National Library
of Canada

Bibliothèque nationale
du Canada

Canadian Theses Service

Services des thèses canadiennes

Ottawa, Canada
K1A 0N4

CANADIAN THESES

THÈSES CANADIENNES

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

NL-339 (r. 86/06)

Canada

ARYLDIAZENIDO AND DINITROGEN COMPLEXES OF RHENIUM

by

Adalberto Hugo Klahn Oliva
Licenciado en Quimica,
Universidad de Concepcion, Chile, 1979

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Chemistry

SIMON FRASER UNIVERSITY
May 1986

ISBN 0-315-36329-0

APPROVAL

Name: Adalberto Hugo Klahn Oliva

Degree: Doctor of Philosophy

Title of Thesis: Aryldiazenido and Dinitrogen Complexes of Rhenium

Examining Committee:

Chairperson: C.H.W. Jones

D. Sutton, Senior Supervisor

L.K. Peterson, Examining Committee

A.C. Oehlschlager, Examining Committee

F.W.B. Einstein, Internal Examiner

Prof. M. Cowie, External Examiner
University of Alberta

Date Approved: 29 May 1986

PARTIAL COPYRIGHT LICENSE

Title of Thesis/Project/Extended Essay

"Aryldiazenido and Dinitrogen Complexes of Rhenium"

Author:

(signature)

A. Hugo Klahn-Oliva
(name)

June 4, 1986
(date)

ABSTRACT

This thesis describes the synthesis, characterization and selected chemical reactions of the new pentamethylcyclopentadienyl rhenium aryldiazenido complex cations of general formula $[Cp^*Re(CO)_2(N_2Ar)]^+$ ($Cp^*=(\eta\text{-}C_5Me_5)$, Ar=aryl), and their derivatives. These cations are important precursors of other aryldiazenido and some dinitrogen complexes, as indicated by the following reactions: i) in reactions with some nucleophiles, a CO group is replaced or transformed leading to monocarbonyl aryldiazenido complexes of the general type $Cp^*ReX(CO)(N_2Ar)$ with X=Cl, Br, I, NCO, COOR (R=alkyl), $CONH_2$, CONHMe, $CONMe_2$, COOH, COO^- and H. ii) in reaction with $NaBH_4$ the N_2Ar group is transformed to give the new dinitrogen complex $Cp^*Re(CO)_2(N_2)$. This complex also was synthesized by direct reaction of $Cp^*Re(CO)_2(THF)$ (THF=tetrahydrofuran) with N_2 under high pressure. iii) reaction with iodosobenzene (PhIO) in nitriles (NCR; R=methyl, isopropyl and n-propyl) removes a CO group to give the cationic nitrile complexes $[Cp^*Re(CO)(NCR)(N_2Ar)]^+$. Further reaction of the acetonitrile complex (R=methyl) with phosphines gives the phosphine-substituted derivatives $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$ with R=methyl, n-butyl, phenyl, cyclohexyl and methoxy. These phosphine complexes react with alkyl lithiums to produce the corresponding phosphine-substituted dinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$.

The dinitrogen complexes $Cp^*Re(CO)_2(N_2)$ and $Cp^*Re(CO)(PMe_3)(N_2)$ are inert regarding N_2 ligand autoexchange but they substitute N_2 under photochemical and non-photochemical conditions. Both react with X_2 (X=Cl, Br and I) non-photochemically to produce stereospecifically the cis-dihalide complexes $Cp^*Re(CO)(L)X_2$ (L=CO and PMe_3). With HX the dicarbonyl dinitrogen complex yields only the cis-dihalide complexes, which are converted to the trans-isomers by UV irradiation, whereas the phosphine dinitrogen complex gives the complexes trans-$Cp^*Re(CO)(PMe_3)(H)(X)$. Under UV irradiation the complex $Cp^*Re(CO)(PMe_3)(N_2)$ loses the nitrogen ligand very easily, and the 16-electron intermediate then produced reacts with C-H bonds: intra-molecularly in alkanes to give the cyclometallated complex $Cp^*Re(CO)(\eta^2-PMe_2CH_2)(H)$, or intermolecularly in benzene to give the phenylhydrido complex $Cp^*Re(CO)(PMe_3)(Ph)(H)$.

The synthesis and characterization of the trioxo complex Cp^*ReO_3 is also described.

To Patricia and Blanquita

and

To my parents and sister

ACKNOWLEDGEMENTS

The author expresses his sincere gratitude to his supervisor, Professor D. Sutton, for his continued guidance, encouragement and patience throughout the course of this work.

The author would also like to express his recognition to:

Dr. C. Barrientos-Penna for his help and friendship;

Prof. R.K. Pomeroy for his helpful discussions;

Dr. G. Buono-Core for proof reading this thesis and friendship; and

Universidad Catolica de Valparaiso, Chile, for leave of absence.

And to his wife Patricia, the author is grateful for typing this thesis and especially for all her sacrifices, support and encouragement during these years of graduate studies.

TABLE OF CONTENTS

CHAPTER I - Review of Diazenido and Dinitrogen Complexes

1.2. Diazenido Complexes

1.3. Dinitrogen Complexes

CHAPTER II - Synthesis and Characterization of Pentamethyl-Cyclopentadienyl Dicarbonylaryldiazenido Complexes of Rhenium

CHAPTER III - Transformation of the CO Ligand in $[\mathrm{Cp^*Re(CO)_2}(p\text{-}\mathrm{N_2C_6H_4OMe})]^+$ by Reaction with Some Nucleophiles

CHAPTER IV - Substitution of CO in $[Cp^{*}Re(CO)_2(\underline{p}-N_2C_6H_4OMe)]^+$ by Two-electron Donor Ligands

CHAPTER V - Pentamethylcyclopentadienylrhenium Dinitrogen Complexes

CHAPTER VI - Non-photochemical Reactions of Rhenium Dinitrogen Complexes

CHAPTER VII - Photochemical Reactions of $Cp^{*}Re(CO)(L)(N_2)$, L= CO and PMe_3 with Saturated and Unsaturated Hydrocarbons

ABBREVIATIONS

Ar	aryl
bipy	2,2'-bipyridyl
n-Bu	butyl, C_4H_9
t-Bu	*tert*-butyl, C_4H_9
Cp	η^5-cyclopentadienyl (η-C_5H_5)
Cp*	η^5-pentamethylcyclopentadienyl (η-C_5Me_5)
Cy	cyclohexyl (C_6H_{11})
das	*ortho*-phenylenebis(dimethylarsine)
dtc	dithiocarbamate (S_2CNMe_2)
dppe	bis(diphenylphosphine)ethane ($Ph_2PCH_2CH_2PPh_2$)
ether	diethylether
FAB	fast atom bombardment
GC	gas chromatography
IR	infrared
i-Pr	isopropyl
M	metal
Me	methyl, CH_3
MS	mass spectra
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
OMe	methoxy, OCH_3
Ph	phenyl, C_6H_5
THF	tetrahydrofuran

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

Review of Diazenido and Dinitrogen Complexes

1.1. Introduction

The main interest in the research being carried out in our laboratory over the last few years, has been the study of dinitrogen (N_2), aryldiazenido (N_2Ar, Ar= aryl), aryldiazene (NHNAr), arylhydrazido (2-) (NN(R)Ar, R=H or alkyl) and arylhydrazido (1-) (NHN(R)Ar) ligands in transition metal complexes. With regard to nitrogen fixation, analogues of these ligands, i.e., the perhydrogen ones, are believed to be intermediates involved in the nitrogenase-mediated reduction of molecular nitrogen to ammonia.[1-6] Within this context, Chatt and coworkers,[1,2] using molybdenum and tungsten complexes, have suggested the following nitrogenase reaction mechanism as the most plausible one (Fig.1).

In the long term, it is believed that the chemistry displayed by dinitrogen and organodinitrogen ligands at metal sites will contribute not only to our understanding of the enzymatic transformation of molecular N_2 into ammonia, but also to the development of new and more efficient catalysts for industrial production of ammonia and other organonitrogen compounds from atmospheric dinitrogen.[7,8]

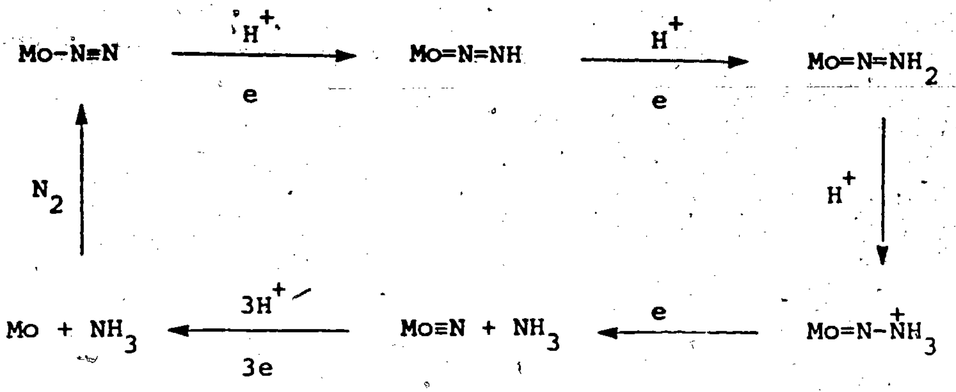


Fig.1. Suggested mechanism for the nitrogenase reaction

The focus of current work has been the synthesis, structural characterization and some chemical reactions of complexes containing the aryldiazenido ligand (N_2Ar). The remarkable chemistry displayed by cationic complexes $[CpM(CO)_2(N_2Ar)]^+$ [9,10] (Cp= η-C_5H_4Me, M=Mn and Cp= η-C_5H_5, M=Re), for example their reaction with some nucleophiles to yield dinitrogen complexes $CpM(CO)_2(N_2)$,[9] stimulated us to continue an investigation of the chemistry of aryldiazenido complexes to determine whether this transformation could be duplicated in related complexes, and to find out what other reactions can be undergone by the N_2Ar group. We therefore designed a program to investigate the effect of replacing the cyclopentadienyl group by the pentamethylcyclopentadienyl group in the synthesis and properties of the rhenium cationic aryldiazenido complexes and their derivatives.

In this chapter, to provide some background to the thesis, a brief review is presented describing our present knowledge of the structure and reactivity of diazenido and dinitrogen complexes, focussing on the more recent developments.

1.2. Diazenido Complexes

1.2.1. Introduction

Current interest in diazenido complexes of transition metals in inorganic chemistry can be viewed from three different aspects. (i) They model one of the possible intermediates formed in the reduction of nitrogen catalyzed by the enzyme nitrogenase.[1-6] (ii) They bear a close relationship to the isoelectronic nitrosyl ligand,[11,12] and (iii) They display varied coordination geometries (see below), which make them chemically,[10,13] structurally[14] and spectroscopically[15,16] attractive.

In the following sections, a literature survey of the structure and reactivity of mononuclear diazenido complexes will be presented.

1.2.2. Structure of Diazenido Ligands

Structural studies have demonstrated that the diazenido ligand in mononuclear complexes can adopt several different coordination geometries. The particular one observed in a given compound presumably depends, at least in part, on the electronic requirements of the metal.[11] Four different coordination modes (A-D) have been distinguished thus far (Fig.2).

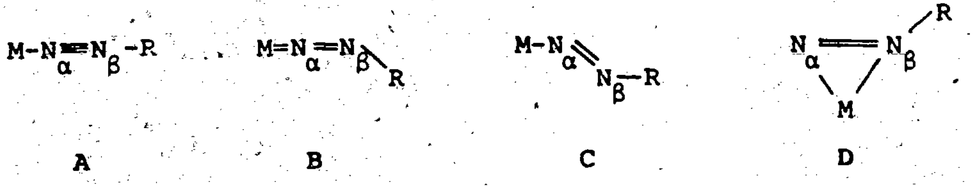


Fig. 2. Coordination modes of diazenido ligand in mononuclear complexes.

In Fig. 2, N_α is the nitrogen atom bonded to the metal M and N_β is the one bonded to the R group (R= alkyl or more commonly aryl). The same convention will be used throughout this thesis.

Only one example of the totally linear structure A has been reported. It is present in the ruthenium diazoborane complex $RuH_2(PPh_3)_3(N_2B_{10}H_8SMe_2)$[17] (RuNN= 175.9(6)°, NNB= 172.7(8)°). In this complex the diazenido ligand can be described as a σ-donor to the metal, with weak π-backbonding from the metal. The diazenido ligand in $[RuCl(bipy)_2(p\text{-}N_2C_6H_4R)]^+$ has also been tentatively assigned the linear form A on the basis of the very high ν(NN) in the IR spectrum,[18] but there has been no structural confirmation.

The side-on configuration D is also a rare example of π-coordination of the diazenido ligand. In fact, it has been observed only once, in the structure determination of the phenyl-diazenido complex $CpTiCl_2(\eta^2\text{-}N_2Ph)$[19] (NTiN= 34.8(2)°, $TiN_\alpha N_\beta$= 70.4(3)°). Of the remaining two forms shown in Fig.2, the doubly-bent structure C can be related to the singly-bent form B by the transfer of two electrons from the metal to the ligand. In C, the ligand can be viewed formally as a neutral one-electron donor, or alternatively can be formulated as a two-electron donor anion N_2Ar^- (analogous to NO^-). From a valence-bond description both nitrogen atoms are sp^2 hybridized, and the metal-diazenido structure has a doubly-bent azobenzene-like geometry. Several complexes which are believed to contain the diazenido ligand with a doubly-bent geometry have been prepared; nevertheless, only a few have been characterized by X-ray crystallography. These include $IrCl_2(CO)(PPh_3)_2(\underline{o}-N_2C_6H_4NO_2)$[20] (IrNN= 115(3)°, NNAr= 118(2)°), $PtCl(PEt_3)_2(\underline{p}-N_2C_6H_4F)$[21] (PtNN= 118(2)°, NNAr=118(2)°) and $[RhCl(L)(N_2Ph)]^+$ [18] (L= tridentate phosphine, RhNN= 125.1(6)°, NNPh= 118.9(8)°).

The singly-bent form B is by far the most common coordination mode of the diazenido ligand. It has been observed in complexes with almost all the transition metals. In the singly-bent configuration, the diazenido ligand may be viewed as a three-electron donor ligand or, equivalently, as the two-electron donor aryldiazonium ion (N_2Ar^+) coordinated through the σ-lone pair on the terminal nitrogen (N_α) together with strong π-back donation from the metal.[11] From a simple valence bond model, both the MN and NN linkages may be considered to be double bonds with sp hybridization at N_α and sp^2 at N_β; i.e., the MNN and NNAr angles should be close to 180° and 120° respectively. In numerous cases, this type of geometry has been characterized by X-ray structural studies. Some of these are: $Mo(S_2CNMe_2)_3(N_2Ph)$[22] (MoNN= 171.5(4)°, NNPh= 120.5(5)°), $OsH(CO)(PPh_3)_2(N_2Ph)$[23] (OsNN= 171.1(6)°, NNPh= 118.5(7)°), $RuCl_3(PPh_3)_2(\underline{p}-N_2C_6H_4Me)$[15]

(RuNN= 171.9(5)°, NNAr= 137.1(5)°), $CpW(CO)_2(N_2Me)$[24] ((WNN= 173.3(3)°, NNMe= 116.5(4)°), $ReCl_2(PPhMe_2)_3(N_2Ph)$[25] (ReNN= 173(2)°, NNPh= 119(2)°) and $[\eta-C_5H_4MeMn(CO)_2(o-N_2C_6H_4CF_3)]^+$ [9] (MnNN= 171.8(8)°, NNAr= 125.6(9)°).

In addition to X-ray crystallography and IR spectroscopy studies, ^{15}N NMR spectroscopy has recently been applied, not only to distinguish the singly and doubly-bent forms, but also for the identification of the individual nitrogen nuclei within the singly-bent geometry of the diazenido ligand.[16,26] It promises to be of great utility since the nitrogen nuclei in singly-bent ligands exhibit resonances in different regions of the spectrum ($\delta_{N\alpha}-\delta_{N\beta} \sim 100$ to 150). On the other hand, when singly and doubly-bent forms are compared, a larger difference in the chemical shifts of the $^{15}N_\alpha$'s is observed. The following examples illustrate the above statements. The ^{15}N NMR spectra of the ^{15}N-enriched complexes $MX(dppe)_2(^{15}N^{15}NR)$ (M= Mo or W, X= Cl or Br, R= Et or COMe), which contain the singly-bent form of the diazenido ligand, exhibit resonances relative to CH_3NO_2 at δ −28 to −60 for N_α, and at much higher field, δ −123 to −165 for N_β.[16] The complexes $RuCl_3(PPh_3)_2(^{15}NNPh)$[16] and $[CpRe(CO)_2(p-^{15}NNC_6H_4R)]^+$ [27] (R= OMe, Me and NEt_2) also have the singly-bent form and $^{15}N_\alpha$ resonances are in the region δ −2.9 to −46.8 (see Table II, Chapter II). In contrast, the complex $RhCl_2(PPh_3)_2(^{15}NNPh)$ which adopts the doubly-bent form, exhibits resonance at 327.1.[16] It is therefore observed that there is a shift of about 350 ppm downfield in the N_α resonance when the geometry at N_α is changed from linear to bent.

