27	-1	8	5	138	137	11	9	5	68	-76
-11	4	5	72	-67	0	5	5	204	194	-14	7	5	74	-75	0	8	5	20	16	12	9	5	28	18
-10	4	5	57	58	1	5	5	83	-72	-13	7	5	48	-58	1	8	5	162	-170	13	9	5	48	61
-9	4	5	175	168	2	5	5	106	-91	-12	7	5	67	62	2	8	5	71	-66	-12	10	5	37	40
-8	4	5	78	-86	3	5	5	33	25	-11	7	5	63	58	3	8	5	137	141	-10	10	5	68	-83
-7	4	5	140	-136	4	5	5	89	-80	-10	7	5	102	-83	4	8	5	84	59	-8	10	5	129	147
-6	4	5	93	91	10	5	5	51	-46	-9	7	5	78	-79	5	8	5	57	-54	-7	10	5	53	57
-5	4	5	36	26	11	5	5	78	82	-8	7	5	101	106	7	8	5	22	-25	-6	10	5	147	-157
-4	4	5	46	-52	12	5	5	70	59	-6	7	5	71	-79	8	8	5	28	17	-5	10	5	70	-78
-1	4	5	73	-67	13	5	5	67	-50	-5	7	5	76	78	9	8	5	74	78	-4	10	5	127	136
0	4	5	40	-53	14	5	5	57	-57	-4	7	5	42	-36	10	8	5	27	-46	-2	10	5	21	-13
1	4	5	194	180	15	5	5	60	60	-3	7	5	150	-148	11	8	5	69	-74	-1	10	5	67	59
2	4	5	74	66	-15	6	5	30	-38	-2	7	5	20	-7	13	8	5	39	56	0	10	5	27	-39
3	4	5	178	-166	-13	6	5	35	36	-1	7	5	79	79	-14	9	5	28	-28	1	10	5	35	41
4	4	5	104	-97	-11	6	5	23	-18	0	7	5	227	230	-12	9	5	70	69	2	10	5	121	134
5	4	5	48	41	-10	6	5	102	82	1	7	5	61	-58	-10	9	5	67	-76	4	10	5	47	-42
6	4	5	21	17	-8	6	5	144	-127	2	7	5	275	-271	-9	9	5	76	-86	5	10	5	67	-73
7	4	5	125	116	-7	6	5	98	-102	4	7	5	176	165	-8	9	5	54	61	7	10	5	46	47
8	4	5	36	-28	-6	6	5	143	134	5	7	5	91	82	-7	9	5	139	151	8	10	5	62	79
9	4	5	119	-110	-5	6	5	124	113	6	7	5	172	-152	-6	9	5	47	-47	10	10	5	38	-53
10	4	5	27	14	-4	6	5	53	-53	7	7	5	125	-129	-5	9	5	164	-171	12	10	5	27	32
11	4	5	76	63	-3	6	5	152	-139	8	7	5	195	194	-3	9	5	179	178	-12	11	5	31	-58
13	4	5	38	-33	-2	6	5	39	-34	9	7	5	87	86	-2	9	5	71	82	-10	11	5	39	65
-13	5	5	26	-22	0	6	5	119	117	10	7	5	82	-87	-1	9	5	219	-227	-8	11	5	22	-19
-12	5	5	35	-35	1	6	5	98	-83	-14	8	5	36	-54	0	9	5	76	-77	-5	11	5	101	-121
-11	5	5	29	12	2	6	5	161	-147	-13	8	5	50	64	1	9	5	104	102	-4	11	5	34	50

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJP1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	11	5	196	229	-6	13	5	35	49	-3	15	5	133	-128	-1	17	5	57	48	-4	20	5	29	19
-2	11	5	24	-11	-5	13	5	40	53	-2	15	5	101	112	0	17	5	59	-60	-3	20	5	36	-28
-1	11	5	130	-172	-4	13	5	35	-37	-1	15	5	115	113	1	17	5	71	-65	0	20	5	28	-3
0	11	5	44	-56	-3	13	5	44	-59	0	15	5	98	-114	2	17	5	26	10	1	20	5	26	18
1	11	5	104	122	1	13	5	25	33	1	15	5	81	-91	3	17	5	74	87	5	20	5	28	21
2	11	5	89	109	2	13	5	44	56	2	15	5	87	87	4	17	5	49	51	-2	21	5	98	-75
3	11	5	101	-112	3	13	5	35	-68	3	15	5	87	85	5	17	5	81	-71	0	21	5	79	51
4	11	5	103	-131	4	13	5	114	-141	4	15	5	24	-13	6	17	5	60	-60	1	21	5	27	22
5	11	5	58	70	5	13	5	82	87	5	15	5	31	-31	7	17	5	87	87	2	21	5	45	-35
6	11	5	91	119	6	13	5	104	125	6	15	5	28	-15	8	17	5	35	32	-14	0	6	88	-83
8	11	5	51	-67	7	13	5	45	-53	10	15	5	34	37	9	17	5	62	-65	-12	0	6	94	88
10	11	5	23	4	8	13	5	75	-86	-9	16	5	41	-38	-4	18	5	24	13	-10	0	6	141	-126
11	11	5	35	-50	10	13	5	63	72	-8	16	5	49	-43	-3	18	5	25	16	-8	0	6	75	63
13	11	5	52	67	12	13	5	49	-65	-7	16	5	77	76	0	18	5	59	-45	-6	0	6	127	119
-13	12	5	25	-33	-11	14	5	59	56	-6	16	5	54	56	1	18	5	32	-38	-4	0	6	76	-80
-10	12	5	35	-54	-10	14	5	40	43	-5	16	5	78	-88	2	18	5	116	111	-2	0	6	144	-127
-7	12	5	43	-58	-9	14	5	44	-33	-4	16	5	81	-57	3	18	5	29	25	0	0	6	237	218
-6	12	5	32	-44	-8	14	5	60	-74	-2	16	5	39	31	4	18	5	81	-82	2	0	6	124	-115
-5	12	5	43	70	-8	14	5	71	81	-1	16	5	27	15	5	18	5	29	-12	4	0	6	127	125
-4	12	5	55	98	-4	14	5	53	-55	0	16	5	36	-38	7	18	5	21	5	6	0	6	166	-157
-3	12	5	26	36	-3	14	5	24	7	1	16	5	34	-34	-7	19	5	43	-42	8	0	6	76	73
-2	12	5	83	-110	-1	14	5	25	-23	3	16	5	42	47	-6	19	5	53	-47	10	0	6	38	40
-1	12	5	89	-118	0	14	5	34	32	5	16	5	44	-42	-4	19	5	62	57	12	0	6	28	-27
1	12	5	95	131	2	14	5	84	-90	6	16	5	30	-14	-3	19	5	31	26	-13	1	6	36	-37
2	12	5	24	37	3	14	5	24	-21	8	16	5	26	-4	-2	19	5	70	-65	-11	1	6	81	76
3	12	5	77	-101	4	14	5	40	47	9	16	5	34	31	-1	19	5	32	-29	-10	1	6	20	-8
5	12	5	44	54	5	14	5	50	51	-9	17	5	70	60	0	19	5	67	67	-9	1	6	132	-118
9	12	5	27	-25	8	14	5	26	-29	-8	17	5	29	25	2	19	5	53	-47	-8	1	6	48	43
11	12	5	42	51	10	14	5	39	38	-7	17	5	69	-67	3	19	5	24	19	-7	1	6	83	67
-12	13	5	90	-105	11	14	5	27	19	-6	17	5	37	-17	4	19	5	35	21	-6	1	6	18	14
-11	13	5	37	41	-8	15	5	50	-46	-5	17	5	51	47	5	19	5	51	-44	-5	1	6	101	-92
-10	13	5	90	109	-8	15	5	73	76	-4	17	5	25	-14	6	19	5	33	-25	-4	1	6	144	-125
-9	13	5	24	-23	-5	15	5	86	83	-3	17	5	30	-27	7	19	5	59	60	-3	1	6	74	68
-8	13	5	59	-58	-4	15	5	78	-77	-2	17	5	48	48	-5	20	5	93	97	-2	1	6	144	125

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	1	6	46	-37	7	2	6	63	-53	-9	4	6	55	-63	0	5	6	38	-25	10	6	6	38	37
0	1	6	120	-116	8	2	6	26	10	-7	4	6	132	125	2	5	6	59	56	11	6	6	43	38
1	1	6	82	89	9	2	6	49	46	-6	4	6	83	-86	3	5	6	45	40	12	6	6	28	-20
2	1	6	66	82	11	2	6	89	-93	-5	4	6	159	-150	4	5	6	27	-34	-14	7	6	22	-19
3	1	6	103	-94	13	2	6	42	35	-4	4	6	27	24	5	5	6	124	-114	-12	7	6	45	-58
4	1	6	85	-82	14	2	6	25	-4	-3	4	6	172	159	6	5	6	103	98	-10	7	6	72	67
5	1	6	188	178	-12	3	6	25	-1	-2	4	6	48	45	7	5	6	161	160	-9	7	6	37	41
6	1	6	38	38	-11	3	6	66	-53	-1	4	6	97	-87	8	5	6	131	-127	-8	7	6	54	-51
7	1	6	170	-155	-10	3	6	37	-19	0	4	6	131	-120	9	5	6	123	-125	-7	7	6	72	-70
8	1	6	33	32	-9	3	6	18	26	1	4	6	103	97	10	5	6	73	77	-5	7	6	98	91
9	1	6	100	100	-8	3	6	32	34	2	4	6	78	68	11	5	6	72	74	-4	7	6	21	25
11	1	6	77	-64	-7	3	6	31	16	3	4	6	81	-72	12	5	6	28	-11	-3	7	6	93	-88
12	1	6	27	-22	-6	3	6	30	22	4	4	6	116	-114	13	5	6	35	-28	-2	7	6	145	-143
13	1	6	47	39	-4	3	6	116	-110	5	4	6	73	71	-14	6	6	80	83	-1	7	6	188	157
14	1	6	32	30	-3	3	6	15	-7	8	4	6	94	88	-13	6	6	60	-62	0	7	6	157	152
-14	2	6	40	-40	-2	3	6	208	192	8	4	6	29	-37	-12	6	6	82	-73	1	7	6	183	-174
-12	2	6	57	57	-1	3	6	127	-116	10	4	6	44	-37	-11	6	6	41	45	2	7	6	121	-114
-11	2	6	52	46	0	3	6	195	-188	11	4	6	30	-7	-10	6	6	81	42	3	7	6	63	62
-10	2	6	88	-88	1	3	6	137	129	12	4	6	32	28	-8	6	6	63	-50	5	7	6	42	-45
-9	2	6	145	-127	2	3	6	190	178	13	4	6	18	9	-6	6	6	99	96	6	7	6	43	42
-7	2	6	58	48	3	3	6	28	-26	14	4	6	19	-22	-5	6	6	56	47	7	7	6	55	56
-7	2	6	134	125	4	3	6	110	-99	-14	5	6	24	29	-4	6	6	95	-90	8	7	6	63	-64
-6	2	6	58	-60	5	3	6	58	-55	-13	5	6	46	47	-3	6	6	67	-70	9	7	6	70	-70
-5	2	6	153	-148	6	3	6	72	65	-12	5	6	28	-14	-2	6	6	66	62	10	7	6	43	42
-4	2	6	108	104	7	3	6	17	10	-11	5	6	73	-66	0	6	6	54	-50	11	7	6	54	55
-3	2	6	200	190	8	3	6	25	-23	-10	5	6	46	39	1	6	6	82	78	12	7	6	24	-22
-2	2	6	73	-70	12	3	6	27	-23	-9	5	6	114	116	2	6	6	101	100	13	7	6	42	-36
-1	2	6	152	-141	14	3	6	61	54	-8	5	6	102	-97	3	6	6	145	-135	14	7	6	21	-23
0	2	6	35	33	-15	4	6	35	38	-7	5	6	92	-84	4	6	6	110	-101	-14	8	6	23	-10
2	2	6	64	-61	-14	4	6	50	57	-6	5	6	95	93	5	6	6	110	107	-13	8	6	18	39
3	2	6	89	85	-13	4	6	53	-54	-5	5	6	100	88	6	6	6	49	46	-11	8	6	26	-27
4	2	6	166	157	-12	4	6	61	-53	-3	5	6	32	29	7	6	6	39	-44	-10	8	6	29	35
5	2	6	25	-25	-11	4	6	73	74	-2	5	6	34	40	8	6	6	49	-42	-8	8	6	116	-104
8	2	6	58	-58	-10	4	6	26	39	-1	5	6	51	-59	9	6	6	20	-26	-7	8	6	81	-32