In this thesis we show, for the first time, that ^{14}N NMR spectroscopy can equally well be used to distinguish the nitrogen nuclei in singly-bent diazenido complexes of rhenium (see Chapter II).

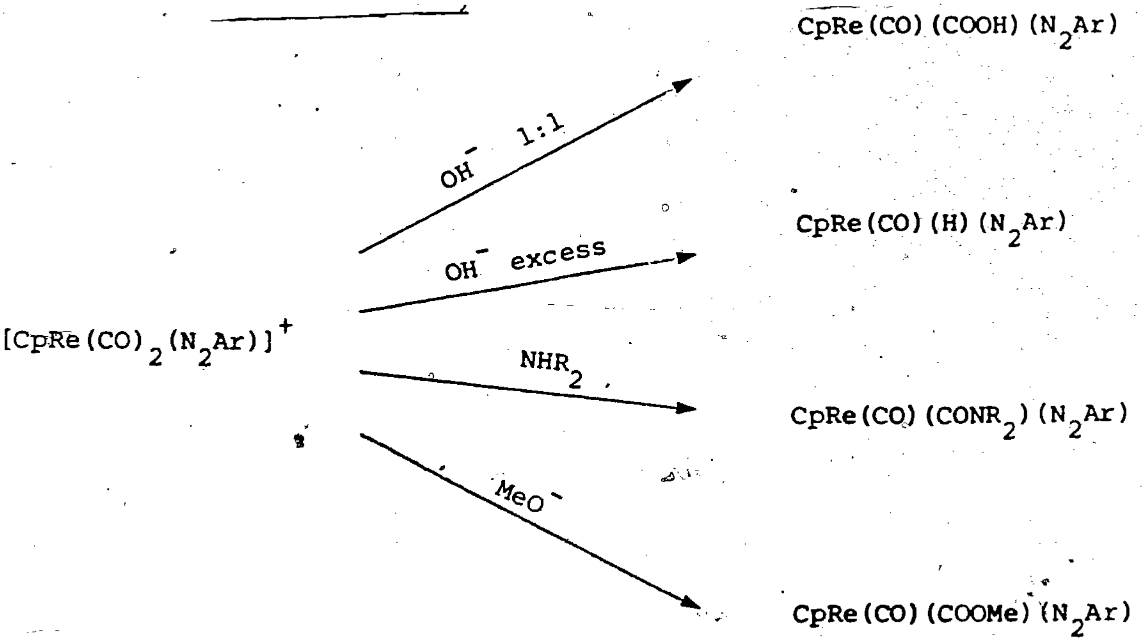
1.2.3. Reactivity of Diazenido Complexes

The reactivity of diazenido complexes has received less attention than their structural and synthetic aspects. It is important to mention that, in addition to the reactions to be presented in this section, there are some other processes that can also occur; for example, counterion metathesis is observed when $[Fe(CO)_2(PPh_3)_2(N_2Ar)][BF_4]$ reacts with KI to give $[Fe(CO)_2(PPh_3)_2(N_2Ar)][I]$.[28] Complete replacement of the diazenido ligand is also known; as an example, the reaction of $[IrCl(PPh_3)_2(N_2Ph)]^+$ with $NaBH_4$ to give $IrH_3(PPh_3)_2$[29] can be cited.

1.2.3(a). Transformation or Replacement of a Co-ligand

There are very few examples in which reaction of the co-ligand takes place in preference to transformation of the diazenido group. Usually quite the reverse occurs. For instance, the cationic complexes $[(C_6Me_6)Cr(CO)_2(N_2Ar)]^+$ [30] (Ar= p-C_6H_4R, R= H, MeO and NO_2) react with $NaBH_4$ to give the neutral cyclohexadienyl complexes $(C_6Me_6H)Cr(CO)_2(N_2Ar)$[31], and no nucleophilic attack at the CO or at the aryldiazenido ligand is observed. The complexes $[M(das)(CO)_3(N_2Ar)]^+$ [29] (M= Mo, Ar= p-C_6H_4F; M=W, Ar=p-C_6H_4OMe;

das= o-phenylenebisdimethylarsine) react with halides X^- (X= Cl, Br and I) to give the neutral species $M(das)(CO)_2X(N_2Ar)$. A direct nucleophilic attack at the metal, with displacement of one of arsenic atoms of das giving $M(das)(CO)_3X(N_2Ar)$, followed by carbonyl elimination and rechelation of das was suggested to be the mechanism.[31] Simple ammonia replacement has been observed when $ReCl_2(NH_3)(PMe_2Ph)(N_2Ph)$ is treated with a phosphine or carbon monoxide to give $ReCl_2(L)(PMe_2Ph)(N_2Ph)$ (L= CO and PMe_2Ph).[32] More recently it has been found in our laboratory that the carbonyl group in $[CpRe(CO)_2(N_2Ar)]^+$ complexes can be replaced or transformed by reactions with some nucleophiles.[27,33] These reactions are summarized in Scheme I.



Scheme I

All the products shown in Scheme I possess a singly-bent diazenido ligand on the basis of IR spectroscopy.[27,33]

1.2.3(b). Singly-bent - Doubly-bent Isomerization

Reactions where the isomerization of the diazenido ligand takes place are scarce. One example of this is the reaction of the five-coordinate singly-bent diazenido complexes $[M(CO)_2(PPh_3)_2(N_2Ph)]^+$ with anions X^- to produce the neutral six-coordinate doubly-bent species $MX(CO)_2(PPh_3)_2(N_2Ph)$[13] (M= Os, X= Cl, Br, I, NCO, N_3, HCO_3 and CH_3COO; M= Ru, X= Cl, Br, I and NCO). Interestingly, in the $OsH(CO)_2(PPh_3)_2(N_2Ph)$ complex the reverse transformation has been observed. This complex contains a doubly-bent diazenido ligand and eliminates one CO group under UV irradiation to give the pentacoordinated singly-bent complex $OsH(CO)(PPh_3)_2(N_2Ph)$.[13]

1.2.3(c). Reactions of Diazenido Complexes with Electrophiles

These types of reactions have been the most extensively studied, usually in connection with protonations or alkylations to give diazene (substitution at N_α) or hydrazido (2-) (substitution at N_β) derivatives.

Simple protonation or alkylation of diazenido ligands can occur at N_α or at N_β, depending on the type of configuration of the ligand (singly or doubly-bent). In all the examples so far known, a doubly-bent diazenido ligand is always protonated at

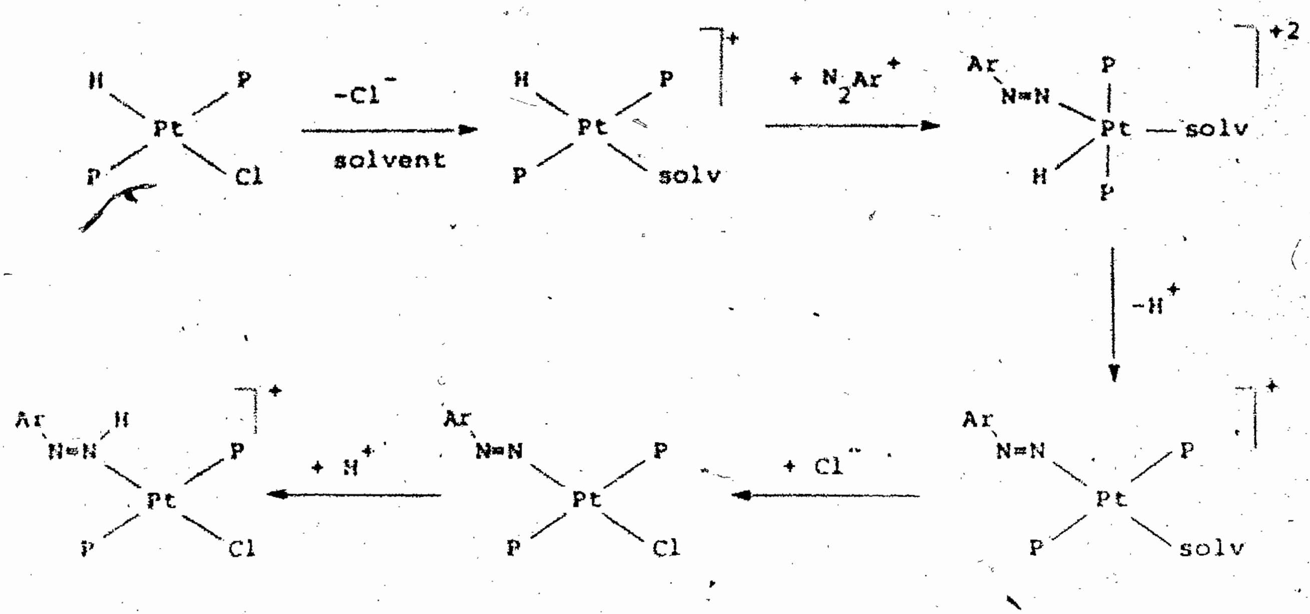
N_α, which seems to be the more basic nitrogen atom. As examples, the following aryldiazene complexes were obtained by direct protonation of doubly-bent diazenido complexes: $[PtCl(PEt_3)_2(NHNC_6H_4R\text{-}p)]^+$ [34] (R= H and F), $[IrCl_2(CO)(PPh_3)_2(NHNPh)]^+$ and $[RuCl(CO)_2(PPh_3)(NHNPh)]^+$.[35] Very recently, kinetic studies have shown that the apparent "insertion" of diazonium cations into a metal-hydride bond to give the diazene complexes ~~[PtCl~~ $(PEt_3)_2(NHNAr)]^+$ [36] and $RhCl_3(PEtPh_2)_2(NHNAr)$[37] (Eqs. 1 and 2)

$$PtH(Cl)(PEt_3)_2 \ + \ N_2Ar^+ \longrightarrow [(Et_3P)_2ClPt(NHNAr)]^+ \qquad \text{Eq.1.}$$

$$RhHCl_2(PEtPh_2)_3 + N_2Ph^+ + Cl^- \longrightarrow (PEtPh_2)_2Cl_3Rh(NHNAr) \ + \ PEtPh_2 \qquad \text{Eq.2.}$$

Ar= $p\text{-}C_6H_4R$, R= NO_2, Cl, H, ~~Me~~ and MeO.

do not proceed by a simple intramolecular hydrogen migration from the metal to the ligand. Instead, proton loss from the metal and then its recapture by the "inserting" ligand i.e. doubly-bent diazenido, has been suggested[36,37] (see Scheme II).



Scheme II

Protonation (or alkylation) reactions involving singly-bent diazenido complexes have been more extensively studied. In these cases, protonation is expected to occur at N_β, due to the presence of a lone pair. The ligand so formed is commonly called "hydrazido (2-)"[38] (some authors have also referred to this ligand as "iso-diazene").[39,40] The complexes $[ReCl_2(NH_3)(PMe_2Ph)_2(NN(H)Ph)]^+$ [32], $WI_2(PMe_2Ph)(NN(H)SiMe_3)$[41], $[WBr(diphos)_2(NN(H)Me)]^+$ and $[Mo(S_2CN(CH_2)_5)_3(NN(Et)Ph)]^+$ [42] are examples of the protonation or alkylation at N_β. In all these cases a linear geometry of the hydrazido (2-) ligand (NN(R)R') was confirmed by X-ray crystallography. More recently, a bent geometry for this ligand has been determined by X-ray crystal structure studies in $ReBr_2(NNPh)(PPh_3)_2(NN(H)Ph)$.[43] In the absence of X-ray data, ^{15}N NMR spectroscopy has proved to be a useful technique for determining whether a hydrazido (2-) ligand is present with a linear or a bent structure. For instance, the molybdenum complexes of the type MoX(dppe)(NN(H)R) (R= H, Me or Et; X= Cl, Br, I or HSO_4) with a linear hydrazido (2-) ligand exhibit ^{15}N resonances at δ -68 ($\pm$10) for N_α and -226 ($\pm$12) for N_β.[44,45] On the other hand, the complexes $ReBr_2(L)(PPh_3)_2$ (NN(H)Ph), which contain a bent ligand, exhibit resonances at δ 238.7 (N_α) and -135.5 (N_β) for L= NO, and at δ 190.0 (N_α) and -153.0 (N_β) for L= NNPh.[39] Thus, bent hydrazido (2-) ligands are characterized by a large downfield shift for N_α and large upfield shift for N_β, when compared with their linear analogues.

1.2.3.(d) Reactions of Diazenido Ligands with Nucleophiles

This research area has been developed in our laboratory over the past few years.[9,10,27] It has been demonstrated that the diazenido ligand in the cationic complexes $[CpM(CO)_2(N_2Ar)]^+$ (M= Mn and Re) can be converted into the dinitrogen $CpM(CO)_2(N_2)$[9], diazene $CpRe(CO)_2(NHNAr)$[10] and hydrazido (2-) $CpRe(CO)_2(NN(R)Ar)$[10] (R= Me, *n*-Bu and Ph) complexes by reaction with nucleophiles such as I^-, H^- and alkyl lithiums respectively. The hydrazido (1-) complex $[CpRe(CO)_2(NHN(Me)Ar)]^+$ was obtained by further protonation of the hydrazido (2-) complex.[46] (Eq.3.)

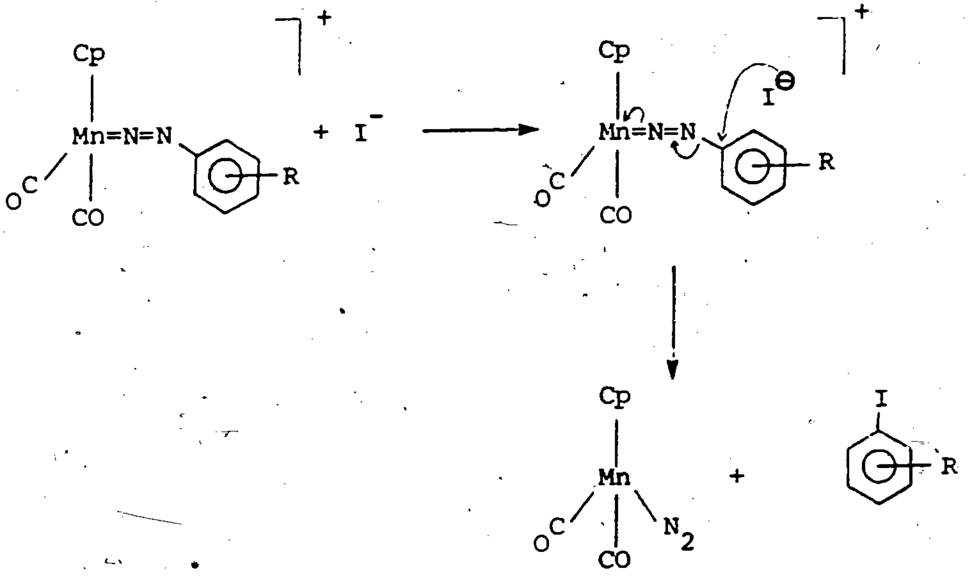
$$Cp(CO)_2Re(NN(Me)Ar) \xrightarrow{H^+} [Cp(CO)_2Re(NHN(Me)Ar)]^+ \qquad \text{Eq.3.}$$

The most remarkable features of these reactions involve the synthesis of the dinitrogen complexes $CpM(CO)_2(N_2)$. These were the first examples of dinitrogen complex formation from characterizable aryldiazenido complexes. The singly-bent N_2Ar ligand in $[CpM(CO)_2(N_2Ar)]^+$ (established by a single-crystal X-ray structure determination for Cp= η-C_5H_4Me and Ar= $\underline{o}$-$C_6H_4CF_3$)[9] is extremely susceptible to attack by nucleophiles such as iodide to give the dinitrogen complex (Eq.4.).

$$[CpMn(CO)_2(N_2Ar)]^+ \quad + \quad I^- \longrightarrow CpMn(CO)_2(N_2) \quad + \quad IAr \qquad \text{Eq.4.}$$

$$Cp= \eta\text{-}C_5H_4Me$$

The products of this reaction are those that would be expected as a result of direct nucleophilic displacement at the ipso carbon on the aromatic ring, ~~as~~ shown in Scheme III.



Scheme III

However, the reaction pathway shown in Scheme III for the manganese complexes, is more complicated in the rhenium analogues due to the formation of other products such as $CpReI(CO)(N_2Ar)$ and $CpRe(CO)_2I_2$. A radical mechanism has been proposed for these reactions.[27]

1.3. Dinitrogen Complexes

1.3.1. Introduction

The importance of the dinitrogen ligand in transition metal complexes has been already mentioned. Since the first metal complex containing dinitrogen as a ligand ($M-N_2$) was reported in 1965,[47] a large number of reports, including several reviews,[1,2,5] has been published emphasizing preparative methods,[1] theoretical aspects,[48-50] spectroscopic characterization[50-52] and chemical reactions.[2,5]

The structure and reactivity of mononuclear dinitrogen complexes will be reviewed in the following sections.

1.3.2. Bonding and Characterization of Dinitrogen Complexes

The mode of bonding of N_2 to a transition metal in mononuclear complexes can be represented by only two coordination geometries shown in Fig.3.

Fig.3. Coordination modes of a dinitrogen ligand in mononuclear complexes

The side-on coordination mode has never been structurally characterized in mononuclear complexes. The compound RhCl $(PPr_3i)_2(N_2)$ was claimed by X-ray crystallography[53] to possess this type of coordination. However, a redetermination of the X-ray crystal structure indicated the actual coordination of the N_2 in this complex to be end-on. This evidence was supported by ^{15}N NMR spectroscopy.[54] There is only one known example where the nitrogen molecule is probably bonded side-on to the metal. The zirconium complex ~~$Cp_2Zr(CH(SiMe_3)_2)(N_2)$~~,[55] ~~which is paramagnetic,~~ is believed to contain a side-on N_2-ligand on the basis of its e.s.r. spectrum which shows coupling to two equivalent nitrogens (a quintuplet in the $^{14}N_2$ complex and a triplet in the $^{15}N_2$ complex respectively), but its structure has not been proved by X-ray crystallography.

Monodinitrogen complexes with an end-on configuration have been observed for most of the transition elements. Bis-, and even tris-N_2 complexes are also known, especially in Mo and W complexes. By far the majority of N_2-complexes are of transition metals in their lower oxidation states. This arises because of the nature of the M-N_2 bond, which in the case of mononuclear species, resembles the bonding of carbon monoxide to these metals;[56] i.e., donation of the σ-lone pair to the metal and back donation from the filled metal d orbitals to the empty π-antibonding (π^*) orbital of the dinitrogen.

Many spectroscopic studies of dinitrogen and related complexes have been concerned with the relative σ-donor and π-acceptor properties of dinitrogen compared with analogous ligands such as carbon monoxide; the conclusion of these studies indicates that N_2 is both a weaker σ-donor and a weaker π-acceptor than CO.[1]

Structural studies have shown that the N-N bond lengths in mononuclear complexes are only slightly different from that in the free ligand, and that the MNN angles are very close to 180° as expected for a linear structure. Some recent examples among many others are: $ReCl(CNMe)(P(OMe)_3)_3(N_2)$[57] (N-N= 1.038(2) A, ReNN= 179.3(12)°), $W(PMe_3)_5(N_2)$[58] (N-N= 1.11(2) A, WNN= 179.7(9)°), $ReH(PEt_2Ph)_4(N_2)$[59] (N-N= 1.018(8) A, ReNN=180°), and $Mo(CO)(dppe)_2(N_2)$[60] (N=N= 1.087(18) A, MoNN= 177.0(2)°). In summary, X-ray crystallography brings valuable information about the nature of the MNN bonds. However, it is limited to systems which give single crystals of good quality. Unfortunately, this occurs rather rarely. Structural information for solutions or for unstable complexes may be obtained only from spectroscopy. Within this context, IR spectroscopy has been one of the most valuable routine techniques both for the identification of M-N_2

structures and for obtaining information about the bonding between the metal and the ligand.[61,62] In general, dinitrogen-containing complexes exhibit in their IR spectra a strong band in the 2200-1700 cm^{-1} region attributable to ν(NN). Chatt and coworkers have used ν(NN) to measure the basic strength of some N_2-complexes of Mo, W, Re and Os toward adduct formation with Lewis acids AlR_3 (R= Me, Ph and Cl). They found that complexes with ν(NN) > 2000 cm^{-1} do not form adducts under the experimental conditions used.[63] More recently, the same group have used ν(NN) and oxidation-potential ($E^{ox}{}_{1/2}$) as a criterion of the electron-richness or poorness of dinitrogen complexes.[63-65]

As in diazenido complexes, ^{15}N NMR spectroscopy has also been successfully applied in the characterization of the nitrogen nuclei in the N_2-complexes.[26,44-46] In general for these complexes two resonances are seen, the one at higher field between δ -40 and -130, relative to CH_3NO_2, is assigned to $^{15}N_\alpha$ since this shows the larger coupling to phosphorus ($^2J_{PN}$ ~ 2-4 Hz) in complexes containing phosphine co-ligands. There is an additional coupling to the metal that is observed when this has I= 1/2 as in ^{183}W ($^1J_{WN}$ ~ 55 Hz) and ^{103}Rh ($^1J_{RhN}$ ~ 30 Hz). On the other hand, the resonance assigned to $^{15}N_\beta$ appears at lower field, between δ -30 and -70, usually with unresolved coupling to other nuclei like P ($^2J_{PN}$ > $^3J_{PN}$ < 1 Hz). The ^{15}N chemical shifts of some specific examples are presented in Table VI (Chapter V).

1.3.3. Reactivity of Dinitrogen Complexes

As was mentioned before, the reactions of N_2-complexes have been the subject of considerable interest not only in mononuclear but also in binuclear complexes. This review will be limited to the more important recent developments in two types of reactions.

1.3.3(a). Displacement of the N_2-ligand

This reaction was the first to be observed in N_2-complexes, and in many ways it is the least interesting, especially with regard to attempts to bring about the chemical transformation of N_2 at metal sites. However, since N_2 is an excellent leaving group, N_2-complexes have often been used for the synthesis of new metal-containing compounds. These reactions involve the replacement of N_2 by other ligands with, or without, a change in the oxidation state of the metal. In the former case, oxidation of the central metal causes a weakening of the M-N interaction (because of the weakened capacity of the metal for back donation) and the N_2 is usually evolved. Very often this occurs as a side-reaction in the protonation or alkylation of an N_2 ligand. Typical oxidizing agents are halogens, hydrogen halides and alkyl halides. Examples of such oxidative reactions, among many others, are: (i) $Mo(N_2)_2(Dmpte)_2$ (Dmpte= (di-**m**-tolylphosphino)ethane) with H_2 to give $MoH_4(Dmpte)_2$;[67] (ii) $OsCl_2(PEt_2Ph)_3(N_2)$ with Cl_2 to produce $OsCl_3(PEt_2Ph)_3$;[68] (iii) $Mo(N_2)_2(dppe)_2$ with thiols (RSH) to give $Mo(SR)_2(dppe)_2$;[69] (iv)

$Re(NHPh)(PMe_3)_4(N_2)$ with I_2 to produce $[Re(NHPh)(I)(PMe_3)_4]I$;[59] and (v) cis-$Mo(N_2)_2(PMe_3)_4$ with alkyl halides (RX) yielding trans-$MoX_2(PMe_3)_4$.[70] There are also cases where the dinitrogen ligand is retained bound to the oxidised metal; e.g., $ReCl(PMe_2Ph)_4(N_2)$ is oxidized by Cl_2 to $[ReCl(PMe_2Ph)_4(N_2)]Cl$,[71] and $W(N_2)_2(Ph_2PCH{=}CHPPh_2)_2$ reacts with I_2 to give $[W(N_2)_2(Ph_2PCH{=}CHPPh_2)]I_3$.[72]

Displacement reactions of the N_2 ligand without changes in the oxidation state of the metal are also very common. Some recent examples are: (i) cis-$Mo(N_2)_2(Ph_2PCH_2PPh_2)_2$ reacts with CO to give cis-$Mo(CO)_2(Ph_2PCH_2PPh_2)_2$;[72] (ii) $ReCl(dppe)_2(N_2)$ with terminal acetylenes ($HC{\equiv}CR$) to produce vinylidene complexes $ReCl(C{=}CHR)(dppe)_2$;[73] (iii) cis-$W(N_2)_2(PMe_3)_4$ with C_2H_4 to afford trans-$W(C_2H_4)_2(PMe_3)_4$;[58] and (iv) $Re(NHPh)(PMe_3)_4(N_2)$ with CO_2 yielding $Re(NHPh)(PMe_3)_3(\eta^2\text{-}CO_2)$.[59] In addition to these reactions, there are some others in which only one N_2-ligand in bis-dinitrogen complexes is displaced giving monodinitrogen species; e.g., trans-$Mo(N_2)_2(P\text{-}P)_2$ reacts with CO[74] or nitriles (RCN)[65,75,76] to give trans-$Mo(N_2)(L)(P\text{-}P)_2$ where L= CO or RCN, P-P= $R_2PCH_2CH_2PR_2$, and R= alkyl or aryl.

There is a relatively small number of reactions where other ligands are displaced in preference to N_2. Some of these are: (i) trans-$W(N_2)_2(PMePh_2)_4$ gives trans-$W(N_2)_2(C_5H_5N)(PMePH_2)_3$ on treatment with pyridine,[77] and (ii) cis-$Mo(N_2)_2(PMePH_2)_4$ reacts with $Ph_2PCH_2CH_2SMe$ to give trans-$Mo(N_2)_2(PMePH_2)_2(Ph_2PCH_2CH_2SMe)$.[78]

1.3.3(b). Reactions of Ligating Dinitrogen

The reduction of terminal N_2-ligands in mononuclear complexes has been extensively studied, but these reactions have been limited almost exclusively to those of the cis- and trans-bis-dinitrogen complexes of the formally d^6 transition metals Mo (0) and W (0), in which each metal atom is also coordinated by mono or bidentate phosphines (see Fig.4).

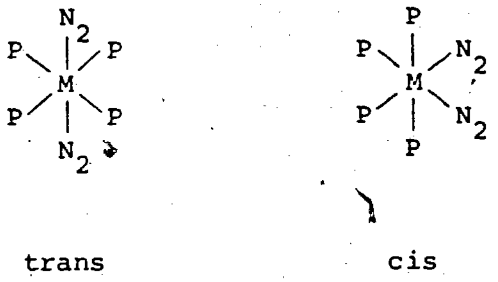
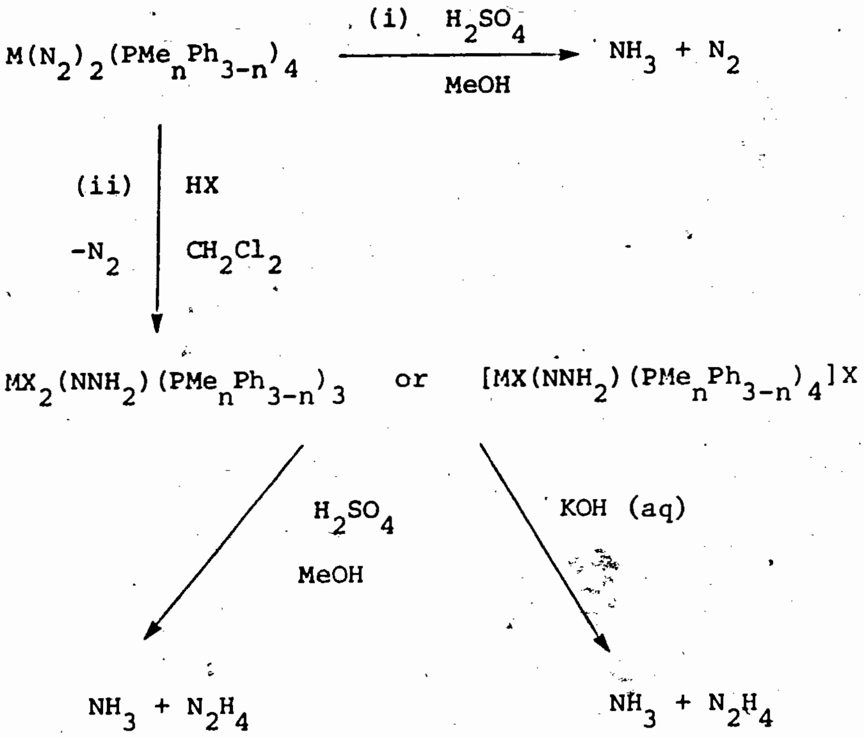


Fig.4. Trans and cis isomers of bis-dinitrogen complexes (M= Mo or W) containing phosphine co-ligands.

In numerous cases these types of complexes react with electrophiles to produce stable compounds containing nitrogen-hydrogen or nitrogen-carbon bonds (N_2R, N_2R_2; R= H or organic group). In other cases they readily react with acids to produce hydrazine or ammonia. The nature of the products depends on the metal, type of phosphine and reaction conditions (see below).

The early chemistry of the complexes shown in Fig.4, which was developed by Chatt and his coworkers about ten years ago, demonstrated that the reaction of $M(N_2)_2P_4$ (M= Mo or W; P= PMe_2Ph or $PMePh_2$) with an excess of acid gives ammonia or hydrazine in addition to molecular dinitrogen, with the yield being critically dependent upon the metal, the acid anion, and the reaction solvent[2,77,79,80] (see Scheme IV).



Scheme IV

The reactions shown in Scheme IV appear to be general when the phosphine co-ligand is monodentate. A quite different reaction occurs between acids and complexes containing a bidentate phosphine such as $M(N_2)_2(dppe)_2$ (M= Mo or W). In these cases, the reaction follows route (ii) in Scheme IV, and stops at the hydrazido (2-) $[MX(NNH_2)(dppe)_2]^+$ with no further production of either ammonia or hydrazine.[79] More recently it has been observed that the presence of at least one monodentate phosphine in the molybdenum bis-dinitrogen complexes is necessary for ammonia to be produced by reaction with acids[81] (Eqs.5 and 6).

$$\text{trans-Mo}(N_2)_2(\text{dppe})(\text{PPh}_2\text{Me})_2 \xrightarrow{\text{HBr}} NH_4Br + [HPPh_2Me]Br + N_2 + \text{MoBr}_3(\text{dppe})(\text{PPh}_2\text{Me}) \qquad \text{Eq.5.}$$

$$\text{trans-Mo}(N_2)_2(\text{triphos})(\text{PPh}_3) \xrightarrow{\text{HBr}} NH_4Br + [HPPh_3]Br + N_2 + \text{MoBr}_3(\text{triphos}) \qquad \text{Eq.6.}$$

$$\text{triphos} = PhP(CH_2CH_2PPh_2)_2$$

The above trend in reactivity as a function of the phosphine ligand seems not to be true for monodinitrogen species. In fact, George et al. have demonstrated that complexes of the type $Mo(N_2)(PPP)(PP)$ (where PPP and PP are respectively tridentate and bidentate phosphines) also produce ammonia and hydrazine by reaction with acids.[82]

In all these protonation reactions, it has been established that the hydrazido (2-) complexes ($MNNH_2$) are intermediates in the reduction process.[80,83] These have been isolated and a linear MNN structure determined on the basis of spectroscopy[44,45] and, in some cases by X-ray crystal structure studies, e.g. $[MoF(NNH_2)$

(dppe)$_2$]$^+$.[84]

On the other hand, complexes containing the diazenido ligand (NNH), which can be considered to represent the first step in the protonation and reduction of ligating dinitrogen have never been isolated directly from protonation reactions of N_2-complexes. They have, however, been prepared by deprotonation of hydrazido (2-) complexes with weak bases, according to Eq.7.[85]

$$\text{trans-}[\mathrm{MX(NNH_2)(dppe)_2}]^+ + \mathrm{Et_3N} \longrightarrow \text{trans-}\mathrm{MX(N_2H)(dppe)_2} + \mathrm{Et_3NH^+} \qquad \text{Eq.7.}$$

M= Mo or W; X= F, Cl or Br

The second important aspect in the reactivity of ligating dinitrogen in mononuclear complexes involves the formation of nitrogen-carbon bonds. These reactions are potentially of great industrial importance in connection with the production of organonitrogen compounds. They have been investigated in parallel with N-H bond formation. Most studies in this area have been limited to complexes of Mo, W, Re and Mn.