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	8	5	172	164	6	9	6	85	-73	-4	11	5	29	39	-4	13	6	18	31	2	15	6	29	-27
-5	8	5	149	147	7	9	6	34	-33	-3	11	6	47	58	-3	13	6	106	150	3	15	6	38	-43
-4	8	5	177	-172	8	9	6	98	94	-1	11	6	82	-90	-2	13	6	31	-43	5	15	6	46	46
-3	8	5	65	-59	9	9	6	33	33	0	11	5	52	-57	-1	13	6	124	-161	6	15	6	73	75
-2	8	5	104	105	10	9	6	82	-71	1	11	6	79	81	0	13	6	34	35	7	15	6	57	-47
0	8	5	52	-42	12	9	6	27	28	2	11	6	17	19	1	13	6	100	132	8	15	6	81	-77
1	8	5	69	-64	13	9	6	15	-21	3	11	6	34	-27	3	13	6	88	-118	9	15	6	54	56
2	8	5	17	-12	-13	10	6	59	81	4	11	6	68	82	5	13	6	48	73	10	15	6	65	65
3	8	5	55	48	-11	10	6	78	-85	5	11	6	17	-5	9	13	6	20	-20	-9	16	6	41	-46
4	8	6	38	22	-9	10	6	36	46	6	11	6	107	-128	-11	14	6	41	40	-8	16	6	30	-30
5	8	5	23	-17	-7	10	6	25	-1	8	11	5	83	98	-10	14	6	40	-49	-7	16	6	34	27
7	8	5	31	-27	-5	10	6	33	37	10	11	6	48	-70	-8	14	6	70	78	-6	16	6	25	27
9	8	5	24	-25	-3	10	6	37	-35	12	11	5	50	71	-7	14	6	38	-44	-4	16	6	48	-44
10	8	5	51	47	-4	10	6	38	-52	-11	12	5	36	-48	-5	14	6	75	-88	-3	16	6	19	22
11	8	5	41	50	-2	10	6	86	94	-10	12	5	23	-58	-5	14	6	75	88	-2	16	6	38	43
12	8	5	51	-54	-1	10	6	79	80	-9	12	5	32	41	-4	14	5	67	84	-1	16	6	36	-35
13	8	5	17	-9	0	10	6	26	-28	-8	12	6	82	95	-3	14	6	59	-56	1	16	6	59	62
-12	9	5	17	16	1	10	6	122	-124	-6	12	6	94	-127	-2	14	5	78	-95	2	16	6	87	-89
-11	9	5	18	21	2	10	6	61	-67	-5	12	6	28	-29	-1	14	6	18	-25	3	16	6	70	-73
-10	9	5	42	-33	3	10	6	142	165	-4	12	6	122	150	0	14	5	59	66	4	16	6	99	100
-9	9	5	67	-74	4	10	6	73	77	-2	12	6	108	-129	1	14	6	40	51	5	16	6	63	67
-8	9	6	89	88	5	10	6	134	-138	-1	12	6	32	48	3	14	6	73	-74	6	16	6	56	-55
-7	9	6	60	58	6	10	6	34	-27	0	12	6	31	41	5	14	6	84	93	7	16	6	41	-32
-6	9	5	67	-65	7	10	6	72	79	1	12	6	38	-40	6	14	6	23	-3	9	16	6	18	13
-5	9	6	32	41	8	10	6	18	24	2	12	6	43	49	7	14	6	45	-53	-8	17	6	31	-16
-3	9	5	154	-163	9	10	6	14	-17	3	12	6	51	63	-10	15	6	79	87	-7	17	6	49	47
-2	9	5	31	-25	10	10	6	23	-24	4	12	5	27	-32	-9	15	6	49	-36	-6	17	6	46	43
-1	9	5	134	136	11	10	6	15	32	5	12	6	51	-89	-8	15	6	76	-82	-4	17	6	35	-36
0	9	6	92	89	-12	11	5	53	76	7	12	6	28	52	-7	15	6	46	37	-3	17	6	59	-54
1	9	6	95	-98	-10	11	6	71	-97	12	12	6	36	41	-6	15	6	81	82	-2	17	6	45	40
2	9	6	116	-120	-9	11	6	23	6	-12	13	6	16	-13	-2	15	6	30	-36	-1	17	6	84	76
3	9	5	127	129	-8	11	6	72	88	-9	13	6	30	35	-1	15	6	16	-15	0	17	6	92	-91
4	9	5	78	75	-6	11	6	55	-66	-8	13	6	18	-28	0	15	6	54	58	1	17	6	67	-62
5	9	5	44	-47	-5	11	6	59	-71	-7	13	5	27	-41	1	15	6	27	21	2	17	6	86	83

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	17	E	45	40	-9	0	7	51	53	-14	2	7	64	-65	-6	3	7	110	-101	1	4	7	127	117
4	17	E	33	-28	-7	0	7	87	-82	-13	2	7	41	43	-5	3	7	144	-131	2	4	7	117	-107
6	17	E	18	19	-5	0	7	211	202	-12	2	7	107	96	-4	3	7	34	32	3	4	7	32	40
7	17	E	46	-47	-3	0	7	262	-244	-11	2	7	44	-37	-3	3	7	80	70	4	4	7	187	158
8	17	E	32	-29	-1	0	7	299	284	-10	2	7	182	-165	-2	3	7	51	-59	5	4	7	73	-75
-7	18	E	80	81	1	0	7	230	-217	-9	2	7	35	36	-1	3	7	16	-15	6	4	7	85	-76
-6	18	E	49	32	3	0	7	140	132	-8	2	7	161	156	1	3	7	103	-98	7	4	7	28	25
-5	18	E	127	-127	5	0	7	38	-34	-7	2	7	89	-82	2	3	7	60	54	8	4	7	34	38
-4	18	E	51	-54	7	0	7	30	29	-6	2	7	24	-25	3	3	7	24	-14	10	4	7	29	-31
-3	18	E	94	88	9	0	7	18	16	-5	2	7	114	99	4	3	7	111	-110	12	4	7	38	37
-2	18	E	49	49	13	0	7	48	-46	-4	2	7	50	-50	5	3	7	67	58	13	4	7	23	16
-1	18	E	32	-24	-14	1	7	34	-27	-3	2	7	89	-84	6	3	7	57	46	-14	5	7	27	27
0	18	E	24	-23	-13	1	7	33	28	-1	2	7	44	36	7	3	7	55	-60	-13	5	7	34	-33
3	18	E	28	21	-12	1	7	27	23	0	2	7	29	12	8	3	7	38	38	-12	5	7	18	13
5	18	E	55	-50	-11	1	7	30	17	1	2	7	92	-89	9	3	7	92	79	-11	5	7	20	-6
7	18	E	29	28	-9	1	7	57	-56	2	2	7	61	-56	10	3	7	43	-42	-9	5	7	19	30
-5	19	E	27	24	-8	1	7	95	-78	3	2	7	74	66	11	3	7	83	-79	-8	5	7	73	66
-4	19	E	30	-28	-7	1	7	55	47	4	2	7	111	105	13	3	7	67	60	-7	5	7	38	-38
-2	19	E	70	68	-6	1	7	97	85	5	2	7	51	-47	14	3	7	22	-14	-6	5	7	48	-48
0	19	E	94	-87	-5	1	7	128	-116	6	2	7	180	-172	-14	4	7	58	-59	-5	5	7	34	39
1	19	E	38	-40	-3	1	7	91	84	8	2	7	147	140	-13	4	7	21	33	-4	5	7	17	17
2	19	E	64	57	-2	1	7	91	-88	9	2	7	19	-10	-12	4	7	74	77	-3	5	7	31	-35
3	19	E	40	37	0	1	7	106	96	10	2	7	63	-53	-11	4	7	55	-63	-2	5	7	63	67
4	19	E	27	-12	1	1	7	93	-83	11	2	7	20	10	-10	4	7	61	-54	-1	5	7	25	-26
5	19	E	36	-30	2	1	7	124	-113	12	2	7	18	13	-9	4	7	42	24	0	5	7	134	-133
-4	20	E	16	20	3	1	7	23	9	13	2	7	25	-20	-8	4	7	58	58	1	5	7	126	122
-3	20	E	30	31	4	1	7	113	112	-14	3	7	19	17	-7	4	7	19	8	2	5	7	192	186
-1	20	E	24	-30	5	1	7	24	30	-13	3	7	25	16	-6	4	7	116	-111	3	5	7	140	-140
0	20	E	47	-37	6	1	7	104	-101	-12	3	7	31	-32	-5	4	7	51	-49	4	5	7	110	-109
1	20	E	17	2	7	1	7	17	-18	-11	3	7	25	15	-4	4	7	130	130	5	5	7	90	88
2	20	E	80	77	8	1	7	31	18	-10	3	7	26	2	-3	4	7	138	128	6	5	7	33	33
3	20	E	36	27	9	1	7	27	27	-9	3	7	72	-68	-2	4	7	102	-93	7	5	7	59	-58
-13	0	7	28	15	11	1	7	56	-52	-8	3	7	92	84	-1	4	7	187	-181	8	5	7	18	17
-11	0	7	33	29	13	1	7	46	48	-7	3	7	88	73	0	4	7	104	106	9	5	7	44	42