The first demonstration of N-C bond formation from ligating N_2 was the acylation of Mo and W dinitrogen complexes shown in Eq.8.[86]

$$\text{trans-M(N}_2\text{)}_2\text{(dppe)}_2 + \text{MeCOCl} \longrightarrow \text{MCl(N}_2\text{COMe)(dppe)}_2 + \text{N}_2 \qquad \text{Eq.8.}$$

M= Mo or W

Similar reactions also occurred with rhenium complexes ReCl $(PR_3)_3(L)(N_2)$, L= pyridine or PR_3.[86] Subsequently, it was shown that alkyl halides (RX) react photochemically with trans-$M(N_2)_2$ $(dppe)_2$ to give alkyldiazenido compounds trans-$MX(N_2R)$ $(dppe)_2$.[86-88] A free radical mechanism has been proposed for (these reactions.[88,90] The resulting diazenido complexes (acyl or alkyl) can be readily protonated to give the hydrazido (2-) species (Eq.9).

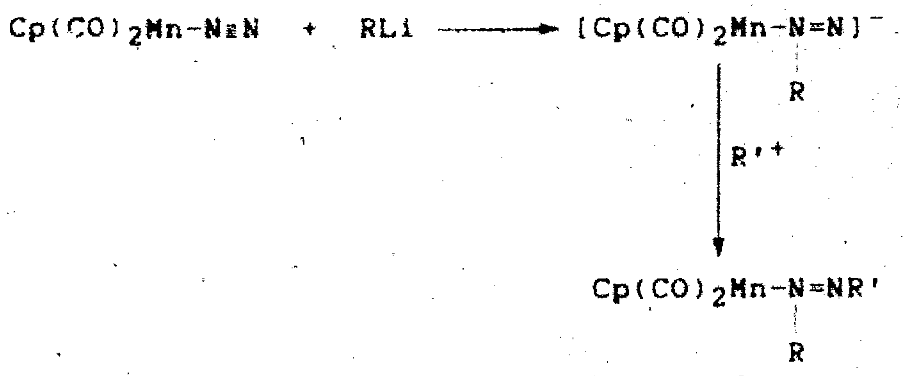
$$\text{trans-MX(N}_2\text{R)(dppe)}_2 + \text{HX} \longrightarrow \text{[MX(NN(H)R)(dppe)}_2\text{]X} \qquad \text{Eq.9.}$$

M= Mo or W; R= alkyl, acyl or aryl

The dimethylhydrazido (2-) complex $[WBr(NNMe_2)(dppe)_2]Br$ could be prepared directly from the bis-dinitrogen complex with an excess of MeBr, but the molybdenum analogue could not be obtained.[86]

Attempts have been made to obtain simple organonitrogen compounds from organodiazenido and organohydrazido (2-) complexes. In general, treatment with strong concentrated acids such as H_2SO_4 leads to considerable N-C bond cleavage and overall yields of amines are poor,[91] but significant yields of primary and secondary amines as well as ammonia are obtained using aluminium or boron hydrides in methanol.[88,91]

Finally, Sellmann and Weiss have demonstrated that the formation of N-C bonds also can be achieved by using a totally different synthetic approach. They showed that the dinitrogen complexes $CpM(CO)_2(N_2)$ (M= Mn and Re) which are electron-poor relative to the phosphine , such as $ReCl(PR_3)_4(N_2)$, react with nucleophiles like phenyllithium to give, after treatment with acid, a phenyldiazene ligand. The manganese complex reacts similarly with MeLi, and subsequent treatment with Me_3O^+ gives the dimethyldiazene complex.[92] (see Scheme V).



$$\mathrm{Cp(CO)_2Mn{-}N{\equiv}N} + \mathrm{RLi} \longrightarrow [\mathrm{Cp(CO)_2Mn{-}\underset{R}{N}{=}N}]^- \xrightarrow{R'^+} \mathrm{Cp(CO)_2Mn{-}\underset{R}{N}{=}NR'}$$

R= Ph, R'= H; R=R'=Me

Scheme V

It has been proposed that the alkyl anion attacks the α-nitrogen atom, and subsequent electrophilic attack occurs at the β-nitrogen to give the diazene products.[92]

CHAPTER II

Synthesis and Characterization of Pentamethylcyclopentadienyl Dicarbonylaryldiazenido Complexes of Rhenium

2.1. Introduction

Recent work in this laboratory on the characterization and study of complexes containing the aryldiazenido ligand (N_2Ar; Ar= aryl) has been centered on the cationic dicarbonylcyclopentadienylrhenium derivatives $[CpRe(CO)_2(N_2Ar)]^+$.[9,10] The rich chemistry displayed by these cations, which has been discussed in chapter I, stimulated us to investigate the effect of replacing the cyclopentadienyl (Cp) ligand by pentamethylcyclopentadienyl (Cp^*) on the chemistry of these systems.

In this chapter, the synthesis and characterization of the new pentamethylcyclopentadienyl aryldiazenido complexes of rhenium are described.

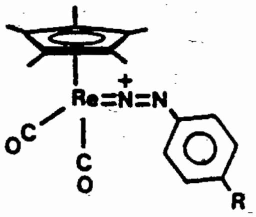
2.2. Synthesis

The pentamethylcyclopentadienyldicarbonylrhenium aryldiazenido complexes of the general formula $[Cp^*Re(CO)_2(\underline{p}\text{-}N_2C_6H_4R)][BF_4]$ ($\underline{1}$: R= (a) OMe, (b) Me, (c) Br, (d) F and (e) H) were prepared in an analogous manner to $[CpRe(CO)_2(N_2Ar)][BF_4]$[10] from the reaction of the corresponding arenediazonium tetrafluoroborate salt with the $Cp^*Re(CO)_2(THF)$ complex generated "in situ" from irradiation of $Cp^*Re(CO)_3$ in THF. Attempts to isolate the THF derivative were unsuccessful due to the low stability of this complex during chromatography, and its reluctance to crystallize from THF solution at low temperature (ca. -78°C); $CpRe(CO)_2(THF)$ crystallizes at this temperature quite readily.[10] The synthesis and characterization of 1a has been reported previously.[93] In all the cases the new aryldiazenido complexes 1 were obtained as orange, red or maroon microcrystalline solids in better than 60% yields.

2.3. Characterization

All the new cationic aryldiazenido complexes 1 are air-stable, both in solution in polar solvents and as solids. Solid samples have been exposed to normal laboratory atmosphere for periods in excess of one year without appreciable deterioration. They have been fully characterized by elemental analysis, IR, ^1H NMR and in two cases, by nitrogen NMR (1a-$^{15}N_\alpha$ and 1e-$^{15}N_\beta$ by ^{15}N NMR and 1a and 1e by ^{14}N NMR), ^{13}C NMR and by MS (FAB).

Infrared and nitrogen NMR spectroscopy show clearly that these complexes are structurally similar to the cyclopentadienyl analogues of manganese and rhenium, i.e. they contain the aryl-diazenido ligand coordinated in a singly-bent geometry (cf., X-ray structure for $[(C_5H_4Me)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$)[9] as shown below.



1

Like the complexes $[(C_5H_4R)M(CO)_2(N_2\ Ar)][BF_4]$ (R= H or Me, M= Mn and R= H, M= Re),[9,10] the IR spectra of these cationic complexes (1) show two very strong ν(CO) bands at ca. 2050 and 2000 cm^{-1} and one strong and broad ν(NN) band at ca. 1730 cm^{-1} (Table I).

The two ν(CO) absorptions in these complexes are not affected by the electronic nature of the *para* substituent in the aromatic ring of the diazenido ligand. However, significant changes are observed in the ν(NN) absorptions which are lowered about 10 cm^{-1} (in CH_2Cl_2 solution) when H, Me or OMe groups (i.e. 1e, 1b and 1a) are replaced by the electron-withdrawing groups Br and F in 1c and 1d.

The assignment of ν(NN) has been confirmed by ^{15}N isotopic substitution at the metal-bound nitrogen position N_α in 1a-$^{15}N_\alpha$, and at the ring-bound nitrogen position N_β in 1e-$^{15}N_\beta$. In both complexes a shift of ν(NN) by 24 cm^{-1} to lower frequency was observed. This shift is similar to those observed in the complexes $[(C_5H_4R)M(CO)_2(N_2C_6H_4R')]^+$ (R= Me, R'= *p*-F, M= Mn;[9] R= H, R'= *p*-Me, *p*-OMe and *p*-NEt_2, M= Re[10]) upon ^{15}N-substitution at N_α and for the same complex (R= H, R'= H, M= Re)[10] when ^{15}N-substituted at the N_β position, and is indicative of a singly-

Table I. Infrared ν(CO) and ν(NN) Data for Rhenium Aryldiazenido Complexes in CH_2Cl_2 Solution.

Compound	ν(CO)[a]	ν(NN)[a]	Ref.
$Cp^*Re(CO)_2(\underline{p}\text{-}N_2C_6H_4R)][BF_4]$			
R= OMe, 1a	2051 vs, 1995 vs	1736 s (br) (1708 s)[b]	t/w[d]
R= Me, 1b	2053 vs, 1997 vs	1736 s (br)	t/w
R= Br, 1c	2057 vs, 2002 vs	1726 s (br)	t/w
R= F, 1d	2056 vs, 2001 vs	1729 s (br)	t/w
R=H, 1e	2055 vs, 2000 vs	1736 s (br) (1711 s)[c]	t/w
$CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4R)][BF_4]$			
R= OMe	2078 vs, 2020 vs	1770 s (br) (1735 s)[b]	10, 27
R= Me	2080 vs, 2021 vs	1769 s (br)	10, 27
R= H	2075 vs, 2016 vs	1768 s (br) (1740 s)[c]	10, 27

[a] Frequencies in cm^{-1}. Abbreviations: vs, very strong; s, strong; br, broad. [b] $\nu(^{15}N^{14}N)$.
[c] $\nu(^{14}N^{15}N)$. [d] This work.

bent aryldiazenido ligand.

The ^{1}H NMR spectra of these complexes in $CDCl_3$ show no unusual features. In general, a single resonance for the C_5Me_5 ring is observed at δ 2.36-2.38; *para*-substitution in the benzene ring of the diazenido ligand shows a typical AA'BB' spectrum in the region δ 7.10-7.80. In addition, single resonances for the OMe group in **1a** and the Me group in **1b** are observed. Similarly, the $^{13}C\{^{1}H\}$ NMR spectra of **1a** and **1e** show resonances expected for these types of complexes. The single resonance at ca. δ 190 is assigned unequivocally to the magnetically equivalent CO groups; the aromatic carbons show their expected resonances in the region δ 114-164, and single resonances for the methyl and ring carbons of the pentamethylcyclopentadienyl ligand are observed at ca. δ 10.5 and 109.0, respectively.

Additional information about the structure of the diazenido ligand has been obtained from nitrogen NMR spectroscopy. The ^{15}N NMR spectra of **1a**-$^{15}N_\alpha$ and **1e**-$^{15}N_\beta$ (96% enriched) show single resonances at δ -7.3 and δ -118.5 relative to external $MeNO_2$, respectively. With the chemical shift positions for the N_α and N_β nitrogens thus determined we were interested in the possibility of utilizing ^{14}N NMR as an alternative. Despite the low resolution, as shown by the relatively broad lines, we have found ^{14}N NMR spectroscopy to be quite adequate for the identification of the nitrogen nuclei in these rhenium aryldiazenido complexes. Two broad resonances, at δ -6.7 and δ

-123.0 are observed for 1a. The former is in good agreement with the δ -7.3 resonance observed in the ^{15}N NMR spectrum of 1a-$^{15}N_{\alpha}$ and the latter resonance is assigned to $^{14}N_{\beta}$. Analogously, the ^{14}N NMR spectrum of 1e (Fig.5) shows two broad resonances at δ -8.5 and δ -118.0. In this case the high field resonance is in good agreement with the δ -118.5 value in the ^{15}N NMR spectrum of 1e-$^{15}N_{\beta}$, and thus is unambiguously assigned to $^{14}N_{\beta}$. These chemical shifts are in the region expected for N_{α} and N_{β} nitrogen nuclei in singly-bent diazenido ligands (Table II).[16,26,27]

Additional characterization of complexes 1 was obtained by determining the mass spectra of 1a and 1e and their ^{15}N-isotopomers 1a-$^{15}N_{\alpha}$ and 1e-$^{15}N_{\beta}$ using the fast atom bombardment (FAB) technique, whereas no worthwhile mass spectra could be obtained using the conventional electron impact (EI) technique. The FAB mass spectrum of 1a is shown in Fig.6. In all the cases, the unfragmented cations $[Cp^{*}Re(CO)_2(N_2C_6H_4R)]^{+}$ were observed as molecular ions (M^{+}). Fragments corresponding to the loss of the diazenido ligand (M^{+}-diazo) and the simultaneous loss of 2 CO and N_2 (M^{+}-84) ((M^{+}-85) when ^{15}N-substituted), were also observed.

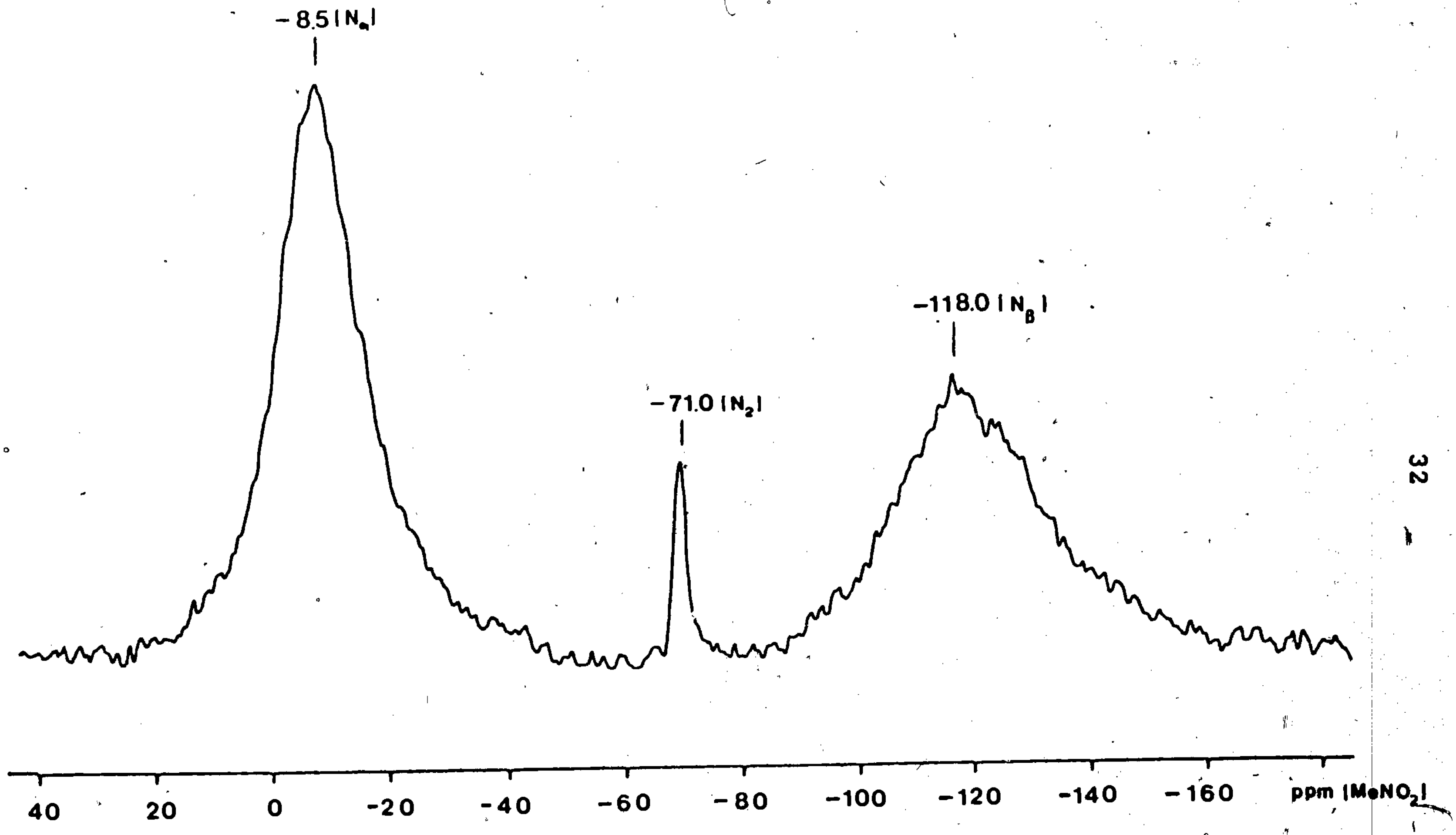


Fig.5. ^{14}N NMR spectrum of $[Cp^*Re(CO)_2(N_2C_6H_5)][BF_4]$ (1e) in acetone/acetone-d_6 (at 28.9 MHz) (the N_2 resonance arises from dissolved molecular N_2 in the solvent).