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
12	5	7	19	11	-3	7	7	43	54	10	8	7	29	29	11	10	7	25	18	9	12	7	26	-50
-13	6	7	63	-82	-2	7	7	30	30	11	8	7	34	-48	12	10	7	21	-35	-10	13	7	44	-60
-12	6	7	46	-33	-1	7	7	70	-67	-13	9	7	21	34	-12	11	7	17	-8	-9	13	7	22	30
-11	6	7	54	65	0	7	7	39	-22	-10	9	7	37	45	-9	11	7	47	-48	-8	13	7	28	58
-10	6	7	58	60	1	7	7	58	67	-8	9	7	75	-74	-8	11	7	35	35	-7	13	7	27	-35
-9	6	7	62	-68	2	7	7	52	50	-6	9	7	42	48	-7	11	7	58	79	-6	13	7	38	-58
-7	6	7	104	108	3	7	7	69	-73	-4	9	7	33	-43	-6	11	7	55	-58	-4	13	7	23	46
-6	6	7	57	-56	5	7	7	56	54	-3	9	7	42	27	-5	11	7	19	-20	-2	13	7	23	-21
-5	6	7	209	-193	7	7	7	19	12	-1	9	7	54	58	-4	11	7	51	45	0	13	7	41	-60
-4	6	7	106	99	8	7	7	56	-56	0	9	7	86	82	-3	11	7	64	-75	2	13	7	31	54
-3	6	7	154	153	9	7	7	78	-77	1	9	7	105	-103	-1	11	7	92	101	3	13	7	35	-49
-2	6	7	120	-122	10	7	7	77	86	2	9	7	101	-108	1	11	7	105	-108	6	13	7	42	-62
-1	6	7	59	-55	11	7	7	52	50	3	9	7	105	106	3	11	7	118	131	8	13	7	55	59
0	6	7	118	118	12	7	7	45	-44	5	9	7	48	-47	4	11	7	17	-24	9	13	7	17	-17
1	6	7	104	102	13	7	7	17	-20	6	9	7	54	59	5	11	7	84	-81	10	13	7	47	-53
2	6	7	72	-66	-13	8	7	74	-82	7	9	7	39	39	9	11	7	18	22	-9	14	7	57	65
3	6	7	108	-107	-12	8	7	51	-49	8	9	7	70	-67	10	11	7	31	-40	-7	14	7	42	-43
4	6	7	38	-31	-11	8	7	98	103	9	9	7	40	-40	-11	12	7	84	-90	-6	14	7	48	-59
5	6	7	36	50	-9	8	7	97	-105	10	9	7	45	45	-10	12	7	36	51	-5	14	7	22	8
6	6	7	80	80	-8	8	7	18	-2	12	9	7	32	-44	-9	12	7	69	83	-4	14	7	65	84
7	6	7	33	-31	-7	8	7	82	80	-12	10	7	17	-4	-8	12	7	42	-66	-3	14	7	29	-29
8	6	7	52	-56	-6	8	7	42	47	-10	10	7	17	20	-7	12	7	24	-25	-2	14	7	77	-103
9	6	7	50	51	-4	8	7	45	-53	-8	10	7	38	-48	-6	12	7	33	49	-1	14	7	58	81
11	6	7	54	-48	-3	8	7	42	-44	-7	10	7	20	-9	-4	12	7	62	-79	0	14	7	49	74
12	6	7	25	29	-2	8	7	19	21	-6	10	7	99	110	-3	12	7	18	22	1	14	7	66	-91
13	6	7	36	34	0	8	7	38	-36	-5	10	7	53	62	-2	12	7	84	108	3	14	7	61	82
-12	7	7	30	34	1	8	7	61	65	-4	10	7	159	-163	-1	12	7	18	25	4	14	7	35	-46
-11	7	7	19	0	2	8	7	103	97	-3	10	7	34	-42	0	12	7	60	-81	5	14	7	65	-80
-9	7	7	75	70	3	8	7	112	-111	-2	10	7	202	204	1	12	7	35	-42	6	14	7	40	45
-8	7	7	58	-57	4	8	7	124	-122	-1	10	7	46	-53	3	12	7	64	77	7	14	7	52	53
-7	7	7	123	-124	5	8	7	119	114	0	10	7	162	-169	4	12	7	19	21	8	14	7	22	-10
-6	7	7	114	120	6	8	7	49	50	2	10	7	67	64	5	12	7	86	-110	9	14	7	30	-28
-5	7	7	84	77	7	8	7	109	-109	5	10	7	32	26	7	12	7	74	103	-9	15	7	29	29
-4	7	7	61	-56	9	8	7	86	87	10	10	7	16	10	8	12	7	17	-18	-8	15	7	16	-15

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-7	15	7	91	-62	-3	14	7	26	13	-8	1	8	79	-72	2	2	8	81	75	-12	4	8	48	43
-6	15	7	33	-28	-2	14	7	31	24	-7	1	8	40	-36	3	2	8	135	129	-11	4	8	67	-64
-5	15	7	47	51	-1	14	7	27	-10	-6	1	8	158	138	4	2	8	69	-66	-10	4	8	135	-129
-1	15	7	66	-71	1	14	7	23	22	-5	1	8	102	81	5	2	8	39	-37	-9	4	8	69	67
0	15	7	46	50	2	14	7	60	-62	-4	1	8	125	-114	6	2	8	44	35	-8	4	8	151	142
1	15	7	60	65	3	14	7	45	-36	-3	1	8	81	-62	7	2	8	26	-13	-7	4	8	77	-81
2	15	7	51	-70	4	14	7	90	92	-2	1	8	60	60	9	2	8	45	42	-6	4	8	60	-55
3	15	7	82	-75	5	14	7	39	40	-1	1	8	55	56	10	2	8	39	32	-5	4	8	133	123
4	15	7	37	52	-4	13	7	17	-11	0	1	8	22	-28	12	2	8	31	-34	-3	4	8	126	-112
5	15	7	32	39	-3	13	7	17	-11	1	1	8	40	29	13	2	8	17	-25	-2	4	8	67	69
-8	16	7	43	48	-2	13	7	36	29	2	1	8	62	-54	-13	3	8	53	53	-1	4	8	97	90
-7	16	7	37	-29	-1	13	7	24	23	3	1	8	91	-75	-12	3	8	21	18	0	4	8	126	-126
-6	16	7	63	-68	0	13	7	47	-41	4	1	8	127	112	-9	3	8	40	-44	1	4	8	87	-89
-5	16	7	90	82	1	13	7	30	-27	5	1	8	57	53	-8	3	8	57	-43	2	4	8	64	60
-4	16	7	70	72	2	13	7	53	43	6	1	8	125	-116	-7	3	8	37	29	3	4	8	108	99
-3	16	7	81	-83	3	13	7	33	30	7	1	8	20	-9	-6	3	8	104	94	5	4	8	103	-98
-2	16	7	61	-54	-12	0	8	78	-71	8	1	8	18	-19	-5	3	8	101	-96	6	4	8	99	-86
-1	16	7	35	46	-10	0	8	192	189	10	1	8	19	17	-4	3	8	110	-101	7	4	8	72	61
0	16	7	50	44	-8	0	8	272	-250	11	1	8	82	54	-3	3	8	154	145	8	4	8	106	101
2	16	7	40	-36	-6	0	8	140	125	12	1	8	23	-11	-2	3	8	22	25	9	4	8	60	-52
4	16	7	10	19	-4	0	8	19	11	13	1	8	51	-56	-1	3	8	71	-70	10	4	8	74	-70
5	16	7	38	47	-2	0	8	25	-25	-12	2	8	32	-31	0	3	8	63	57	11	4	8	48	55
7	16	7	47	-45	0	0	8	52	42	-11	2	8	50	53	1	3	8	109	-109	12	4	8	35	27
8	16	7	24	25	2	0	8	21	15	-10	2	8	43	43	2	3	8	101	-92	13	4	8	33	-38
-7	17	7	28	34	4	0	8	46	-34	-9	2	8	20	-15	3	3	8	126	117	-13	5	8	53	57
-6	17	7	37	22	6	0	8	157	138	-8	2	8	51	-47	4	3	8	103	91	-12	5	8	63	-66
-5	17	7	36	-46	8	0	8	188	-170	-6	2	8	71	63	5	3	8	67	-54	-11	5	8	38	-36
-4	17	7	35	-19	10	0	8	129	116	-5	2	8	53	46	6	3	8	91	-81	-10	5	8	49	57
0	17	7	65	75	12	0	8	54	-60	-4	2	8	78	-71	7	3	8	41	29	-8	5	8	43	43
2	17	7	61	-65	-13	1	8	62	-64	-3	2	8	179	-156	8	3	8	30	30	-7	5	8	68	61
3	17	7	19	-15	-12	1	8	39	37	-2	2	8	73	68	9	3	8	27	-34	-6	5	8	114	-114
6	17	7	30	18	-11	1	8	54	49	-1	2	8	352	332	11	3	8	24	-18	-5	5	8	98	-95
7	17	7	40	-39	-10	1	8	30	-21	0	2	8	61	-60	13	3	8	30	35	-4	5	8	83	78
-6	18	7	26	-14	-9	1	8	21	3	1	2	8	304	-294	-13	4	8	64	65	-3	5	8	57	60

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	5	A	48	-51	11	6	8	53	53	1	8	8	35	29	-3	10	8	32	21	7	12	8	22	-43
1	5	A	38	-31	12	6	8	38	51	2	8	8	140	-154	3	10	8	47	-40	9	12	8	23	26
2	5	A	40	45	-12	7	8	18	-16	3	8	8	74	-76	4	10	8	28	-27	-8	13	8	28	43
3	5	A	74	73	-9	7	8	29	33	4	8	8	62	66	5	10	8	81	81	-7	13	8	38	55
4	5	A	98	-95	-8	7	8	25	26	5	8	8	62	63	7	10	8	90	-101	-6	13	8	34	-63
5	5	A	47	-51	-7	7	8	61	-61	7	8	8	29	-20	8	10	8	18	18	-5	13	8	40	-50
6	5	A	66	71	-6	7	8	41	-44	8	8	8	21	-29	9	10	8	80	95	-4	13	8	32	49
7	5	A	24	22	-5	7	8	87	90	9	8	8	19	20	11	10	8	38	-84	-2	13	8	29	-34
10	5	A	47	-42	-4	7	8	90	92	11	8	8	39	-42	-9	11	8	18	-35	1	13	8	19	0
11	5	A	38	-39	-3	7	8	106	-112	-12	9	8	35	48	-7	11	8	40	53	2	13	8	33	42
12	5	A	44	41	-2	7	8	45	-54	-10	9	8	33	-46	-5	11	8	36	-42	3	13	8	20	35
-13	6	A	35	30	-1	7	8	19	31	-9	9	8	19	18	-4	11	8	26	-45	4	13	8	28	-59
-12	6	A	41	43	0	7	8	25	-15	-8	9	8	20	-29	-3	11	8	42	53	5	13	8	35	-53
-11	6	A	72	-79	1	7	8	81	78	-7	9	8	58	-57	-2	11	8	40	47	6	13	8	25	43
-10	6	A	38	-28	2	7	8	72	77	-6	9	8	65	73	1	11	8	34	-43	7	13	8	17	28
-9	6	A	97	97	3	7	8	105	-105	-5	9	8	35	71	2	11	8	38	-51	-9	14	8	50	71
-8	6	A	35	27	4	7	8	50	-50	-4	9	8	60	-61	3	11	8	52	66	-8	14	8	40	-55
-7	6	A	98	-103	5	7	8	76	85	-3	9	8	19	-27	4	11	8	18	9	-7	14	8	32	-46
-6	6	A	82	-80	7	7	8	59	-65	-1	9	8	18	8	5	11	8	33	-45	-6	14	8	37	45
-5	6	A	51	47	9	7	8	27	30	2	9	8	30	-31	6	11	8	25	28	-4	14	8	30	-34
-4	6	A	159	160	10	7	8	24	-7	3	9	8	69	-61	7	11	8	28	31	-3	14	8	18	31
-3	6	A	27	23	12	7	8	27	31	4	9	8	64	63	-9	12	8	32	-52	-2	14	8	43	72
-2	6	A	127	-124	-11	8	8	43	46	5	9	8	78	77	-7	12	8	31	52	-1	14	8	25	3
-1	6	A	112	-106	-10	8	8	20	22	6	9	8	19	-30	-5	12	8	30	-19	0	14	8	53	-78
0	6	8	77	74	-9	8	8	46	-37	7	9	8	34	-38	-4	12	8	57	-70	2	14	8	39	51
1	6	8	90	95	-8	8	8	28	-30	9	9	8	22	-14	-3	12	8	29	32	4	14	8	39	-40
2	6	A	108	-104	-7	8	8	40	43	10	9	8	41	44	-2	12	8	121	141	5	14	8	28	-38
4	6	A	130	128	-6	8	8	47	-48	11	9	8	26	31	-1	12	8	87	-78	6	14	8	37	45
5	6	A	53	-49	-5	8	8	70	-78	-11	10	8	77	90	0	12	8	100	-124	7	14	8	49	59
6	6	A	71	-66	-4	8	8	99	106	-10	10	8	23	-4	1	12	8	59	70	8	14	8	34	-43
7	6	A	98	98	-3	8	8	58	51	-9	10	8	108	-126	2	12	8	64	72	-5	15	8	24	32
8	6	A	29	21	-2	8	8	173	-175	-7	10	8	101	114	3	12	8	33	-37	-4	15	8	33	30
9	6	A	101	-98	-1	8	8	19	-17	-5	10	8	87	-67	4	12	8	32	-36	-2	15	8	29	-33
10	6	A	40	-38	0	8	8	169	171	-4	10	8	23	-29	6	12	8	23	34	0	15	8	27	-17

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	15	8	18	4	5	0	9	55	44	6	2	9	64	60	-4	4	9	144	-132	-9	6	9	48	49
2	15	8	39	44	7	0	9	42	-29	7	2	9	57	-57	-3	4	9	28	-23	-8	6	9	64	69
4	15	8	25	-27	-11	1	9	33	35	8	2	9	111	-113	-2	4	9	116	106	-7	6	9	39	-35
-7	16	8	40	-33	-8	1	9	53	54	9	2	9	43	45	-1	4	9	144	140	-6	6	9	38	-32
-6	16	8	33	36	-6	1	9	110	-102	10	2	9	115	110	0	4	9	72	-71	-5	6	9	66	80
-5	16	8	47	37	-4	1	9	91	85	11	2	9	28	-36	1	4	9	158	-155	-4	6	9	31	-35
-4	16	8	27	-19	-3	1	9	74	-64	12	2	9	47	-55	2	4	9	65	64	-3	6	9	52	-57
-3	16	8	58	-59	-2	1	9	74	-62	-12	3	9	33	39	3	4	9	71	69	-2	6	9	74	72
-2	16	8	38	-31	-1	1	9	63	66	-11	3	9	70	64	4	4	9	65	-66	-1	6	9	45	42
-1	16	8	58	62	0	1	9	48	38	-10	3	9	51	-52	5	4	9	20	-11	0	6	9	90	-91
0	16	8	39	39	1	1	9	52	42	-9	3	9	72	-66	6	4	9	52	53	1	6	9	62	-54
1	16	8	44	-50	3	1	9	85	-57	-7	3	9	45	60	8	4	9	38	-32	2	6	9	110	111
2	16	8	22	8	4	1	9	20	-17	-6	3	9	75	70	9	4	9	21	30	3	6	9	104	105
3	16	8	48	48	5	1	9	55	53	-4	3	9	56	-55	10	4	9	52	48	4	6	9	80	-84
4	16	8	34	-44	6	1	9	62	60	-3	3	9	44	-39	-9	5	9	44	-38	5	6	9	91	-89
5	16	8	52	-45	7	1	9	21	-25	-2	3	9	35	36	-7	5	9	59	43	7	6	9	67	63
6	16	8	29	34	8	1	9	28	-31	0	3	9	42	-37	-6	5	9	32	38	8	6	9	45	37
-5	17	8	23	15	10	1	8	18	0	1	3	9	47	49	-5	5	9	76	-75	9	6	9	53	-53
-4	17	8	25	-31	-12	2	9	19	-32	3	3	9	52	-48	-4	5	9	81	-72	10	6	9	39	-38
-2	17	8	32	-40	-11	2	9	26	30	4	3	9	56	56	-3	5	9	117	122	11	6	9	38	51
4	17	8	25	21	-10	2	9	110	110	5	3	9	58	55	-2	5	9	110	104	-11	7	9	37	-44
5	17	8	37	33	-9	2	9	34	-24	6	3	9	94	-98	-1	5	9	80	-82	-10	7	9	64	65
-3	18	8	67	-66	-8	2	9	158	-159	7	3	9	70	-60	0	5	9	71	-66	-9	7	9	33	35
-2	18	8	38	-35	-7	2	9	31	17	8	3	9	31	39	1	5	9	36	-38	-8	7	9	20	-20
-1	18	8	49	46	-6	2	9	144	138	9	3	9	24	19	3	5	9	73	76	-7	7	9	20	10
0	18	8	29	27	-5	2	9	53	-57	11	3	9	27	7	4	5	9	34	32	-6	7	9	30	-38
1	18	8	52	-45	-4	2	9	88	-53	-12	4	9	24	-41	5	5	9	33	-31	-5	7	9	40	-53
2	18	8	18	-23	-3	2	9	53	50	-11	4	9	25	40	6	5	9	53	-52	-4	7	9	35	33
3	18	8	51	41	-2	2	9	27	19	-10	4	9	27	31	7	5	9	27	18	-3	7	9	58	58
-5	0	9	38	-32	-1	2	9	61	-55	-9	4	9	18	-25	8	5	9	33	34	-1	7	9	54	-61
-3	0	9	88	72	1	2	9	61	56	-8	4	9	21	-22	9	5	9	20	-13	0	7	9	37	-39
-1	0	9	226	-198	2	2	9	19	-13	-7	4	9	48	48	-12	6	9	18	-18	1	7	9	38	41
1	0	9	252	244	3	2	9	76	-67	-6	4	9	79	70	-11	6	9	44	-50	2	7	9	39	32
3	0	9	147	-148	5	2	9	68	63	-5	4	9	28	-31	-10	6	9	33	-33	3	7	9	23	9

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	7	9	55	-54	-2	9	9	87	-78	6	11	9	38	-44	4	14	9	27	-28	-11	1	10	52	-53
5	7	9	62	-62	-1	9	9	64	63	7	11	9	37	-34	5	14	9	21	23	-10	1	10	22	20
6	7	9	60	62	0	9	9	37	44	8	11	9	26	24	6	14	9	21	20	-9	1	10	71	69
7	7	9	53	57	2	9	9	19	2	-9	12	9	53	-84	7	14	9	36	-29	-7	1	10	77	-65
8	7	9	20	-31	3	9	9	44	-58	-7	12	9	64	100	-6	15	9	27	-35	-6	1	10	42	-37
10	7	9	23	-16	4	9	9	28	-23	-5	12	9	84	-79	-5	15	9	42	-38	-5	1	10	70	57
11	7	9	16	-1	5	9	9	34	33	-4	12	9	17	-25	-4	15	9	40	55	-4	1	10	54	45
-11	8	9	39	-45	6	9	9	34	27	0	12	9	30	44	-3	15	9	36	30	-2	1	10	33	-28
-9	8	9	78	83	7	9	9	19	-26	2	12	9	40	-43	-2	15	9	45	-50	0	1	10	63	60
-8	8	9	23	5	8	9	9	33	-33	4	12	9	40	40	-1	15	9	41	-37	1	1	10	19	-20
-7	8	9	112	-117	9	9	9	22	14	6	12	9	18	-46	0	15	9	22	29	2	1	10	57	-55
-6	8	9	61	-62	10	9	9	17	20	7	12	9	38	-54	1	15	9	34	55	3	1	10	46	48
-5	8	9	110	111	-8	10	9	15	-8	8	12	9	31	48	2	15	9	18	13	4	1	10	18	4
-4	8	9	96	107	-6	10	9	24	-1	-8	13	9	34	47	4	15	9	16	-27	5	1	10	48	-43
-3	8	9	60	-59	-3	10	9	23	-17	-7	13	9	17	23	5	15	9	17	-23	6	1	10	24	26
-2	8	9	71	-74	-2	10	9	89	-88	-6	13	9	27	-48	-4	16	9	17	-19	7	1	10	53	43
-1	8	9	24	6	0	10	9	119	136	-5	13	9	21	-43	-2	16	9	22	24	8	1	10	19	-17
0	8	9	43	48	1	10	9	19	-24	-4	13	9	18	-16	-1	16	9	31	-18	9	1	10	36	-45
1	8	9	26	25	2	10	9	137	-144	-3	13	9	30	42	0	16	9	38	-34	-10	2	10	25	-14
2	8	9	41	-40	3	10	9	24	-27	-2	13	9	37	57	1	16	9	46	36	-9	2	10	19	-28
3	8	9	22	-9	4	10	9	79	96	-1	13	9	25	-23	2	16	9	48	48	-8	2	10	21	15
4	8	9	27	38	5	10	9	23	30	4	13	9	25	14	3	16	9	51	-57	-6	2	10	26	-20
5	8	9	24	-26	8	10	9	48	-63	5	13	9	22	-38	4	16	9	50	-52	-5	2	10	28	26
6	8	9	25	-13	8	10	9	22	24	7	13	9	17	23	-2	17	9	43	-49	-4	2	10	45	37
7	8	9	58	59	-7	11	9	18	-24	-7	14	9	45	54	-10	0	10	31	-36	-2	2	10	38	-33
9	8	9	74	-85	-6	11	9	26	37	-6	14	9	28	-32	-8	0	10	101	108	-1	2	10	83	-80
10	8	9	17	-19	-5	11	9	49	59	-5	14	9	38	-50	-6	0	10	121	-114	0	2	10	29	27
-10	9	9	36	39	-4	11	9	41	-56	-4	14	9	24	34	-4	0	10	94	80	1	2	10	109	96
-8	9	9	28	42	-3	11	9	77	-76	-3	14	9	41	57	-2	0	10	76	-68	2	2	10	30	-41
-8	9	9	27	-23	-2	11	9	30	29	-1	14	9	51	-84	0	0	10	57	60	3	2	10	66	-65
-7	9	9	58	-63	-1	11	9	56	69	0	14	9	42	-60	2	0	10	44	-49	4	2	10	34	18
-6	9	9	21	23	1	11	9	53	-62	1	14	9	44	72	4	0	10	31	-11	5	2	10	74	63
-5	9	9	71	83	2	11	9	40	-37	2	14	9	48	59	8	0	10	69	70	6	2	10	21	-18
-3	9	9	77	-90	4	11	9	34	33	3	14	9	36	-38	10	0	10	74	-77	7	2	10	58	-53