Table II. ^{14}N and ^{15}N Chemical Shifts for Singly-Bent Diazenido Complexes.[a]

Compound	δ ($^{15}N_{\alpha}$)	δ ($^{14}N_{\alpha}$)	δ ($^{15}N_{\beta}$)	δ ($^{14}N_{\beta}$)	solvent	Ref.
$[Cp^*Re(CO)_2(\underline{p}\text{-}N_2C_6H_4OMe)]^+$ 1a	-7.3	-6.7	-	-123.0	acet./acet.-d_6	t/w[b]
$[Cp^*Re(CO)_2(N_2C_6H_5)]^+$ 1e	-	-8.5	-118.5	-118.0	" "	t/w
$[CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4OMe)]^+$	-16.9	-16.1	-	-125.5	" "	t/w, 27
$[CpRe(CO)_2(N_2C_6H_5)]^+$	-	-	-125.1	-	" "	27
$[CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4Me)]^+$	-12.3	-	-	-	" "	27
$[CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4NEt_2)]^+$	-2.9	-	-	-	" "	27
$ReCl_2(N_2COC_6H_5)(C_5H_5N)(PPh_3)$	-55.9	-	-148.6	-	toluene	16
$RuCl_3(N_2C_6H_5)(PPh_3)_2$	-46.8	-	-	-	CH_2Cl_2	16
$MoBr(N_2Et)(dppe)_2$	-29.0	-	-146.8	-	THF	16
$WBr(N_2Et)(dppe)_2$	-28.0	-	-164.7	-	"	16
$WF(N_2H)(dppe)_2$	-24.6	-	-182.6	-	"	66
$MoCl(N_2COCH_3)(dppe)_2$	-35.4	-	-123.7	-	"	16

[a] Chemical shifts relative to external CH_3NO_2. [b] This work.

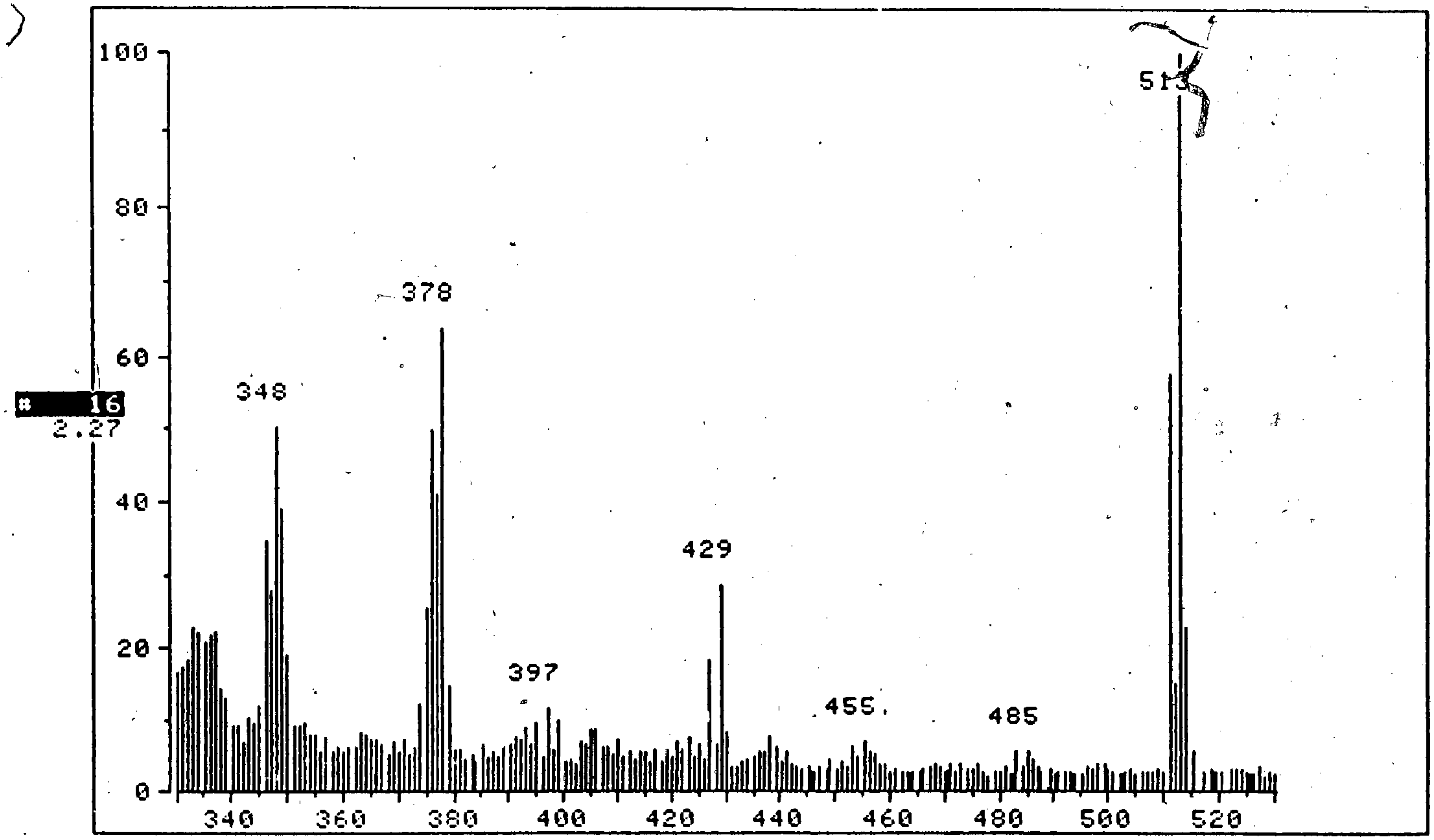


Fig.6. Mass Spectrum (FAB) of [$Cp^{*}Re(CO)_2(\underline{p}\text{-}N_2C_6H_4OMe)$][$BF_4$] (<u>1a</u>) (xenon, sulfolane) in the region m/z 330-530; m/z values (^{187}Re) are 513 (M^+), 429 $(M\text{-}2CO\text{-}N_2)^+$, 378 $(M\text{-}N_2Ar)^+$.

2.4. Discussion

The pentamethylcyclopentadienylaryldiazenido complexes of rhenium (1) are similar in their spectroscopic parameters, color and other physical properties to the Cp species, but are noticeably more soluble in polar organic solvents and in water (in which they are slightly soluble).

The high values of ν(CO) and ν(NN) in the IR spectra (Table I) may be partly accounted for by the positive charge on the complexes, resulting in decreased back-bonding from the metal to the CO and N_2R groups, compared with that of similar neutral compounds. This is well substantiated by the pair of complexes $[(C_5H_4Me)Mn(CO)_2(N_2C_6H_5)]^+$ (ν(CO) 2085, 2038; ν(NN) 1790 cm^{-1})[9] and $(CpCr(CO)_2(N_2C_6H_5)$ (ν(CO) 1996, 1930; ν(NN) 1570 cm^{-1}),[94] and the present compounds may be expected to exhibit a similar trend with the, as yet, unknown neutral analogue $Cp^*W(CO)_2(N_2Ar)$. A comparison of ν(CO) for complexes 1 with values for $[Cp^*Re(CO)_2(NO)]^+$ (ν(CO) 2092, 2036 cm^{-1})[95,96] shows how similar NO and N_2R ligands are in their π-acceptor properties in these compounds, with N_2R being the poorer.[15]

The IR spectra of complexes 1 are of special interest when compared to the spectra of the cyclopentadienyl analogues (see Table I). In particular, it is noteworthy that the carbonyl stretching frequencies ν(CO) for the Cp^* complexes are shifted by ca. 20-27 cm^{-1} to lower wavenumbers, relative to the values for the corresponding Cp complexes. The same behaviour is observed for ν(NN), which is shifted by about 33 cm^{-1} to lower wavenumber. Comparable shifts have been observed in the ν(CO) and ν(NO) absorptions in the isoelectronic complexes $[CpRe(CO)_2(NO)]^+$ and $[Cp^*Re(CO)_2(NO)]^+$.[95] These shifts are approximately those predicted empirically[97] for the introduction of five methyl substituents into the cyclopentadienyl ring of complexes **1**. They can be explained by the increased π-back-bonding to the CO and the diazenido ligands that results from the increase in electron density on the metal atom caused by the presence of the more electron-donating methyl groups.

The nitrogen NMR chemical shifts also change significantly when the Cp^* ligand replaces Cp in these rhenium aryldiazenido complexes. In the ^{15}N NMR spectrum of the p-OMe derivative **1a**-$^{15}N_\alpha$, the ^{15}N resonance occurs 9.6 ppm downfield relative to the unsubstituted analogue (see Table II). To make a more general comparison, the ^{14}N NMR spectrum of the complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ was measured (acetone/acetone-d_6, relative to $MeNO_2$, δN_α -16.1 and δN_β -125.5). In this case a downfield shift of 9.4 and 2.5 ppm was observed for the N_α and N_β resonances, respectively. The first is in very good agreement with the shift observed in the ^{15}N NMR spectra (9.6 ppm). The same effect was observed in the ^{15}N NMR spectra of **1e**-$^{15}N_\beta$ and $[CpRe(CO)_2(N^{15}NC_6H_5)]^+$,[27] where a downfield shift of 6.6 ppm in N_β occurred on replacing the Cp ligand by Cp^*. The relative deshielding of both nitrogen nuclei in the diazenido ligand can be associated with an increase in back-bonding in the M=N=N moiety, caused by the presence of the pentamethylcyclopentadienyl ligand. Thus, the ^{15}N or ^{14}N shifts provide useful supplementary data to those obtained by IR spectroscopy in the elucidation of the structure of the diazenido ligand in the rhenium complexes.

2.5. Experimental Section

(a) General

All reactions were carried out under dry N_2 in Schlenk apparatus connected to a switchable double manifold providing low vacuum or nitrogen. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Reaction yields are based on the rhenium reagent used.

Photochemical reactions of $Cp^*Re(CO)_3$ were carried out at atmospheric pressure in a Pyrex vessel (400 mL) equipped with a water-cooled quartz finger joined to the vessel by 60/50 standard taper joint. A 200 Watt ultraviolet source (Hanovia high-pressure mercury lamp) was placed inside the quartz finger. Nitrogen was passed through the reaction vessel prior to the introduction of the solvent and starting materials, and slow passage of nitrogen or argon was maintained during the reaction. Other photochemical reactions were carried out in quartz tubes (10, 20 or 100 mL) placed beside the quartz finger. During the photolysis a slow flux of N_2 was maintained, unless otherwise specified.

Infrared spectra were measured by using Perkin-Elmer models 599B or 983 instruments, calibrated against polystyrene or carbon monoxide. CaF_2 cells (0.1 mm) were used to measure the IR spectra in solution, with the appropriate solvent in the reference cell. NMR spectra were recorded in the NMR Services of S.F.U. by Mrs. M. Tracey on a Bruker WM-400 instrument at 400, 100, 28.9 and 40.5 MHz for ^1H, ^{13}C, ^{14}N and ^{15}N, respectively. Chemical shifts (δ) are reported in ppm, downfield positive, ^1H and ^{13}C relative to internal tetramethylsilane (TMS) and, ^{14}N and ^{15}N relative to external $MeNO_2$. A Varian XL-100 Fourier Transform instrument was used to record some of the proton spectra. Mass spectra were obtained by Mr. G. Owen on a Hewlett-Packard Model 5985 spectrometer using fast atom bombardment (F.A.B., Phrasor Scientific, Inc., accessory). The m/z values are referred to ^{187}Re. Microanalyses were performed by Mr. M.K. Yang of the microanalytical laboratory of S.F.U.

(b) Starting Materials

Diazonium tetrafluoroborate salts were prepared by diazotization of substituted anilines (Aldrich) with $NaNO_2$; these were recrystallized from acetone/diethyl ether. The ^{15}N isotopic label was introduced at N_α with $Na^{15}NO_2$ (96% ^{15}N, MSD Isotopes) or N_β with $^{15}NH_2C_6H_5$ (99% ^{15}N, Stohler Isotopes). Pentamethylcyclopentadiene and decacarbonyldirhenium (Strem Chemicals) were used directly as purchased. $Cp^*Re(CO)_3$ was synthesized by the method used by Graham.[98]

Preparation of $[Cp^*Re(CO)_2(\underline{p}\text{-}N_2C_6H_4OMe)][BF_4^-]$ (**1a**) and (**1a**-$^{15}N_\alpha$)

$Cp^*Re(CO)_3$ (1.10 g, 2.71 mmol) was irradiated in freshly distilled THF (400 mL) under nitrogen or argon for 120 min, at 0°C. (This time is sufficient to provide a reasonable conversion to the THF complex without too much ensuing decomposition). The solution was concentrated to one-third volume, then [*p*-$N_2C_6H_4$OMe][BF_4] or [*p*-^{15}NNC_6H_4OMe][BF_4] (0.46 g, 2.07 mmol) in acetone (15 mL) was added dropwise with continuous stirring at room temperature. The solution changed from yellow-brown to dark red. After 1 h stirring, the solution was concentrated to 50 mL by rotary evaporation, then diethyl ether was added slowly until no more solid precipitated (ca. 150 mL). Supernatant solvent was removed by pipet and the solid washed twice with 30 mL of diethyl ether. Recrystallization from CH_2Cl_2/ether gave 1.23 g (76%) of a maroon microcrystalline solid M.p. 128-130°C. IR (CH_2Cl_2): 2051 vs, 1995 vs ν(CO), 1736 s (1708 in **1a**-$^{15}N_\alpha$), ν(NN) and 1060 br, m, ν(BF_4) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.37 s (15H, Cp*), 3.92 s (3H, OMe), 7.14 d (2H, C_6H_4) and 7.38 d (2H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.50 s (C_5<u>Me</u>$_5$) 56.07 s (O<u>Me</u>), 108.83 s (<u>C</u>$_5$Me$_5$), 114.80 s, 116.70 s, 125.25 s and 164.07 s (C_6H_4), 190.65 s (CO). ^{14}N NMR (acetone/acetone-d_6): δ -123.0 br, s (N_β), -6.7 br, s (N_α). ^{15}N NMR for **1a**-$^{15}N_\alpha$ (acetone/acetone-d_6): δ -7.30 s (N_α). MS (FAB, sulfolane, xenon) (Fig.6): m/z 513 (514 in **1a**-$^{15}N_\alpha$) (M$^+$ of cation), 429 (M$^+$-2CO-N_2), 378 (M$^+$-diazo). Anal. Calcd. for **1a**: C, 38.06; H, 3.67; N, 4.67. Found: C, 38.11; H, 3.45; N, 4.53.

Preparation of [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4$Me)][BF_4] (**1b**)

This complex was synthesized analogously to **1a**, as dark-red microcrystals (after recrystallization from CH_2Cl_2/ether) using [p-$N_2C_6H_4Me$][BF_4], in 60% yield, m.p. 133-135°C. IR (CH_2Cl_2): 2053 vs, 1997 vs ν(CO), 1736 s ν(NN) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.38 s (15H, Cp*), 2.54 s (3H, Me), 7.27 d (2H, C_6H_4), 7.43 d (2H, C_6H_4). Anal. Calcd. for 1b: C, 39.11; H, 3.77; N, 4.80. Found: C, 39.29; H, 3.70; N, 4.70.

Preparation of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4Br)][BF_4]$ (1c)

This complex was prepared similarly in 67% yield, as orange microcrystals, m.p. 183-185°C. IR (CH_2Cl_2): 2057 vs, 2002 vs ν(CO), 1726 s ν(NN) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.38 s (15H, C_5Me_5), 7.32 d (2H, C_6H_4), 7.77 d (2H, C_6H_4). Anal. Calcd. for 1c: C, 33.33; H, 2.93; N, 4.31. Found: C, 33.36; H, 2.81; N, 4.12.

Preparation of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4F)][BF_4]$ (1d)

A similar procedure to that used for 1a gave 1d as bright-orange microcrystals in 68% yield, m.p. 155-157°C. IR (CH_2Cl_2): 2056 vs, 2001 vs ν(CO), 1729 ν(NN) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.38 s (15H, Cp*), 7.38 d (2H, C_6H_4), 7.45 d (2H, C_6H_4). Anal. Calcd. for 1d: C, 36.80; H, 3.23; N, 4.77. Found: C, 36.40; H, 3.30; N, 4.65.