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
9	2	10	27	29	-6	5	10	29	-20	-7	7	10	31	31	0	9	10	20	-28	-6	13	10	15	7
10	2	10	27	-28	-5	5	10	33	-29	-5	7	10	54	-53	1	9	10	62	62	-5	13	10	32	48
-10	3	10	18	-10	-3	5	10	19	19	-4	7	10	28	-33	3	9	10	48	-51	-3	13	10	34	-51
-9	3	10	17	14	-2	5	10	26	-42	-3	7	10	74	74	4	9	10	33	-42	-1	13	10	45	53
-6	3	10	48	-41	1	5	10	16	-11	-2	7	10	75	72	6	9	10	37	42	0	13	10	18	-33
-4	3	10	83	82	2	5	10	25	12	-1	7	10	87	-80	7	9	10	28	36	1	13	10	46	-74
-3	3	10	44	-36	3	5	10	18	-20	0	7	10	59	-58	8	9	10	32	-33	3	13	10	43	64
-2	3	10	99	-89	4	5	10	28	16	1	7	10	42	33	-8	10	10	22	-4	-5	14	10	32	-42
-1	3	10	74	73	5	5	10	19	33	2	7	10	30	36	-7	10	10	82	-80	-3	14	10	23	23
0	3	10	94	84	6	5	10	55	-62	4	7	10	28	16	-6	10	10	25	-13	-1	14	10	16	-29
2	3	10	71	-64	7	5	10	47	-45	6	7	10	25	-28	-5	10	10	81	93	0	14	10	34	42
3	3	10	28	-20	8	5	10	43	45	8	7	10	26	35	-4	10	10	25	52	2	14	10	37	-50
5	3	10	20	-9	9	5	10	35	45	-10	8	10	24	21	-3	10	10	66	-73	3	14	10	26	35
-9	4	10	20	-27	-10	6	10	27	31	-8	8	10	17	3	-1	10	10	41	49	4	14	10	37	49
-8	4	10	53	-49	-8	6	10	23	-22	-6	8	10	26	-11	4	10	10	24	-8	-2	15	10	25	33
-6	4	10	63	47	-7	6	10	40	35	-5	8	10	18	12	7	10	10	17	19	0	15	10	22	-34
-5	4	10	28	-35	-6	6	10	37	39	-3	8	10	25	-31	-8	11	10	38	-66	2	15	10	21	6
-4	4	10	47	-37	-5	6	10	56	-51	-2	8	10	28	28	-6	11	10	54	79	-9	0	11	47	50
-3	4	10	81	68	-4	6	10	85	-93	0	8	10	50	-50	-5	11	10	26	28	-5	0	11	30	-21
-2	4	10	30	22	-3	6	10	65	63	2	8	10	84	81	-3	11	10	44	-42	-3	0	11	58	59
-1	4	10	84	-88	-2	6	10	69	75	3	8	10	49	48	-2	11	10	35	-33	1	0	11	34	-44
1	4	10	24	27	-1	6	10	25	-18	4	8	10	86	-87	-1	11	10	41	48	3	0	11	48	47
3	4	10	58	-60	0	6	10	34	-21	5	8	10	56	-61	0	11	10	23	26	5	0	11	57	-43
4	4	10	53	47	1	6	10	29	-33	6	8	10	58	61	1	11	10	34	-27	7	0	11	62	62
5	4	10	79	78	2	6	10	37	32	7	8	10	24	24	8	11	10	22	25	9	0	11	51	-50
7	4	10	85	-70	3	6	10	39	39	8	8	10	27	-27	-7	12	10	20	-46	-9	1	11	39	31
8	4	10	27	-37	4	6	10	51	-52	9	8	10	16	-9	-6	12	10	28	23	-8	1	11	17	-12
9	4	10	51	46	5	6	10	29	-18	-9	9	10	25	38	-5	12	10	21	31	-7	1	11	66	-68
10	4	10	39	36	6	6	10	52	57	-8	9	10	47	-42	-1	12	10	25	32	-6	1	11	32	31
-11	5	10	51	58	8	6	10	29	-26	-6	9	10	33	20	0	12	10	40	49	-5	1	11	86	89
-10	5	10	82	-71	9	6	10	33	23	-5	9	10	31	-45	1	12	10	34	-40	-4	1	11	55	-47
-9	5	10	65	-70	10	6	10	28	27	-4	9	10	27	-18	2	12	10	63	-77	-3	1	11	35	-34
-8	5	10	59	56	-9	7	10	35	-50	-3	9	10	61	63	4	12	10	53	61	-2	1	11	45	47
-7	5	10	47	46	-8	7	10	27	37	-1	9	10	61	-56	6	12	10	39	-51	-1	1	11	20	-10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJ91

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	1	11	59	-59	-9	4	11	40	-43	4	8	11	29	45	5	9	11	38	47	4	1	12	75	-70
1	1	11	23	2	-7	4	11	18	30	5	8	11	47	51	-2	10	11	19	-31	5	1	12	18	10
2	1	11	98	89	-6	4	11	18	-15	6	8	11	44	-47	2	10	11	35	37	6	1	12	48	47
4	1	11	76	-71	-4	4	11	42	48	7	8	11	35	-36	3	10	11	17	20	-7	2	12	44	-51
5	1	11	19	-13	-3	4	11	61	-58	8	8	11	35	31	4	10	11	45	-47	-3	2	12	66	71
6	1	11	34	33	-2	4	11	32	-40	-8	7	11	61	71	5	10	11	23	-31	-1	2	12	73	-78
7	1	11	18	10	-1	4	11	46	41	-7	7	11	42	47	6	10	11	34	47	1	2	12	42	41
9	1	11	17	-24	0	4	11	18	18	-6	7	11	60	-60	-5	11	11	23	-36	3	2	12	17	-6
-8	2	11	17	4	3	4	11	30	-32	-5	7	11	27	-25	-4	11	11	20	-24	5	2	12	29	-20
-6	2	11	83	-87	4	4	11	31	28	-4	7	11	50	48	-3	11	11	45	49	7	2	12	40	42
-4	2	11	55	58	5	4	11	44	34	-2	7	11	63	-69	-1	11	11	35	-54	-7	3	12	21	-26
-3	2	11	32	-21	6	4	11	25	-36	0	7	11	38	50	1	11	11	57	72	-5	3	12	54	53
-2	2	11	51	-47	7	4	11	41	-47	1	7	11	49	-51	3	11	11	60	-77	-4	3	12	26	-19
-1	2	11	23	19	-9	5	11	29	37	3	7	11	42	43	4	11	11	21	3	-3	3	12	45	-47
0	2	11	71	67	-7	5	11	29	-6	6	7	11	30	-33	5	11	11	24	31	-2	3	12	36	36
2	2	11	25	-29	-4	5	11	28	28	7	7	11	28	-33	-3	12	11	30	-41	0	3	12	61	-67
5	2	11	35	-32	-3	5	11	29	-19	-7	8	11	18	15	-1	12	11	16	42	1	3	12	37	38
7	2	11	24	27	-2	5	11	67	-87	-6	8	11	23	25	1	12	11	24	-38	2	3	12	90	93
9	2	11	22	-15	-1	5	11	65	66	-5	8	11	50	-52	1	13	11	15	-8	3	3	12	38	-28
-9	3	11	70	69	0	5	11	73	85	-4	8	11	41	-47	-6	0	12	23	-7	4	3	12	79	-83
-8	3	11	41	-49	1	5	11	61	-63	-3	8	11	62	70	-2	0	12	35	40	5	3	12	34	34
-7	3	11	91	-94	2	5	11	75	-89	-1	8	11	66	-64	0	0	12	98	-98	6	3	12	63	61
-6	3	11	37	44	3	5	11	48	44	1	8	11	30	26	2	0	12	79	86	-7	4	12	20	18
-5	3	11	92	86	4	5	11	47	39	2	8	11	17	-7	4	0	12	19	-12	-4	4	12	28	25
-3	3	11	53	-43	5	5	11	43	-49	7	8	11	16	11	6	0	12	19	-31	-2	4	12	40	-47
-1	3	11	24	20	7	5	11	34	40	-6	9	11	54	-67	-7	1	12	73	71	0	4	12	78	79
0	3	11	19	0	-8	6	11	18	11	-4	9	11	34	33	-6	1	12	25	-24	2	4	12	55	-54
1	3	11	20	-11	-5	6	11	19	-4	-3	9	11	31	31	-5	1	12	98	-10	6	4	12	17	35
2	3	11	39	-34	-4	6	11	36	-23	-1	9	11	57	-58	-3	1	12	83	78	-7	5	12	58	-59
4	3	11	34	30	-2	6	11	30	22	0	9	11	19	-26	-2	1	12	18	-24	-6	5	12	58	63
5	3	11	27	-30	-1	6	11	29	-22	1	9	11	54	54	-1	1	12	28	-34	-5	5	12	69	72
7	3	11	51	46	0	6	11	31	-26	2	9	11	17	10	1	1	12	24	12	-4	5	12	56	-58
8	3	11	17	-13	1	6	11	20	16	3	9	11	43	-40	2	1	12	70	64	-3	5	12	63	-62
9	3	11	40	-47	3	6	11	37	-43	4	9	11	17	11	3	1	12	26	-27	-2	5	12	78	77

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	1	11	59	-59	-3	4	11	40	-43	4	6	11	29	45	5	9	11	38	47	4	1	12	76	-70
1	1	11	23	2	-7	4	11	18	30	5	6	11	47	51	-2	10	11	19	-31	5	1	12	10	10
2	1	11	98	89	-6	4	11	18	-15	6	6	11	44	-47	2	10	11	35	37	6	1	12	48	47
4	1	11	78	-71	-4	4	11	42	48	7	6	11	35	-36	3	10	11	17	20	-7	2	12	44	-51
5	1	11	14	-13	-3	4	11	61	-58	8	6	11	35	31	4	10	11	45	-47	-3	2	12	66	71
6	1	11	34	33	-2	4	11	32	-40	-8	7	11	61	71	5	10	11	23	-31	-1	2	12	73	-78
7	1	11	18	10	-1	4	11	46	41	-7	7	11	42	47	6	10	11	34	47	1	2	12	42	41
9	1	11	17	-24	0	4	11	18	18	-6	7	11	60	-60	-5	11	11	23	-36	3	2	12	17	-6
-8	2	11	17	4	3	4	11	30	-32	-5	7	11	27	-25	-4	11	11	20	-24	5	2	12	29	-20
-6	2	11	69	-57	4	4	11	31	28	-4	7	11	50	48	-3	11	11	45	49	7	2	12	40	42
-4	2	11	56	53	5	4	11	44	34	-2	7	11	63	-69	-1	11	11	35	-54	-7	3	12	21	-26
-3	2	11	32	-21	6	4	11	25	-36	0	7	11	38	50	1	11	11	57	72	-5	3	12	54	63
-2	2	11	51	-47	7	4	11	41	-47	1	7	11	49	-51	3	11	11	60	-77	-4	3	12	28	-19
-1	2	11	23	19	-8	5	11	29	37	3	7	11	42	43	4	11	11	21	3	-3	3	12	45	-47
0	2	11	71	67	-7	5	11	29	-6	6	7	11	30	-33	5	11	11	24	31	-2	3	12	36	36
2	2	11	25	-29	-4	5	11	28	24	7	7	11	28	-33	-3	12	11	30	-41	0	3	12	61	-67
5	2	11	35	-32	-3	5	11	29	-19	-7	8	11	18	15	-1	12	11	16	42	1	3	12	37	38
7	2	11	24	27	-2	5	11	67	-87	-6	8	11	23	25	1	12	11	24	-38	2	3	12	90	93
9	2	11	22	-15	-1	5	11	65	66	-5	8	11	50	-52	1	13	11	15	-8	3	3	12	36	-28
-9	3	11	70	69	0	5	11	73	85	-4	8	11	41	-47	-6	0	12	23	-7	4	3	12	79	-83
-8	3	11	41	-49	1	5	11	61	-63	-3	8	11	62	70	-2	0	12	35	40	5	3	12	34	34
-7	3	11	91	-94	2	5	11	75	-69	-1	8	11	86	-84	0	0	12	98	-98	6	3	12	63	61
-6	3	11	37	44	3	5	11	48	44	1	8	11	30	26	2	0	12	79	86	-7	4	12	20	18
-5	3	11	82	86	4	5	11	47	39	2	8	11	17	-7	4	0	12	19	-12	-4	4	12	28	25
-3	3	11	53	-43	5	5	11	43	-49	7	8	11	16	11	6	0	12	19	-31	-2	4	12	40	-47
-1	3	11	24	20	7	5	11	34	40	-8	9	11	54	-67	-7	1	12	73	71	0	4	12	78	79
0	3	11	18	0	-8	6	11	18	11	-4	9	11	36	33	-6	1	12	25	-24	2	4	12	55	-54
1	3	11	20	-11	-5	6	11	19	-4	-3	9	11	31	31	-5	1	12	98	-101	5	4	12	17	35
2	3	11	39	-34	-4	6	11	36	-23	-1	9	11	57	-58	-3	1	12	83	78	-7	5	12	58	-59
4	3	11	34	30	-2	6	11	30	22	0	9	11	19	-26	-2	1	12	18	-24	-6	5	12	58	63
5	3	11	27	-30	-1	6	11	29	-22	1	9	11	54	54	-1	1	12	28	-34	-5	5	12	69	72
7	3	11	51	46	0	6	11	31	-26	2	9	11	17	10	1	1	12	24	12	-4	5	12	56	-58
8	3	11	17	-13	1	6	11	20	16	3	9	11	43	-40	2	1	12	70	64	-3	5	12	63	-62
9	3	11	40	-47	3	6	11	37	-43	4	9	11	17	11	3	1	12	26	-27	-2	5	12	78	77