Preparation of $[Cp^*Re(CO)_2(N_2C_6H_5)][BF_4]$ (1e and (1e-$^{15}N_\alpha$)

This complex was prepared following the procedure of 1a, using [$N_2C_6H_5$][BF_4] or [$N^{15}NC_6H_5$][BF_4] in 61% yield, as orange microcrystals, m.p. 153-155°C. IR (CH_2Cl_2): 2055 vs, 2000 vs ν(CO), 1736 (1711 in $\underline{1e}$-$^{15}N_\beta$) s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.36 s (15H, Cp*), 7.39 d (2H, C_6H_5), 7.50 t (1H, C_6H_5), 7.62 t (2H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.47 s ($C_5\underline{Me}_5$), 109.15 s ($\underline{C}_5Me_5$), 123.13 s, 125.42s, 131.08 s and 133.41 s (C_6H_5), 189.88 s (CO). ^{14}N NMR (acetone/acetone-d_6) (Fig.4): δ -118.0 br, s (N_β), -8.5 br, s (N_α). ^{15}N NMR for $\underline{1e}$-$^{15}N_\beta$ (acetone/acetone-d_6) δ -118.5 s (N_β). MS (FAB, xenon, sulfolane): m/z 483 (484 in $\underline{1e}$-$^{15}N_\beta$) (M^+ of cation), 399 (M^+-2CO-N_2), 378 (M^+-diazo). Anal. Calcd. for $\underline{1e}$: C, 37.96; H, 3.51; N, 4.92. Found: C, 37.58; H, 3.47; N, 4.81.

CHAPTER III

Transformation of the CO Ligand in $[Cp^{*}Re(CO)_2(\underline{p}\text{-}N_2C_6H_4OMe]^{+}$ by Reaction with some Nucleophiles

3.1. General

Intermolecular nucleophilic attack at carbon in transition metal carbonyl complexes has been demonstrated in several different chemical situations. A wide variety of such reactions has been discovered, involving different nucleophilic reagents. The most common and extensively studied include reactions of Grignard and organolithiums to produce acyl derivatives[99,100] (MCOR), and of hydride containing reagents to give formyl complexes[101] (MCOH). More recently, the nucleophilic attack of hydroxide ion at coordinated carbon monoxide to produce metallocarboxylic acids (MCOOH) and/or hydride (MH) complexes has received considerable attention.[102] In an analogous manner, carbamoyl ($MCONR_2$) and alkoxycarbonyl (MCOOR) complexes have been prepared using amines (or ammonia) and alkoxides respectively[103] as nucleophiles.

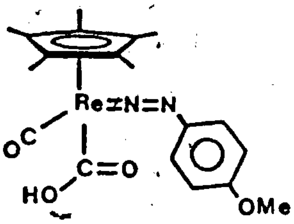
In the following sections of this chapter, a brief review of metallocarboxylic acids, carbamoyl and alkoxycarbonyl complexes will be considered. At the same time, our work on the synthesis, characterization and chemical properties of these types of complexes derived from the dicarbonylpentamethylcyclopentadienylrheniumaryldiazenido complex **1a**, will be discussed.

3.2. Hydroxycarbonyl, Formate, Carboxylate and Hydride Derivatives of [$Cp^*Re(CO)_2$(*p*-$N_2C_6H_4OMe$)][BF_4]

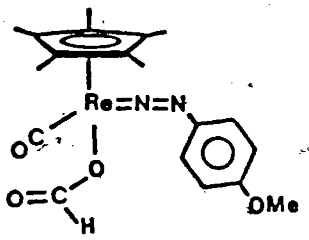
3.2.1. Introduction

Hydroxycarbonyl complexes (or metallocarboxylic acids) have been proposed as key intermediates in several important reactions involving carbon monoxide. They include homogeneous catalysis of the water gas shift reaction[102,104,105] and the formation of hydride ligands by water or hydroxide ion attack on coordinated carbonyl groups.[106,107] However, relatively few hydroxycarbonyl complexes have been isolated and characterized and little is known about their chemistry. Reasonably stable compounds of this class include $IrCl_2(CO)(PMe_2Ph)_2(COOH)$,[108], $CpM(CO)(PPh_3)(COOH)$, M= Fe[109] and Ru,[110] $CpRe(CO)(NO)(COOH)$,[107] $CpRe(PPh_3)(NO)(COOH)$,[111] $Pt(C_6H_9)(P-P)(COOH)$[112] (C_6H_9= 1-cyclohexenyl, P-P= various chelating phosphines), $CpMo(CO)_2(PPh_3)(COOH)$,[113] $PtCl(PEt_3)_2(COOH)$[114] and $CpRe(CO)(N_2Ar)(COOH)$.[33] Particularly interesting is the latter compound, because its isolation, characterization and transformation to the hydride complex $CpReH(CO)(N_2Ar)$ stimulated us to study the reactions of the dicarbonyl pentamethylcyclopentadienyl cationic complex **1a** with hydroxide ion in order to compare the effect of the Cp^* ligand on the properties of these compounds.

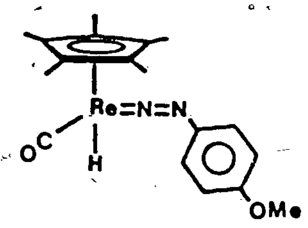
In this section the synthesis and characterization of the stable hydroxycarbonyl complex of formula Cp*Re(CO)(*p*-$N_2C_6H_4OMe$)(COOH) 2 is discussed. The isomeric formate complex Cp*Re(CO)(*p*-$N_2C_6H_4OMe$)(OCHO) 3 has also been synthesized for comparison. The chemistry of complex 2, particularly with reference to the conditions for its conversion to the hydride complex Cp*ReH(CO)(*p*-$N_2C_6H_4OMe$) 4 and the anionic carboxylate complex [Cp*Re(CO)(*p*-$N_2C_6H_4OMe$)(COO)]$^-$ 5 is also discussed. Some of this work was carried out in parallel with the cyclopentadienylrhenium analogues. This study has already been published.[93]



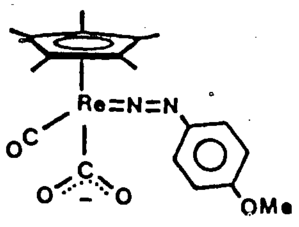
2



3



4



5

3.2.2. Synthesis and Characterization

In analogous manner to the cyclopentadienyl complexes [CpRe(CO)$_2$(N_2Ar)]$^+$, the reactions of the pentamethylcyclopentadienyl complex 1a with alkali-metal hydroxides are exceedingly dependent on the experimental conditions, the solvents, the alkali metal and whether excess hydroxide is present. It is therefore possible to obtain the hydroxycarbonyl complex 2, the hydride complex 4 and the anionic carboxylate complex 5.

The hydroxycarbonyl complex 2 was obtained analytically pure as a golden-yellow microcrystalline precipitate by the slow addition of a stoichiometric amount of 0.1 M aqueous NaOH to a suspension of 1a in water. Complex 2 is air- and thermally-stable as a solid, but it decomposes without melting above 90°C. It is insoluble in water, when pure and free from traces of base, but dissolves in organic solvents such as acetone, CH_2Cl_2, THF and ether, in which solvents it is moderately stable; a small amount of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ was detected by IR when 2 was kept in a THF solution for 1-2 h. Total decomposition was observed after an overnight NMR experiment in C_6D_6 at room temperature, and the IR and capillary GC-MS of the solution then showed the presence of $Cp^*Re(CO)_3$, $Cp^*Re(CO)_2(N_2)$, C_6H_5OMe and $C_6D_5C_6H_4OMe$ among other unidentified minor products.

Compound 2 was fully characterized by elemental analysis, IR and ^1H NMR spectroscopies. The IR spectrum in solution shows a very strong terminal $\nu(CO)$ absorption at about 1930 cm^{-1} and two strong and broad bands at about 1620-1580 cm^{-1} which correspond to $\nu(NN)$ of the N_2Ar group and to $\nu(CO)$ and δ (COH) (bending mode) of the carboxylic group. It was not possible to identify unambiguously a particular band corresponding to $\nu(NN)$, since several bands shifted under ^{15}N-isotopic substitution at N_α in the complex $CpRe(CO)(p\text{-}^{15}NNC_6H_4OMe)(COOH)$ compared with its unsubstituted parent, indicating that $\nu(NN)$ is strongly coupled to other vibrational modes in the same region.[33,93]

Additional confirmatory evidence of the formulation of 2 as a hydroxycarbonyl complex was obtained from the ^1H NMR spectrum. It shows a broad resonance at δ 9.41 (in acetone-d_6) which integrates as 1 H and is assigned to the carboxylic proton. This value is in good agreement with those reported for other hydroxycarbonyl complexes e.g. CpRe(CO)(NO)(COOH)[95] (9.5, CD_2Cl_2), CpRe(CO)(p-$N_2C_6H_4OMe$)(COOH)[33] (8.9, $CDCl_3$) and Pt(C_6H_9)(P-P)(COOH)[112] (9.2-9.8, $(CD_3)SO$).

Electron-impact mass spectral analysis did not give the molecular peak for compound 2, even when low electron voltage (12 eV) and lower temperature (ion source= 40°C) were used. Instead, the molecular peak of the hydrido complex 4 was obtained. This thermal decomposition of the hydroxycarbonyl 2 to the hydride 4 during the run was clearly observed by simultaneously recording the liberation of CO_2 (m/z= 44) and the generation of the ion with m/z= 486 (which corresponds to the molecular peak of complex 4, based on ^{187}Re). Using fast atom bombardment (FAB) the spectrum of 2 was dominated by the $(M-OH)^+$ peak which corresponds to the cation 1a. No formation of the hydride 4 was observed under these conditions.

The lithium salt of the carboxylate complex 5 $[Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(COO)]^-Li^+$ was obtained as a yellow solid using two alternative synthetic methods (see Experimental Section). The fastest and easiest is by direct reaction of the cationic dicarbonyl complex 1a dissolved in CH_2Cl_2 with an excess of saturated aqueous LiOH. Attempts to isolate the sodium or potassium salt of 5 were unsuccesful; instead the hydride complex 4 was obtained (see below). Compound 5 as a Li salt is stable as a solid under a dry atmosphere of N_2. It is insoluble in non-polar solvents, but it dissolves in water to give a bright yellow solution that slowly generates the insoluble hydroxycarbonyl 2. In CH_2Cl_2 and THF the lithium salt is reasonably stable, and only minor decomposition to give the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ and 2 respectively was observed (by IR) after 1 h. The IR spectrum of the lithium salt of 5 shows a strong ν(CO) band at 1928 cm^{-1} in CH_2Cl_2 (1907 cm^{-1} in THF) in addition to one at 1614 cm^{-1} assigned to ν(NN) and the carboxylate group. The ^1H NMR spectrum of this anion 5 could be obtained quickly from the Li salt in D_2O. This shows a resonance at δ 2.03 (Cp^*) and other resonances due to the p-$N_2C_6H_4OMe$ protons.

The hydrido complex 4 can also be synthesized by two methods (see Experimental Section). The more convenient involves the reaction of the cationic complex 1a, dissolved in CH_2Cl_2, with 5 M aqueous NaOH or KOH, followed by removal of the solvent and extraction with THF or acetone. After purification, compound 4 can be obtained analytically pure as a yellow solid which decomposes over 95°C. As a neutral compound, it is soluble in the majority of organic solvents and insoluble in water, but it rapidly reacts with $CHCl_3$ and $CHBr_3$ to give the chloro and bromo complexes $Cp^*ReX(CO)(p\text{-}N_2C_6H_4OMe)$, X= Cl and Br respectively (see Chapter IV).

The IR spectrum of 4 in CH_2Cl_2 shows a very strong terminal ν(CO) band at 1906 cm^{-1} (1925 cm^{-1} in hexane) and a strong band at 1618 cm^{-1} attributable to ν(NN). The occurrence of ν(NN) in this region is evidence that this hydrido complex contains the singly-bent three-electron donor aryldiazenido ligand. No ν(ReH) could be observed in the region 2200-1980 cm^{-1} of the spectrum even in very concentrated solutions. However, the presence of the hydride ligand is indicated by the upfield resonance at δ −5.88 (in C_6D_6) in the ^{1}H NMR spectrum. This resonance is rather broad and the aryl proton resonance is not the usual AA'BB' normally observed in compounds bearing this p-substituted aryldiazenido group. The high-field aromatic resonances (probably H$_\alpha$, i.e., the protons α to the CNN skeleton) appear as a broad doublet, and a similar phenomenon was observed in the cyclopentadienyl analogues.[33,93] The broadening of this and the Re-H resonances may be rhenium quadrupolar in origin.[95] The electron-impact mass spectrum of complex 4 shows the molecular ion as the base peak at m/z= 486 (based on ^{187}Re).

The formate complex $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(OCHO)$ 3 was prepared by reaction of the cationic acetonitrile complex $[Cp^*Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe))]^+$ (to be described in Chapter IV) and sodium formate. This compound was isolated as a red-orange solid melting without decomposition at 65-67°C and soluble in organic solvents, in which it is very stable. In the IR spectrum (CH_2Cl_2 solution) compound 3 shows a very strong ν(CO) at 1925 cm^{-1} and two extra bands at 1642 (medium) and 1624 (strong), cm^{-1} presumably due to ν(CO) of the formate group and ν(NN) respectively. No confirmatory evidence for this assignment was attempted. The resonance of the formate proton, which appears as a sharp singlet, occurs slightly upfield compared with that of the hydroxycarbonyl one δ 7.81 (in acetone-d_6) (cf. δ 9.41 for 2).

This value agrees well with those reported for other formate complexes e.g. $[M(CO)_5(OCHO)]^-$[105] δ 8.28, 8.23 and 7.95 for M= Cr, Mo and W respectively (in CD_3CN) and $CpRe(PPh_3)(NO)(OCHO)$,[115] 8.06 ($CDCl_3$). The electron-impact mass spectrum of 3 exhibits (M^+), $(M-CO)^+$ and $(M-CO_2)^+$ ions in ratio 1:5:3; the generation of CO_2 was evident from the mass 44 ion-current.

3.2.3. Discussion

As was mentioned before, the chemistry of hydroxycarbonyl complexes has been little exploited, presumably due to the usual instability of these compounds. The most recent and comprehensive studies of their intermediacy in the reactions of metal carbonyl complexes with bases to give the corresponding metal-hydride species are those reported by Sweet and Graham[95] for CpRe(CO)(NO)(COOH) and, for $CpRe(CO)(N_2Ar)(COOH)$[33] from our laboratory. In both cases it was suggested that the decarboxylation mechanism, to give the hydrido species CpReH(CO)(L) L= NO and N_2Ar, involves first deprotonation of the acid by OH^- to give the carboxylate anion $[CpRe(CO)(L)(COO)]^-$ from which CO_2 loss then readily occurs (see Eq.10).

$$\mathrm{CpRe(CO)(L)(COOH)} \xrightarrow{OH^-} [\mathrm{CpRe(CO)(L)(COO)}]^- \xrightarrow[H_2O]{-CO_2} \mathrm{CpReH(CO)(L)}$$

Eq.10.

L= NO and N_2Ar

In both cases the carboxylate anion could not be isolated but strong indirect evidence for its formation was provided.[95,33]

In the pentamethylcyclopentadienyl system the isolation of the hydroxycarbonyl complex <u>2</u> by reaction of the cationic complex <u>1a</u> with stoichiometric amount of OH^-, has allowed it to be identified and fully characterized. In general, this compound exhibits chemical properties similar to those observed in the nitrosyl and aryldiazenido cyclopentadienyl analogues. For example, it displays amphoteric behaviour since it dissolves in dilute mineral acids to generate the parent dicarbonyl cation <u>1a</u>, and dissolves in excess aqueous hydroxide to give a bright yellow solution considered to contain the anionic carboxylate complex <u>5</u>. The latter, when treated with acid, regenerates first the hydroxycarbonyl and then the parent cation according to Eq.11.

$$\begin{tikzcd}
{[Cp^*Re(CO)_2(N_2Ar)]^+} \arrow[r, shift left, "OH^-"] & Cp^*Re(CO)(N_2Ar)(COOH) \arrow[l, shift left, "H^+"] \arrow[d, shift left, "OH^-"] \\
\underline{1a} & \underline{2} \\
& Cp^*Re(CO)(N_2Ar)(COO)]^- \arrow[u, shift left, "H^+"] \\
& \underline{5}
\end{tikzcd} \qquad \text{Eq.11.}$$

In the IR spectrum, the presence of the more electron-donating Cp^* ligand in the $Re(CO)(N_2Ar)(COOH)$ fragment is reflected in the $\nu(CO)$ of the metal carbonyl group, which appears 21 cm^{-1} at lower wavenumber (in CH_2Cl_2) compared with the cyclopentadienyl analogue. This effect has already been discussed for the cationic complexes described in Chapter II, and is generally observed for all the related Cp and Cp^* complexes involved in this thesis.

Despite the strong probability, on the basis of the foregoing evidence (and the method of synthesis), that compound 2 is indeed a hydroxycarbonyl complex, the formate complex $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(OCHO)$ 3 was prepared to demonstrate that we were not in fact dealing with the isomeric species. Though it is unlikely, the possibility did exist that the hydroxide addition step might be followed by a rearrangement of the COOH group to OCHO (though it is difficult to believe that the OCHO ligand would exhibit the observed amphoteric behaviour). In fact both species are completely different in their physical (color, m.p.) and chemical properties (formate complex 3 was recovered unreacted when treated with dilute HCl or NaOH in CH_2Cl_2 solution). However, they are (as expected) quite similar in their spectroscopic parameters. For example, in both groups the ^1H NMR resonance occurs at low field (δ 9.41 for COOH and 7.81 for OCHO, in acetone-d_6) but this resonance appears as a sharp singlet in the case of the formate complex; $\nu(CO)$ of the metal carbonyl in both compounds also occurs at similar wavenumbers ($\Delta\nu(CO) = 8\ cm^{-1}$ in CH_2Cl_2), therefore IR cannot easily be used to differentiate these complexes.

Much greater differences are observed in the electron-impact mass spectra of these isomeric complexes. Formate 3 exhibits (M^+) and the $(M-CO)^+$ fragment which were not observable above the background in the hydroxycarbonyl 2. However, both show a peak at m/z 486 (being more intense in 2) which corresponds to the cation of the hydride complex 4. The liberation of CO_2 was clearly observed from monitoring the mass 44 ion-current.

It has already been mentioned in this discussion that the hydroxycarbonyl complex 2 is soluble in excess of aqueous hydroxide to form a bright yellow solution that is considered to contain the carboxylate anion 5 (Eq.11). Corresponding metallo-carboxylate anions have been suggested to be formed in similar reactions of the hydroxycarbonyls CpRe(CO)(NO)(COOH),[95] CpRe(CO)(N_2Ar)(COOH)[33] and CpFe(PPh_3)(CO)(COOH)[109] with excess aqueous hydroxide. Only in the latter case was the anion isolated, but no details of its characterization or properties were given.

The presence of the carboxylate anion 5 is suggested by two experimental observations. (i) The formation of the yellow aqueous solution obtained by reaction of 1a with excess of OH^-, is reversed by the addition of aqueous acid, which regenerates first the insoluble hydroxycarbonyl 2 and then the parent dicarbonyl cation 1a in agreement with Eq.11. (ii) Reaction of 2 with MeLi in hexane yields a yellow precipitate which is soluble in water. Furthermore, the IR spectrum of this precipitate (in CH_2Cl_2) corresponds exactly with that observed when a CH_2Cl_2 solution of 1a is treated with excess of saturated aqueous LiOH.

Subsequently by using the reaction of 1a with LiOH, the lithium salt of the carboxylate anion 5 [Cp^*Re(CO)(p-$N_2C_6H_4$OMe)(COO)]Li was isolated and fully characterized. The sodium and potasium salts of $\underline{5}$ could not be isolated under these conditions, instead the hydride complex $\underline{4}$ was obtained (see below). No calcium salt could be obtained using an analogous procedure, as the reaction proceeded only as far as the hydroxycarbonyl $\underline{2}$. In contrast, the calcium salt of the cyclopentadienyl anion $[CpRe(CO)(N_2Ar)(COO)]_2Ca$ could be isolated and fully characterized.[93]

The IR spectrum of the lithium salt of $\underline{5}$ has a strong $\nu(CO)$ band at 1906 cm^{-1} in CH_2Cl_2 (compared with 1933 cm^{-1} for $\underline{2}$ and 1906 cm^{-1} for $\underline{4}$ in the same solvent) which is some 16 cm^{-1} lower than that of the corresponding cyclopentadienyl compound.

The pure lithium salt of $\underline{5}$ is soluble in water but slowly deprotonates water to generate the insoluble hydroxycarbonyl $\underline{2}$ (Eq.12).

$$[Cp^{*}Re(CO)(N_2Ar)(COO)]^{-} + H_2O \longrightarrow Cp^{*}Re(CO)(N_2Ar)(COOH) + OH^{-} \qquad \text{Eq.12.}$$

The reaction shown in Eq.12 does not occur in the cyclopentadienyl analogues $[Cp\ Re(CO)(N_2Ar)(COO)]^{-}$ (Li or Ca salts) indicating that the more electron-releasing Cp^{*} group significantly increases the basicity of the anion $\underline{5}$. Thus, the lithium salt of $\underline{5}$ in solution appears not to generate the hydride $\underline{4}$ under any of the mild conditions used.

On the other hand, a good yield of the pentamethylcyclopentadienyl hydride complex $\underline{4}$ was obtained by the addition of excess 5 M aqueous KOH or NaOH to a CH_2Cl_2 solution of $\underline{1a}$.

An alternative but less convenient method for the preparation of 4 is that from $NaBH_4$ and the acetonitrile complex $[Cp^*Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)]^+$. Replacement of the labile CH_3CN ligand by hydride occurs largely in preference to hydride attack at the aryldiazenido group. This is notably different from the parent dicarbonyl cation 1a in which carbonyl substitution normally does not occur, and borohydride reacts preferentially at the diazenido group to give the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ (see chapter V).

The foregoing discussion has demonstrated that it is possible to observe in solution and to isolate and characterize the dicarbonyl cation 1a, the hydroxycarbonyl 2 and the carboxylate anion 5. Although it is insoluble in water, the hydroxycarbonyl is very soluble in polar organic solvents, and we were curious to find out what evidence there might be for dissociation in these solvents. A purely organic carboxylic acid is well-known to be capable of weak dissociation as shown in Eq.13.

$$RCOOH \rightleftharpoons RCOO^- + H^+ \qquad \text{Eq.13.}$$

In the case of the hydroxycarbonyl complex 2 this would require dissociation to the carboxylate anion 5 according to Eq.14.

$$\underset{\mathbf{2}}{Cp^*Re(CO)(N_2Ar)(COOH)} \rightleftharpoons \underset{\mathbf{5}}{[Cp^*Re(CO)(N_2Ar)(COO)]^-} + H^+ \qquad \text{Eq.14.}$$

An alternative mode of dissociation of complex 2 is shown in Eq.15.

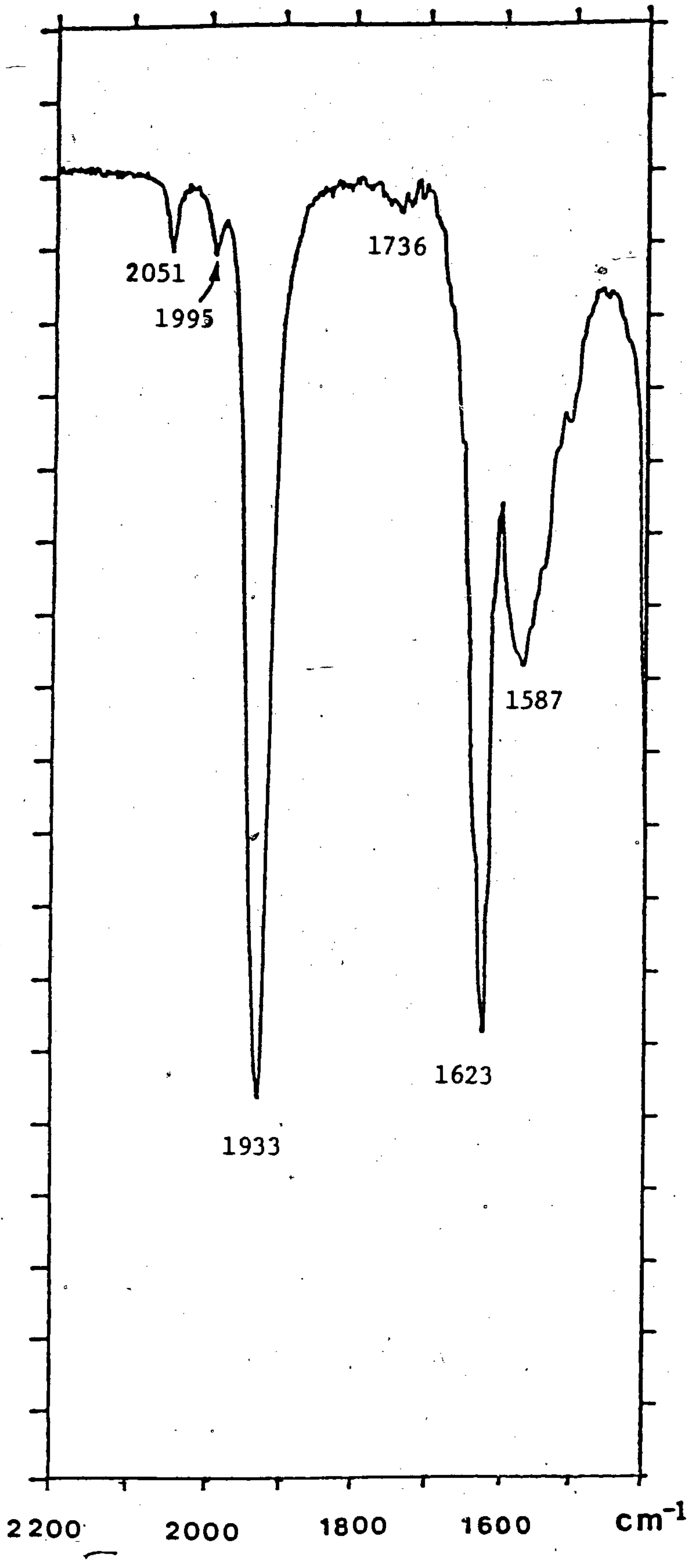
$$\underset{\underline{2}}{Cp^*Re(CO)(N_2Ar)(COOH)} \rightleftharpoons \underset{\underline{1a}}{[Cp^*Re(CO)_2(N_2Ar)]^+} + OH^- \qquad \text{Eq.15.}$$

Eq.15 is simply the reverse of the method of synthesis from the dicarbonyl cation 1a.

In CH_2Cl_2 solution, the hydroxycarbonyl 2 shows the same amphoteric behaviour observed in water (Eq.11). Bubbling HCl produces the IR spectrum typical of cation 1a, whereas stirring with solid LiOH slowly produces the IR spectrum of the anion 5. Thus, dissociation of the hydroxycarbonyl group according to either Eqs.14 or 15 can be driven by adding H^+ or OH^- in CH_2Cl_2.

A close examination of the IR spectrum of a freshly prepared solution of the pure hydroxycarbonyl complex 2 in CH_2Cl_2 reveals weak absorptions present at positions typical of the ν(CO) and ν(NN) absorptions of the dicarbonyl cation 1a, (see Fig.7). The presence of the cation was also observed in the IR spectrum of 2 in acetonitrile and nitromethane. Compound 2 is also soluble in benzene and THF, and in these solvents it appears to be undissociated. Interestingly, the IR spectrum of 2 in methanol shows no evidence of ionization (i.e. absorptions for 1a); instead a single compound with ν(CO) at 1937 cm^{-1} and ν(NN) at 1632 cm^{-1} (in MeOH) was observed. Evaporation of MeOH gave a yellow residue which was soluble in hexane (note that the

Fig.7. IR spectrum of $Cp^{*}Re(CO)(\underline{p}\text{-}N_2C_6H_4OMe)(COOH)$ __2__ in CH_2Cl_2 solution. Absorptions at 2051 and 1995 cm^{-1} $\nu(CO)$ and 1736 cm^{-1} $\nu(NN)$ correspond to cationic complex __1a__.


2051
1995
1933
1736
1623
1587
2200
2000
1800
1600
cm^{-1}

hydroxycarbonyl 2 is insoluble in hexane). Subsequently, the residue was identified as the methoxycarbonyl complex $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(COOMe)$, by comparison with an authentic sample. Thus, reaction of 2 with methanol to form the methoxycarbonyl complex probably proceeds by initial dissociation of OH^- which abstracts the alcoholic proton generating "in situ" MeO^- which then attacks the cationic dicarbonyl and leads to the observed product (see Eq.16).

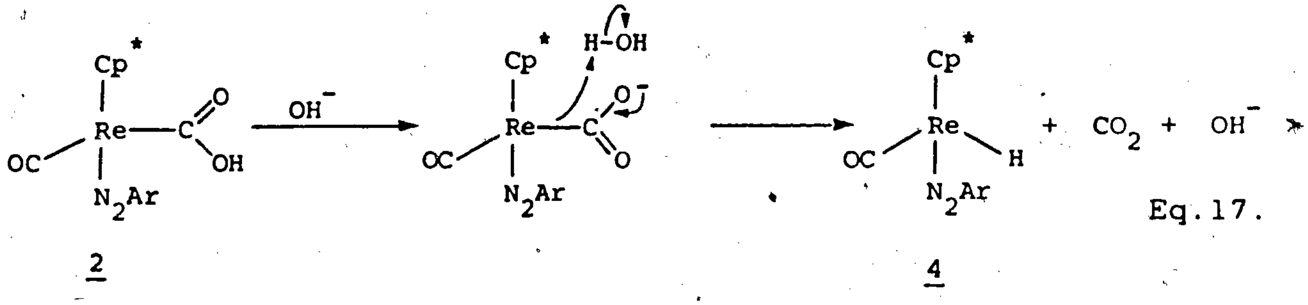
$$\begin{tikzcd}
Cp^*Re(CO)(N_2Ar)(COOH) \arrow[r, shift left] & {[Cp^*Re(CO)_2(N_2Ar)]^+ + OH^-} \arrow[l, shift left] \arrow[d, "MeOH"] \\
\underline{2} & Cp^*Re(CO)(N_2Ar)(COOMe) + H_2O
\end{tikzcd}$$

Eq.16.

The observation above was confirmed by observing the immediate formation of the methoxycarbonyl upon dissolving 1a in methanol in the presence of OH^-. The reaction occurs equally well using NEt_3 as a base.

Finally, another important aspect involving the hydroxycarbonyl complex 2 is its decarboxylation. It has already been discussed that the solutions of 2 do not decarboxylate and that no hydride 4 is observed when base is excluded, but that 2 gives the hydride complex 4 in good yield when its CH_2Cl_2 solution is treated with excess of aqueous NaOH or KOH. These results suggest that the actual species undergoing facile decarboxylation in organic solvents under the basic conditions employed is the carboxylate anion 5 as its sodium or potassium salt (note that the lithium salt does not give the hydride 4).

Based on these results, and in agreement with Sweet and Graham,[95] the schematic mechanism for the decarboxylation shown in Eq.17 seems to be plausible.



Eq.17.

The results using CH_2Cl_2 as a solvent for Cp and Cp* carboxylate anions indicate that the tendency of these species to decarboxylate is decreased with small or more highly charged cations (Li^+, Ca^{2+}), presumably because these are more effective at removing charge from the carboxylate group by close ion-pair association with it.

3.3. Carbamoyl, Alkoxycarbonyl and Isocyanate Derivatives of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$

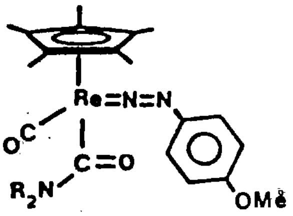
3.3.1. Introduction

Carbamoyl and alkoxycarbonyl complexes of transition metals have received considerable attention in recent years owing to their recognition as intermediates in several important catalytic processes such as the carbonylation of amines or alcohols.[116] These compounds have usually been synthesized by the reaction of a variety of metal carbonyl complexes (especially cationic complexes) with primary and secondary amines and alkoxides.[117]

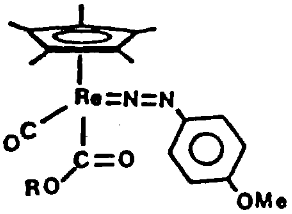
Angelici[103] and Darensbourg[118] have suggested that the tendency of a CO ligand to react with amines, or with other nucleophiles, depends upon the electron density on the carbon atom, which is related to the C-O bond force constant. In terms of ν(CO), it has been observed that the carbonyl complexes with ν(CO) below 2000 cm^{-1} do not yield carbamoyl or alkoxycarbonyl complexes.