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DJR1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	4	12	17	24	0	7	12	17	31	-2	8	12	47	-51	3	0	13	27	33	-1	3	13	61	-61
0	5	12	40	-45	1	7	12	62	-66	0	9	12	32	31	-3	1	13	54	57	1	3	13	39	39
4	5	12	28	30	2	7	12	28	-43	1	9	12	33	-38	-1	1	13	17	-29	2	3	13	18	19
6	5	12	21	1	3	7	12	64	66	2	9	12	16	-8	2	1	13	53	-57	3	3	13	15	-16
-3	6	12	40	-53	4	7	12	30	32	3	9	12	43	57	-2	2	13	23	8	-1	4	13	62	-70
-1	6	12	57	69	5	7	12	60	-65	-1	10	12	26	-40	0	2	13	41	-61	0	4	13	18	16
1	6	12	44	-42	-4	8	12	18	-26	1	10	12	32	34	2	2	13	40	53	1	4	13	47	54
3	6	12	27	4	-2	8	12	40	44	-3	0	13	31	-40	-4	3	13	34	32	2	4	13	17	-14
-6	7	12	22	34	0	8	12	40	-44	-1	0	13	66	73	-3	3	13	68	68	0	5	13	16	-15
-4	7	12	17	-26	-4	9	12	51	55	1	0	13	47	-51	-2	3	13	41	-42	1	5	13	45	54
-1	7	12	42	54																				

Appendix D

LIST 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 $M_2(CO)_8(Bu^tNC)_2$ (M=Mn,Re) ", J. Chem. Soc., Chem. Commun., in press.

(b) E. A. Darling, D. J. Robinson and N. J. Coville, "The Palladium Catalysed Reactions of $MnRe(CO)_{10}$ and Isonitriles and the Crystal and Molecular Structure of $Mn(CO)_5Re(CO)_4(Bu^tNC)$.", manuscript in preparation.

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

REFERENCES

1. R. Ugo, Catal. Rev., 1975, 11, 225.
2. E. L. Muetterties, Bull. Soc. Chim. Belg., 1975, 84, 959.
3. E. L. Muetterties, Bull. Soc. Chim. Belg., 1976, 85, 451.
4. E. L. Muetterties, Science, 1977, 196, 839.
5. E. L. Muetterties, Angew. Chem., Int. Ed. Engl., 1978, 17, 545.
6. E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, Chem. Rev., 1979, 79, 91.
7. J. Y. Saillard and R. Hoffmann, J. Am. Chem. Soc., 1984, 106, 2006.
8. E. L. Muetterties, Chem. Eng. News, 1982, 30 Aug., 28.
9. J. B. Johnson and W. G. Klemperer, J. Am. Chem. Soc., 1977, 99, 7132.
10. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 1967, 2nd Ed., Wiley, New York.
11. R. L. Mond, C. Langer and F. Quincke, J. Chem. Soc., 1890, 57, 749.
12. R. L. Mond and F. Quincke, J. Chem. Soc., 1891, 59, 604.
13. M. Bertheldt, Comp. Rend., 1981. 112, 1343.

14. L. F. Dahl, E. Ishishi and R. E. Rundle, J. Chem. Phys., 1957, 26, 1750.

15. M. R. Churchill, K. N. Amoh and H. J. Wasserman, Inorg. Chem., 1981, 20, 1609.

16. G. Bor and K. Noack, J. Organomet. Chem., 1974, 64, 367.

17. S. Onaka and D. F. Shriver, Inorg. Chem., 1976, 15, 915.

18. G. Bor, U. K. Dietler and K. Noack, J. Chem. Soc., Chem. Commun., 1976, 914.

19. J. Dewar and H. O. Jones, Proc. R. Soc. (London), 1905, A76, 558.

20. H. M. Powell and R. V. G. Ewens, J. Chem. Soc., 1939, 286.

21. F. A. Cotton and J. M. Troup, J. Chem. Soc., Dalton Trans., 1974, 800.

22. C. R. Eady, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., 1975, 2606.

23. E. H. Braye and W. Hubel, Inorg. Synth., 1966, 8, 178.

24. H. G. Cutforth and P. W. Selwood, J. Am. Chem. Soc., 1943, 65, 2414.

25. M. I. Bruce and F. G. A. Stone, J. Chem. Soc. A, 1967, 1238.

26. P. Chini and B. T. Heaton, Topics Curr. Chem., 1977, 71, 1.

27. P. Chini, G. Longoni and U. G. Albano, Adv. Organomet. Chem., 1976, 14, 285.

28. G. A. Ozin, Catal. Rev.- Sci. Eng., 1977, 16, 191.

29. M. P. Schubert, J. Am. Chem. Soc., 1933, 55, 4563.

30. R. Hoffmann, Angew. Chem., Int. Ed. Engl., 1982, 21.

31. U. Anders and W. A. G. Graham, J. Am. Chem. Soc., 1967, 89, 539.

32. J. K. Ruff, Inorg. Chem., 1968, 7, 1818.

33. J. R. Johnson, R. J. Ziegler and W. M. Risen, Jr., Inorg. Chem., 1973, 12, 2349.

34. J. R. Johnson, D. M. Duggan and W. R. Risen, Jr., Inorg. Chem., 1975, 14, 1053.

35. U. Honrath and H. Vahrenkamp, Z. Naturforsch., Tiel B, 1979, 34, 1190.

36. A. N. Nesmeyanov, M. I. Rybinskaya, V. S. Kaganovich, and K. L. Korneva, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 722.

37. R. A. Levenson and H. B. Gray, J. Am. Chem. Soc., 1975, 97, 6042.

38. T. Madack and H. Vahrenkamp, Chem. Ber., 1980, 113, 2675.

39. G. Beysel, J. Grobe and W. Mohr, J. Organomet. Chem., 1979, 170, 319.

40. T. Kruck and M. Höfler, Chem. Ber., 1964, 97, 2289.

41. G. Sbringnadello, G. Bor and L. Maresca, J. Organomet. Chem., 1972, 46, 345.

42. K. K. Joshi and P. L. Pauson, Z. Naturforsch., Tiel B, 1962, 17, 565.

43. G. Bor, J. Organomet. Chem., 1974, 65, 81.

44. G. Beysel, J. Grobe and U. Mohr, Z. Anorg. Allg. Chem., 1975, 418, 121.

45. E. S. Mooberry and R. K. Sheline, J. Chem. Phys., 1972, 56, 1852.

46. W. T. Wozniak and R. K. Sheline, J. Inorg. Nucl. Chem., 1973, 35, 1199.

47. G. Sbringnaello, G. Tomat, L. Magon and G. Bor, Inorg. Nucl. Chem. Lett., 1973, 9, 1073.

48. M. S. Wrighton and D. S. Ginley, J. Am. Chem. Soc., 1975, 97 2065.

49. G. O. Evans, W. T. Wozniak and R. K. Sheline, Inorg. Chem., 1970, 9, 979.

50. R. A. Levenson, H. B. Gray and G. P. Ceasar, J. Am. Chem. Soc., 1970, 92, 3653.

51. J. P. Fawcett and A. Poë, J. Chem. Soc., Dalton Trans., 1976, 2039.

52. D. Sonnenberger and J. D. Atwood, J. Am. Chem. Soc., 1980, 102, 3484.

53. J. P. Fawcett, A. Poë and K. R. Sharma, J. Am. Chem. Soc., 1976, 98, 1401.

54. R. A. Jackson and A. J. Poë, Inorg. Chem., 1978, 17, 997.

55. A. N. Nesmeyanov, K. N. Anisimov, H. Ye. Kolobova and I. S. Kolemnikov, Izv. Adad. Nauk. SSSR. Otd. Khim. Nauk, 1963, 194.

56. N. Flitcroft, D. K. Huggins and H. D. Kaesz, Inorg. Chem., 1964, 3, 1123.

57. S. A. R. Knox, R. J. Hoxmeier and H. D. Kaesz, Inorg. Chem., 1971, 10, 2636.

58. G. A. Junk and H. J. Svec, J. Chem. Soc. A, 1970, 2102.

59. E. W. Abel, R. A. N. McLean and S. Moorhouse, Inorg. Nucl. Chem. Lett., 1971, 7, 587.

60. I. G. deJong and D. R. Wiles, Inorg. Chem., 1973, 12, 2519.

61. B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, J. Chem. Soc. A, 1967, 341.

62. G. Kramer, J. Patterson and A. Poë, J. Chem. Soc., Dalton Trans., 1979, 1165.

63. D. A. Brown, W. J. Chambers, N. J. Fitzpatrick and R. W. Rawlinson, J. Chem. Soc. A, 1971, 720.

64. T. Kruck, M. Höfler and M. Noack, Chem. Ber., 1966, 99, 1153.

65. G. Sbrignadello, G. Battiston and G. Bor, Inorg. Chim. Acta, 1975, 14, 69.

66. W. T. Wozniak, G. O. Evans and R. K. Sheline, Inorg. Chim. Acta, 1975, 14, L53.

67. W. T. Wozniak, G. O. Evans and R. K. Sheline, J. Inorg. Nucl. Chem., 1975, 37, 105.

68. C. Q. Quicksall and T. G. Spiro, Inorg. Chem., 1964, 3, 1123.

69. P. Lemoine, M. Gross, M. Diot and J. Bousquet, J. Organomet. Chem., 1976, 104, 221.

70. M. Diot, J. Bousquet, P. Lemoine and M. Gross, J. Organomet. Chem., 1976, 112, 79.

71. G. O. Evans and R. K. Sheline, J. Inorg. Nucl. Chem., 1968, 30, 2862.

72. E. O. Fischer, E. Offhaus, J. Müller and D. Nöthe, Chem. Ber., 1972, 105, 3027.

73. H. J. Svec and G. A. Junk, J. Am. Chem. Soc., 1967, 89, 2836.

74. H. M. Gager, J. Lewis and M. J. Ware, J. Chem. Soc., Chem. Commun., 1966, 616.

75. F. A. Cotton and J. M. Troup, J. Chem. Soc., Dalton Trans., 1974, 800.

76. M. I. Bruce, Comp. Organomet. Chem., 1982, Vol. 4, p.663, Pergamon Press, New York.

77. J. R. Moss and W. A. G. Graham, J. Chem. Soc., Dalton Trans., 1977, 95.

78. R. B. King and F. G. A. Stone, Inorg. Synth., 1966, 8, 181.

79. W. MacFarlane and G. Wilkinson, Inorg. Synth., 1980, 20, 222.

80. M. I. Bruce and F. G. A. Stone, Angew. Chem., 1968, 80, 460.

81. S. C. Tripathi, S. C. Srivasta, R. P. Manit and A. K. Shrimal, Inorg. Chim. Acta, 1975, 15, 249.

82. M. R. Churchill and B. G. DeBoer, Inorg. Chem., 1977, 16, 878.

83. G. A. Battiston, G. Bor, U. K. Dietler, S. F. A. Kettle, R. Rossetti, G. Sbrignadello and P. L. Stanghellini, Inorg. Chem., 1980, 19, 1961.

84. B. E. Reichert and G. M. Sheldrick, Acta Crystalogr. B, 1977, 33, 173.

85. C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta and G. M. Sheldrick, J. Chem. Soc., Chem. Commun., 1976, 807.

86. E. H. Shubert and R. K. Sheline, Z. Naturforsch., Tiel B, 1965, 20, 1306.

87. M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. LiShingman and J. Takats, J. Am. Chem. Soc., 1976, 98, 4810.

88. D. R. Tyler, R. A. Levenson and H. B. Gray, J. Am. Chem. Soc., 1978, 100, 7888.

89. G. Nagarajan and M. W. Lindauer, Phys. Rev. A, 1972, 5, 557.

90. P. A. Agron, R. D. Ellison and H. A. Levy, Acta Crystalogr., 1967, 23, 1079.

91. G. O. Evans, J. P. Hargarden and R. K. Sheline, J. Chem. Soc., Chem. Commun., 1967, 186.

92. P. A. Agron, R. D. Ellison and H. A. Levy, Chem. Div. Ann. Progr. Rept., 1968, May 20, ORNL - 4306, p.157.

93. P. Braunstein, D. Matt, O. Bars and D. Grandjean, Angew. Chem., Int. Ed. Engl., 1979, 18, 797.

94. U. Anders and W. A. G. Graham, J. Chem. Soc., Chem. Commun., 1966, 291.

95. A. Forrester, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson and W. G. Jackson, J. Chem. Soc., Chem. Commun., 1974, 1042.

96. M. W. Lindauer, G. O. Evans and R. K. Sheline, Inorg. Chem., 1968, 7, 1249.

97. J. Knight and M. J. Mays, J. Chem. Soc., Dalton Trans., 1972, 1022.

98. P. Braunstein and J. Dehand, J. Organomet. Chem., 1975, 88, C24.

99. S. Martinengo, P. Chini, V. G. Albano, F. Cariati and T. Salvatori, J. Organomet. Chem., 1973, 59, 379.

100. B. F. G. Johnson, J. Lewis and T. W. Matheson, J. Chem. Soc., Chem. Commun., 1974, 441.

101. P. M. Lansarot, G. A. Vaglio and M. Valle, Inorg. Chim. Acta, 1979, 35, 227.

102. D. Labroue, R. Queanand and R. Poilbanc, J. Organomet. Chem., 1980, 186, 101.

103. G. Longoni, M. Manassero and M. Sansoni, J. Am. Chem. Soc., 1980, 102, 3242.

104. M. I. Bruce, G. Shaw and F. G. A. Stone, J. Chem. Soc., Dalton Trans. 1972, 1082.

105. A. Fumagali, G. Longoni, P. Chini, A. Albinati and S. Bruckner, J. Organomet. Chem., 1980, 202, 329.

106. A. Fumagali, S. Martinengo, P. Chini, A. Albinati, S. Bruckner and B. T. Heaton, J. Chem. Soc., Chem. Commun., 1978, 195.

107. C. H. Langford and H. B. Gray, Ligand Substitution Processes, W. A. Benjamin, Inc., 1965, New York.

108. R. J. Angelici, Organomet. Chem. Rev., 1968, 3, 173.

109. D. A. Brown, Inorg. Chim. Acta Rev., 1967, 1, 35.

110. H. Werner, Angew. Chem., Int. Ed. Engl., 1968, 7, 930.

111. K. Noack and F. Calderazzo, J. Organomet. Chem., 1967, 10, 101.

112. A. Wojcicki, Adv. Organomet. Chem., 1973, 11, 87.

113. B. H. Byers and T. L. Brown, J. Am. Chem. Soc., 1975, 97, 947.

114. D. J. Darensbourg, Adv. Organomet. Chem., 1982, 21, 113.

115. D. J. Darensbourg and M. J. Incorvia, Inorg. Chem., 1980, 19, 2585.

116. D. J. Darensbourg, B. S. Peterson and R. E. Schmidt Jr., Organomet., 1982, 1, 306.

117. K. J. Karel and J. R. Norton, J. Am. Chem. Soc., 1974, 96, 6812.

118. D. C. Sonnenberger and J. D. Atwood, J. Am. Chem. Soc., 1982, 104, 2113.

119. D. C. Sonnenberger and J. D. Atwood, Organomet., 1982, 1, 649.

120. D. J. Darensbourg and B. J. Baldwin-Zuschke, J. Am. Chem. Soc., 1982, 104, 3906.

121. D. A. Brown and R. T. Sane, J. Chem. Soc. A, 1971, 2088.

122. R. J. Angelici and F. Basolo, J. Am. Chem. Soc., 1962, 84, 2495.

123. F. Zingales, M. Graziani, F. Farsone and U. Belluco, Inorg. Chim. Acta, 1967, 1, 172.

124. D. A. Brown, H. J. Lyons and R. T. Sane, Inorg. Chim. Acta, 1970, 4, 621.

125. A. Wojicki and F. Basolo, J. Am. Chem. Soc., 1961, 83, 525.

126. W. Hieber and K. Wollmann, Chem. Ber., 1962, 95, 1552.

127. B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson and A. Wojicki, J. Chem. Soc. A, 1968, 522.

128. J. D. Atwood and T. L. Brown, J. Am. Chem. Soc., 1975, 97, 3380.

129. J. D. Atwood and T. L. Brown, J. Am. Chem. Soc., 1976, 98, 3155.

130. J. D. Atwood and T. L. Brown, J. Am. Chem. Soc., 1976, 98, 3160.

131. H. Wawersik and F. Basolo, J. Am. Chem. Soc., 1967, 89, 4626.

132. R. J. Mawby, F. Basolo and R. G. Pearson, J. Am. Chem. Soc., 1964, 86, 5043.

133. R. J. Mawby, F. Basolo and R. G. Pearson, J. Am. Chem. Soc., 1964, 86, 3994.

134. F. Calderazzo and F. A. Cotton, Chim. E Ind., 1964, 46, 1165.

135. F. Calderazzo and K. Noack, Coord. Chem. Rev., 1966, 1, 118.

136. R. W. Johnson and R. G. Pearson, Inorg. Chem., 1971, 10, 2091.

137. H. G. Schuster-Woldan and F. Basolo, J. Am. Chem. Soc., 1966, 88, 1657.

138. A. Berry and T. L. Brown, J. Organomet. Chem., 1971, 33, C67.

139. B. H. Byers and T. L. Brown, J. Am. Chem. Soc., 1975, 97, 947.

140. J. P. Fawcett, R. A. Jackson and A. Poë, J. Chem. Soc., Dalton Trans., 1978, 789.

141. A. Fox, J. Malito and A. Poë, J. Chem. Soc., Chem. Commun., 1981, 1052.

142. A. Poë, Transition Met. Chem., 1982, 7, 65.

143. A. Wojicki and F. Basolo, J. Inorg. Nucl. Chem., 1961, 17, 77.

144. R. J. Angelici and W. Loewen, Inorg. Chem., 1967, 6, 682.

145. P. M. Zizelman, C. Amatore and J. K. Kochi, J. Am. Chem. Soc., 1984, 106, 3771.

146. S. Brietschaft and F. Basolo, J. Am. Chem. Soc.. 1966, 88, 2702.

147. J. R. Graham and R. J. Angelici, Inorg. Chem., 1967, 6, 2082.

148. J. A. Connor, Topics Curr. Chem., 1977, 71, 71

149. E. L. Muetterties, B. A. Sosinsky and K. I. Zamariev, J. Am. Chem. Soc., 1975, 97, 5299

150. G. Battison, G. Sbrignadello, G. Bor and J. A. Connor, J. Organomet. Chem., 1977, 131, 445.

151. H. Wawersik and F. Basolo, Inorg. Chim. Acta, 1969, 3, 113.

15 . S. Schmidt, W C. Trogler and F. Basolo, Inorg. Chem., 1982, 21, 1698.

153. W. D. Covey and T. L. Brown, Inorg. Chem., 1973, 12, 2820.

154. A. Marcomini and A. Poë, J. Am. Chem. Soc., 1983, 105, 695?.

155. L. I. B. Haines, D. Hopgood and A. J. Poë, J. Chem. Soc. A, 1968, 421.

156. L. I. B. Haines and A. J. Poë, J. Chem. Soc. A, 1969, 2826.

157. F. Zingales, U. Sartorelli, F. Canziani and M. Raveglia, Inorg. Chem., 1967, 6, 154.

158. F. Zingales and U. Sartorelli, Inorg. Chem., 1967, 6, 1243.

159. D. G. DeWit, J. P. Fawcett and A. J. Poë, J. Chem. Soc., Dalton Trans., 1976, 528.

160. A. Poë, Inorg. Chem., 1981, 20, 4029.

161. L. F. Dahl and R. E. Rundle, Acta Crystallogr., 1963, 16, 419.

162. M. F. Bailey and L. F. Dahl, Inorg. Chem., 1965, 4, 1140.

163. D. M. Chowdhury, A. J. Poë and K. R. Sharma, J. Chem. Soc., Dalton Trans., 1977, 2352.

164. D. R. Bidinosti and N. S. McIntyre, J. Chem. Soc., Chem. Commun., 1966, 555.

165. M. S. Wrighton, Chem. Rev., 1974, 74, 401.

166. M. S. Wrighton and D. Bredesen, J. Organomet. Chem., 1973, 50, C35.

167. D. R. Kidd and T. L. Brown, J. Am. Chem. Soc., 1978, 100, 4095.

168. S. P. Church, H. Herman, F. W. Grevels and K. Schaffner, J. Chem. Soc., Chem. Commun., 1984, 785.

169. J. P. Fawcett, R. A. Jackson and A. J. Poë, J. Chem. Soc., Chem. Commun., 1975, 733.

170. A. Poë, Inorg. Chem., 1981, 20, 4032.

171. J. D. Atwood, Inorg. Chem., 1981, 20, 4032.

172. R. W. Wegman, R. J. Olsen, D. K. Gard, L. R. Faulkner and T. L. Brown, J. Am. Chem. Soc., 1981, 103, 6089.

173. J. L. Hughey IV, C. P. Anderson and T. L. Meyer, J. Organomet. Chem., 1977, 125, C49.

174. A. M. Stolzenberg and E. L. Muetterties, J. Am. Chem. Soc., 1983, 105, 822.

175. N. J. Coville, A. M. Stolzenberg and E. L. Muetterties, J. Am. Chem. Soc., 1983, 105, 2499.

176. R. J. Angelici, F. Basolo and A. J. Poë, J. Am. Chem. Soc., 1963, 85, 2215.

177. B. E. Mann, Adv. Organomet. Chem., 1974, 12, 135.

178. O. A. Gansow, A. R. Burke and G. N. LaMar, J. Chem. Soc. Chem. Commun., 1972, 456.

179. L. J. Todd and J. R. Wilkinson, J. Organomet. Chem., 1974, 77, 1.

180. L. J. Todd and J. R. Wilkinson, J. Organomet. Chem., 1974, 80, C31.

181. S. Aime, G. Gervasio, L. Milone and E. Rosenberg, Transition Met. Chem., 1976, 1, 177.

182. S. Aime and L. Milone, Progress in N.M.R. Spectroscopy, 1977, 11, 183.

183. R. L. Kump and L. J. Todd, J. Organomet. Chem., 1980, 194, C43.

184. H. Wawersik and F. Basolo, J. Chem. Soc., Chem. Commun., 1966, 366.

185. M. S. Wrighton and D. S. Ginley, J. Am. Chem. Soc., 1975, 97, 2065.

186. R. D. Adams and D. F. Chodosh, J. Organomet. Chem., 1975, 87, C48.

187. R. D. Adams and F. A. Cotton, J. Am. Chem. Soc., 1973, 95, 6589.

188. T. J. Marks and J. S. Kirstoff, J. Organomet. Chem., 1972, 42, 277.

189. Y. Yamamato, Coord. Chem. Rev., 1980, 32, 193.

190. E. Singleton and H. E. Oosthuizen, Adv. Organomet. Chem., 1983, 22, 209.

191. S. Grant, J. Newman and A. R. Manning, J. Organomet. Chem., 1975, 96, C11.

192. U. Koelle, J. Organomet. Chem., 1977, 133, 53.

193. U. Koelle, J. Organomet. Chem., 1978, 155, 53.

194. P. N. Prasad, Spectrochim. Acta., 1977, 33A, 335.

195. M. O. Albers and N. J. Coville, S. Afr. J. Chem., 1982, 35, 139.

196. M. O. Albers, J. C. A. Boeyens, N. J. Coville and G. W. Harris, J. Organomet. Chem., 1984, 260, 99.

197. G. W. Harris and N. J. Coville, Organometallics, in press.

198. K. K. Joshi, P. L. Pauson and W. H. Stubbs, J. Orga met. Chem., 1963, 1, 51.

199. H. ehrens, P. Wurstl, P. Merbach and M. Moll, Z. Anorg. Allg. Chem., 1979, 456, 16.

200. H. J. Mueh, Govt. Rep. Announce (U.S.), 1977, 77(1), 94; Chem. Abs. 1977, 86, 776, No. 86132c90K.

201. P. W. Jolly and F. G. A. Stone, J. Chem. Soc., 1965, 5259.

202. F. Nyman, Chem. Ind. (London), 1965, 604.

203. M. Freni, D. Guisto and P. Romiti, J. Inorg. Nucl. Chem., 1967, 29, 761.

204. A. G. Osborne and M. H. B. Stiddard, J. Chem. Soc., 1964, 637.

205. J. Lewis, A. R. Manning and J. R. Miller, J. Chem. Soc. A, 1966, 845.

206. ref. 52, therein ref. 1 - 11.

207. J. D. Atwood, M. J. Wovkulich and D. Sonnenberger, Acc. Chem. Res., 1983, 16, 350.

208. J. P. Fawcett, A. J. Poë and K. R. Sharma, J. Chem. Soc., Dalton Trans., 1979, 1886.

209. D. J. Robinson, G. W. Harris, J. C. A. Boeyens and N. J. Coville, J. Chem. Soc., Chem. Commun., in press.

210. J. R. Graham and R. J. Angelici, Inorg. Chem., 1967, 6, 2082.

211. J. P. Fawcett and A. J. Poë, J. Chem. Soc., Dalton Trans., 1977, 1302.

212. A. Poë, in "Reactivity in Metal-Metal Bonds"; M. H. Chisholm Ed., American Chemical Society: Washington D. C. 1981.

213. R. J. Angelici and F. Basolo, J. Am. Chem. Soc., 1962, 84, 2495.

214. W. Heiber and K. Wollman, Chem. Ber., 1962, 95, 1552.

215. T. L. Brown, Inorg. Chem., 1968, 7, 2673.

216. G. Cetini, O. Gambino, G. A. Vaglio and R. P. Ferrari, Inorg. Chem., 1969, 8, 1371.

217. A. Berry and T. L. Brown, Inorg. Chem., 1972, 11, 1165.

218. R. B. King and F. G. A. Stone, Inorg. Synth., 1963, 7, 198.

219. A. N. Nesmeyanov, G. G. Dvoryantseva, Yu. N. Sheinker, N. E. Kolobova and K. N. Anisimov, Doklady Akademii Nauk SSSR, 1966, 169, 843.

220. G. O. Evans and R. K. Sheline, Inorg. Chem., 1971, 10, 1598, and ref. 2-11 therin.

221. J. A. Gladysz and W. Tam, J. Am. Chem. Soc., 1978, 100, 2545.

222. J. P. Fawcett, A. J. Poë and M. V. Twigg, J. Organomet. Chem., 1973, 61, 315.

223. G. Kramer, J. Patterson, A. J. Poë and L. Ng, Inorg. Chem., 1980, 19, 1161.

224. C. P. Casey and C. R. Cyr, J. Organomet. Chem., 1973, 57, C69.

225. O. Orama, V. Schubert, F. R. Kreisse and E. O. Fischer, Z. Naturforsch., Tiel B, 1980, 35, 82.

226. J. Martin-Gil, J. A. K. Howard, R. Navarro and F. G. A. Stone, J. Chem. Soc., Chem. Commun., 1979, 1168.

227. N. E. Kolobova, A. B. Antonova and O. M. Khitrova, J. Organomet. Chem., 1978, 146, C17.

228. L. H. Staal, G. Van Koten and K. Vrieze, J. Organomet. Chem., 1979, 175, 73.

229. T. Kruck and M. Höfler, Angew. Chem., 1964, 76, 786.

230. M. Gross and P. Lemoine, Bull. Soc. Chim. Fr., 1972, 4461.

231. P. Lemoine, M. Gross and J. Boissier, J. Chem. Soc., Dalton Trans., 1972, 1626.

232. A. J. Poë, J. Am. Chem. Soc., 1981, 103, 135.

233. Y. Yamamoto, K. Aoki and H. Yamazaki, Inorg. Chem., 1979, 18, 1681.

234. M. R. Churchill and R. Bau, Inorg. Chem., 1967, 6, 2086.

235. N. J. Coville, private communication.

236. G. M. Sheldrick, in "Computing in Crystallography", Ed., H. Schenck, R. Olthuf-Hagekamp, H. Van Koningsveld and G. C. Bassi, Delft University Press, 1978.

237. C. K. Johnson, Ortep, Report ORNL - 3794, Oak Ridge National Laboratory, Tennessee, 1965.

238. A. J. Hart-Davis, C. White and R. J. Mawby, Inorg. Chim. Acta, 1970, 4, 441.

239. C. White and R. J. Mawby, J. Chem. Soc. A, 1971, 940.

240. D. J. Jones and R. J. Mawby, Inorg. Chim. Acta, 1972, 6, 157.

241. N. J. Forrow and S. A. R. Knox, J. Chem. Soc., Chem. Commun., 1984, 679.

242. E. O. Fischer and A. Vogler, Z. Naturoforsch., Tiel B, 1962, 17, 421.

243. H. R. Allock, L. J. Wagner and M. L. Levin, J. Am. Chem. Soc., 1983, 105, 1321.

244. B. P. Gracey, S. A. R. Knox, K. A. Macpherson and S. R. Stobart, J. Organomet. Chem., 1984, 272, C45.

245. R. B. King, Organometal. Synth., 1965, 1, 114.

246. R. B. King and M. B. Bisnette, J. Organomet. Chem., 1967, 8, 287.

247. T. Blackmore, M. I. Bruce and F. G. A. Stone, J. Chem. Soc. A, 1968, 2158.

248. O. A. Gansow, A. R. Burke and W. D. Vernon, J. Am. Chem. Soc., 1976, 98, 5817.

249. P. McArdle and A. R. Manning, J. Chem. Soc. A, 1970, 2128.

250. A. P. Humphries and S. A. R. Knox, J. Chem. Soc., Dalton Trans., 1975, 1710.

251. T. A. Wnuk and R. J. Angelici, Inorg. Chem., 1977, 16, 1173.

252. D. H. Gibson, W. L. Hsu, A. L. Steinmetz and B. V. Johnson, J. Organomet. Chem., 1981, 208, 89.

253. S. A. R. Knox, Pure Appl. Chem., 1984, 56, 81.

254. J. Bellerby, M. J. Boylan, M. Ennis and A. R. Manning, J. Chem. Soc., Dalton Trans., 1978, 1185.

255. J. A. S. Howell and A. J. Rowan, J. Chem. Soc., Dalton Trans., 1980, 503.

256. K. K. Joshi, O. S. Mills, P. L. Pauson, R. W. Shaw and N. H. Stubbs, J. Chem. Soc., Chem. Commun., 1965, 181.

257. N. J. Coville, M. O. Albers and E. Singleton, J. Chem. Soc., Dalton Trans., 1982, 1389.

258. M. O. Albers, A. A. Chalmers, G. J. Kruger, D. C. Liles, H. E. Oosthuizen, E. Singleton and N. J. Coville, manuscript in preparation.

259. M. Ennis, R. Kumar, A. R. Manning, J. A. S. Howell, P. Mathur, A. J. Rowan and F. S. Stephens, J. Chem. Soc., Dalton Trans., 1981, 1251.

260. J. V. Caspar and T. J. Meyers, J. Am. Chem. Soc., 1980, 102, 7794.

261. H. B. Abrahamson, M. C. Palazzotto, C. L. Reichel and M. S. Wrighton, J. Am. Chem. Soc., 1979, 101, 4123.

262. A. Eisenstadt, R. Tannenbaum and A. Efraty, J. Organomet. Chem. 1981, 221, 317.

263. R. J. Haines and A. L. duPreez, J. Am. Chem. Soc., 1969, 91, 769.

264. R. J. Haines and A. L. duPreez, J. Chem. Soc. A, 1970, 2341.

265. R. J. Haines and A. L. duPreez, J. Chem. Soc., Dalton Trans., 1972, 944.

266. C. Giannotti and G. Merle, J. Organomet. Chem., 1976, 105, 97.

267. D. R. Tyler, M. A. Schmidt and H. B. Gray, J. Am. Chem. Soc., 1983, 105, 6018.

268. J. A. S. Howell and A. J. Rowan, J. Chem. Soc. Dalton Trans., 1980, 1845.

269. B. D. Fabian and J. A. Labinger, J. Am. Chem. Soc., 1979, 101, 2239.

270. N. J. Coville, J. Organomet. Chem., 1980, 190, C84.

271. N. J. Coville, J. Organomet. Chem., 1981, 218, 337.

272. J. C. A. Boeyens, N. J. Coville and K. Solldenhoff, S. Afr. J. Chem., in press.

273. E. A. Darling and N. J. Coville, J. Organomet. Chem., in press.

274. Y. Yamamoto and N. Hagihwa, Mem. Inst. Sci. Ind. Res., Osaka Univ., 1970, 27, 109.

275. M. O. Albers, N. J. Coville, T. V. Ashworth, E. Singleton and H. E. Swan poel, J. Chem. Soc., Chem. Commun., 1980, 489.

276. M. O. Albers, N. J. Coville and E. Singleton, J. Chem. Soc., Dalton Trans., 1982, 1069.

277. A. R. Manning, Coord. Chem. Rev., 1983, 51, 41.

278. P. A. Agron, R. D. Ellison and H. A. Levy, Chem. Div. Ann. Progr. Rept., May 20, 1967, ORNL - 4164, p. 133.

279. J. P. Collman, Acc. Chem. Res., 1975, 8, 342.

280. W. Hieber and G. Bader, Chem. Ber., 1928, 61, 1717.

281. R. C. Taylor and W. D. Horrocks, Jr., Inorg. Chem., 1964, 3, 584.

282. M. H. Quick and R. J. Angelici, Inorg. Synth., 1979, 19, 161.

283. F. A. Cotton, Inorg. Chem., 1964, 3, 702 and references therein.

284. .. J. Coxand and R. Davis, J. Organomet. Chem., 1980, 186, 347 and references therein.