A large number of these types of complexes has been prepared. Some recent examples are: (i) trans-$[IrCl(COOMe)(dppe)_2]^+$,[119] (ii) $Pt(C_6H_9)(Ph_2PCH_2CH_2CH_2PPh_2)(CONR_2)$,[112] (iii) $MCl(pnp)(COX)$[120] (M= Ni, Pt and Pd; X= OMe and NR_2; pnp= 2,6-bis (diphenylphosphinomethyl)pyridine), (iv) $[IrH(COOMe)(PMe_3)_4]^+$ [121] and (v) $CpFe(CO)(PMe_2Ph)(CONHMe)$.[122]

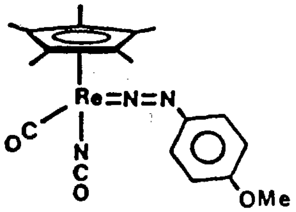
In this section the synthesis and characterization of the carbamoyl complexes $Cp^*Re(CO)(\textit{p}-N_2C_6H_4OMe)(CONR_2)$ 6 (R_2= H_2, 6a; R_2= HMe, 6b; and R_2= Me_2, 6c), the alkoxycarbonyl complexes $Cp^*Re(CO)(\textit{p}-N_2C_6H_4OMe)(COOR)$ 7 (R= Me, 7a and R= Pr^i, 7b) and the isocyanate complex $Cp^*Re(CO)(NCO)(\textit{p}-N_2C_6H_4OMe)$ 8 are discussed. Some of this work was carried out in parallel with their cyclopentadienyl rhenium aryldiazenido analogues and has already been published.[123]



6



7



8

3.3.2. Synthesis and Characterization

(a) Carbamoyl Complexes $Cp^*Re(CO)(\textit{p}-N_2C_6H_4OMe)(CONR_2)$ 6

These complexes were prepared by reaction of the dicarbonyl cation 1a with liquid ammonia (6a, R_2= H_2) or with neat amines $MeNH_2$ (6b, R_2= HMe) and Me_2NH (6c, R_2= Me_2). No reaction occurred with pure tertiary amines such as Me_3N or Et_3N. In all the cases the products were obtained as yellow solids in good yields. They have the expected analytical, spectroscopic and chemical properties and are analogous to the known nitrosyls $CpM(CO)(NO)(CONR_2)$ M= Re and Mn.[124] These compounds are stable at room temperature under nitrogen but easily hydrate under normal atmosphere, especially 6a which is extremely hygroscopic. They dissolve in the majority of organic solvents such as hexane, benzene and THF but in acetone solution they slowly decompose to produce the dinitrogen complex $Cp^*Re(CO)_2(N_2)$. The IR spectra in THF show the expected single ν(CO) absorption at about 1925 cm^{-1} and ν(NN) at 1620, but replacing the THF by CH_2Cl_2 produces a spectrum with weak additional ν(CO) and ν(NN) absorptions in the positions associated with the cation <u>1a</u>. This sequence is reversible.

The ν(NH) in <u>6a</u> and <u>6b</u> appears as a weak broad absorption in the 3400-3200 cm^{-1} region. In addition, one or two strong and broad absorptions in the 1590-1560 cm^{-1} region are also observed. They probably originate from a combination of ν(C=O) and ν(C=N) of the carbamoyl ligands.

The ^1H NMR spectrum of the N-methylcarbamoyl complex <u>6b</u> shows the NH resonance at δ 5.35 in $CDCl_3$, and the methyl resonance remains unchanged as a sharp doublet (J_{HNCH}= 4.8 Hz) over the temperature range -40 to +50°C. These chemical shifts and coupling constants agree well with previously reported values for the N-methylcarbamoyls $CpW(CO)_3(CONHMe)$[125] [δ 6.0, J= 5.0 Hz] and $Re(CO)_5(CONHMe)$[126] [δ 5.45, J= 5.4 Hz]. Notably, the room temperature ^1H NMR spectrum in $CDCl_3$ of the N,N-dimethylcarbamoyl <u>6c</u> shows a single broad resonance for the methyl groups but on cooling to 0°C this splits into two equal intensity singlets from magnetically nonequivalent methyls.

In the three species, electron-impact mass spectra showed neither molecular ions nor $(M-CO)^+$ or $(M-CONR_2)^+$ fragments.

Instead, the mass spectrum of the dinitrogen complex $Cp^{*}Re(CO)_2(N_2)$ was observed. Using FAB, the mass spectrum of <u>6a</u> gave the typical spectrum of the dicarbonyl cation <u>1a</u>, i.e., the molecular ion m/z= 513 (based on ^{187}Re) which corresponds to the fragment $(M-NH_2)^+$.

(b) Alkoxycarbonyl complexes $Cp^{*}Re(CO)(\underline{p}-N_2C_6H_4OMe)(COOR)$ <u>7</u>

The dicarbonyl cation <u>1a</u> reacts with one equivalent of NaOMe in methanol to produce the neutral methoxycarbonyl complex <u>7a</u> as a yellow solid, analytically and spectroscopically pure. The IR spectrum in hexane exhibits the expected single terminal $\nu(CO)$ band at 1944 cm^{-1} and two more bands at 1643 and 1624 cm^{-1} which contain the $\nu(NN)$ and $\nu(C{=}O)$ vibrational modes. No attempts were made to assign unambiguously these absorptions. The ^1H NMR data are as expected , with the resonance from the COOMe group appearing at δ 3.65 ($CDCl_3$).

The methoxycarbonyl complex <u>7a</u> was also isolated in near quantitative yield from the reaction of cation <u>1a</u> with tris(isopropoxy)borohydride in methanol. This reaction was carried out initially with the intention of delivering a hydride. More interestingly instead, in the reaction of <u>1a</u> with this borohydride in THF an isopropoxy group was delivered to produce the isopropoxycarbonyl complex <u>7b</u>. This complex was characterized by spectroscopy. In general it shows similar spectroscopic parameters to those observed for the methoxycarbonyl <u>7a</u>, and its diastereotopic methyl groups were easily recognized in the ^1H

NMR spectrum.

Like the carbamoyl complexes, these alkoxycarbonyl compounds gave the electron-impact mass spectrum of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ even when a low voltage (12 eV) was used, whereas the (FAB) mass spectrum of 7a showed the molecular peak at m/z= 513 which corresponded to $(M-OMe)^+$ (i.e., to the dicarbonyl 1a).

(c) Isocyanate Complex $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(NCO)$ 8

Complex 8 was synthesized from the dicarbonyl cation 1a using either KNCO, NaN_3 or N_2H_4. In either case, the isocyanate complex 8 was obtained in excellent yield. This compound is a red, low melting point solid which is soluble in hexane. Its IR spectrum shows the typical ν(NCO) at 2240 cm^{-1} (in CH_2Cl_2), in addition to ν(CO) at 1926 and ν(NN) at 1626 cm^{-1}. The ^1H NMR spectrum shows the expected resonances for the Cp^* and aryl groups, and the electron-impact mass spectrum exhibits M^+ at m/z= 527 (based on ^{187}Re), and $(M-CO)^+$ at m/z= 499 as the base peak.

3.3.3. Discussion

The production of the monocarbonyl carbamoyl 6 and alkoxycarbonyl 7 complexes from the dicarbonyl cation $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ 1a evidently results from straightforward attack of the nucleophile on the relatively electrophilic carbonyl carbon atoms in this cation. These results are those expected according to Angelici's predictions[103] that carbonyl containing compounds with $\nu(CO) >$ 2000 cm^{-1} should yield these types of complexes. It is important to mention that possible products which were not observed in these reactions include the monocarbonyl amides or alkoxides $Cp^{*}ReX(CO)(\underline{p}\text{-}N_2C_6H_4OMe)$ (where X= NR_2 or OR) resulting from CO substitution. These could have arisen either from direct displacement of a CO group in <u>1a</u> by the alkoxide or amine nucleophile or from a subsequent rearrangement of the carbamoyl or alkoxycarbonyl ligands.

The carbamoyl and alkoxycarbonyl complexes react in the expected manner with HCl or HBF_4 to regenerate the parent dicarbonyl cation according to Eq. 18.

$$Cp^{*}Re(CO)(N_2Ar)(COR) + H^{+} \longrightarrow [Cp^{*}Re(CO)_2(N_2Ar)]^{+} + HR \text{ (or } H_2R^{+}) \qquad \text{Eq.18.}$$

$$Ar = \underline{p}\text{-}C_6H_4OMe;\ R = OMe \text{ or } NR'_2$$

In a similar manner to the hydroxycarbonyl <u>2</u>, the IR spectra of the carbamoyl complexes <u>6</u> suggest that in CH_2Cl_2 solution they partly undergo autodissociation as shown in Eq. 19.

$$Cp^{*}Re(CO)(N_2Ar)(CONR_2) \rightleftharpoons [Cp^{*}Re(CO)_2(N_2Ar)]^{+} + NR_2^{-} \qquad \text{Eq.19.}$$

However, this phenomenon was not observed in the alkoxycarbonyl complexes 7 in CH_2Cl_2 or in even more polar solvents such as methanol and acetonitrile. At this point it is worth noting that the alkoxycarbonyls are stable in the above solvents and that no formation of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ was observed in any case.

The manner in which the carbamoyl complexes 6 are able to generate the dinitrogen complex when they decompose is presently unknown but apparently the autodissociation of these species in CH_2Cl_2 (and also the hydroxycarbonyl complex 2) can be related to the production of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$. This can be understood by a nucleophilic attack of the amide ion NR_2^- (or OH^-) at the ipso carbon of the aromatic ring in the aryldiazenido ligand. Obviously more information is necessary to confirm this assumption.

Finally, the isolation of the isocyanate complex 8 has allowed it to be fully characterized. Any of the three reagents (NCO^-, N_3^- and N_2H_4) can be used to synthesize this compound in excellent yields by reaction with the dicarbonyl cation 1a. It is presumed that the mechanisms of these reactions are analogous to those reported[127] for the very similar reactions of $[CpFe(CO)_3]^+$ with NCO^-, N_3^- and N_2H_4 leading to $CpFe(CO)_2(NCO)$. In particular for N_3^- and N_2H_4, at least, they likely involve initial attack of the nucleophile at the coordinated carbonyl carbon atom. No intermediates were observed in these reactions when they were followed by IR.

3.4. Experimental Section

General synthetic procedures, purification of solvents and spectroscopic measurements, as described in Chapter II. GC analysis were carried out on an OV-1 capillary column using a Hewlett-Packard 5880A gas chromatograph. GC-MS were obtained by using a Hewlett-Packard 5985 mass spectrometer. Gaseous NH_3, NH_2Me and $NHMe_2$ (Matheson), and $K[HB(OCHMe_2)_3]$ (Aldrich, 1 M in THF) were used as purchased.

Preparation of $Cp^*Re(CO)(COOH)(p\text{-}N_2C_6H_4OMe)$ (2)

A suspension of 1a (50 mg, 0.083 mmol) in water (15 mL), in which it is slightly soluble, was vigorously stirred while aqueous 0.10 M NaOH (0.83 mL, 0.083 mmol) was added very slowly. The golden yellow solid which precipitated quantitatively was washed twice with cold water and then dried under vacuum. It decomposed at 90-95°C without melting. IR (CH_2Cl_2): 1933 vs, ν(CO), 1623 s, 1587 m br, cm^{-1} ν(NN) + ν(COOH). ^1H NMR (acetone-d_6): δ 2.11 s (15H, Cp* [illegible] 3.82 s (3H, OMe), 6.96 d (2H, C_6H_4), 7.49 d (2H, C_6H_4), 9.41 br s (1H, COOH). MS (FAB, xenon, sulfolane): m/z 513 ($M-OH^+$), 485 v. weak $(M-COOH)^+$ or $(M-OH-CO)^+$. MS (E.I., 70 eV): 486 $(M-CO_2)^+$. Anal. Calcd. for 2: C, 43.10; H, 4.34; N, 5.29. Found: C, 43.00; H, 4.10; N, 5.09.

Analysis of Decomposition Products of Complex 2 in C_6D_6

A sample of the hydroxycarbonyl complex (2) in C_6D_6 decomposed completely during an overnight NMR experiment at room temperature. The IR and capillary GC-MS (OV-1 column) of the solution showed the presence of $Cp^*Re(CO)_3$, $Cp^*Re(CO)_2(N_2)$ (M^+, 406 (49%)), anisole (M^+, 108 (23%)), $C_6D_5C_6H_4OMe$ (M^+, 189 (19%)), and an unassigned peak of M^+ 134 (10%).

Preparation of $Cp^*Re(CO)(\underline{p}\text{-}N_2C_6H_4OMe)(OCHO)$ (3)

The cationic acetonitrile complex $[Cp^*Re(CO)(NCMe)(\underline{p}\text{-}N_2C_6H_4OMe)]^+$ (70 mg, 0.11 mmol) in acetone (25 mL) was stirred with finely ground solid sodium formate (ca. 200 mg, 2.94 mmol) then water (10 mL) was added and the reaction followed by IR. All of the acetonitrile complex had reacted in 1 h. Solvent was pumped off and the residual water was pipetted off the red-orange product which was then dissolved in ether and filtered through celite. Addition of hexane precipitated a red-orange solid m.p. 65-67°C in 85% yield. IR (acetone): 1931 vs, ν(CO); 1645 m, 1620 s cm^{-1}; (ether) 1941 vs, 1648 m, 1622 s cm^{-1}; (CH_2Cl_2) 1925 vs, 1642 m, 1624 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.04 s (15H, Cp^*), 3.81 s (3H, OMe), 6.92 d (2H, C_6H_4), 7.29 d (2H, C_6H_4), 8.03 s (1H, OCHO); (C_6D_6): δ 1.73 s, 3.22 s, 6.74 d, 7.63 d, 8.37 s. MS (E.I. 15 eV, 75°C): m/z 530 (M^+), 502 $(M-CO)^+$ in 1:5:3 ratio. MS (FAB, xenon, sulfolane): m/z 513 $(M-OH)^+$, 502 $(M-CO)^+$, 485 $(M-HCO_2)^+$, 429 $(M-N_2-CO-HCO_2)^+$. Anal. Calcd. for 3: C, 43.10; H, 4.34; N, 5.29. Found: C, 43.53; H4.40; N, 5.34.

Preparation of $Cp^*ReH(CO)(\underline{p}\text{-}N_2C_6H_4OMe)$ (4)

Method 1. Compound 1a (50 mg, 0.083 mmol) was dissolved in

CH_2Cl_2 (15 mL) and an excess (ca. 2 mL) of aqueous 6 M NaOH was added while vigorously stirring. The CH_2Cl_2 layer became yellow-orange. Solvent was removed by pumping at room temperature. The residue was dissolved in THF (it was insoluble in hexane) and filtered through celite to give an orange solution, having ν(CO) 1910 vs and ν(NN) 1615 s cm^{-1}. The THF was pumped off and the oily residue was now easily extracted into hexane to give an orange solution having ν(CO) 1925 vs and ν(NN) 1619 s cm^{-1}. The hexane solution was chromatographed on neutral alumina. Elution with benzene gave a yellow solution. Benzene was pumped off and the yellow residue was dissolved in pentane from which **4** precipitated as a yellow solid during 6 h at −78°C in 80% yield. It decomposed at 95-98°C. IR (hexane): 1925 vs, ν(CO), 1619 s, cm^{-1} ν(NN). ^1H NMR (C_6D_6): δ −5.88 s (1H, ReH), 1.90 s (15H, Cp*), 3.27 s (3H, OMe), 6.78 d (2H, C_6H_4), 7.61 d (2H, C_6H_4). MS (EI, 16 eV): m/z 486 (M^+), 458 $(M-CO)^+$.

Method 2. The cationic acetonitrile complex $[Cp^*Re(CO)(NCMe)(\underline{p}\text{-}N_2C_6H_4OMe)]^+$ (50 mg, 0.08 mmol) was dissolved in acetone (10 mL) and stirred with an excess of solid $NaBH_4$ (ca. 5 mg, 0.13 mmol) at room temperature. The solution rapidly changed its color from orange to yellow-orange. Evaporation of acetone under vacuum and subsequent extraction with hexane gave only **4** (by IR). Repurification as above yielded 28 mg (70.5%) of the product.

Preparation of $Li[Cp^*Re(CO)(\underline{p}\text{-}N_2C_6H_4OMe)(CO_2)]$ (Li-**5**)

Method 1. The hydroxycarbonyl **2** (100 mg, 0.18 mmol) was suspended in hexane (25 mL) and excess (0.5 mL) of MeLi (1.6 M in diethyl ether) was added under N_2 with vigorous stirring. After 30 min the solvent was removed by pipet and the yellow solid washed twice with 5 mL of hexane. It was redissolved in CH_2Cl_2, filtered under N_2 and reprecipitated by adding hexane as a yellow solid in near quantitative yield. IR (CH_2Cl_2, cm^{-1}): 1928 vs, ν(CO), 1614 s, ν(NN); (THF) 1907 vs, 1612 s. ^1H NMR (D_2O): δ 2.03 (15H, Cp*), 3.81 s (3H, OMe), 7.02 d (2H, C_6H_4), 7.28 d (2H, C_6H_4). Anal. Calcd. for Li-5 (CH_2Cl_2): C, 38.77; H, 3.88; N, 4.52. Found: C, 38.32; H, 4.18; N, 4.76. CH_2Cl_2 was observed to be present by MS.

Method 2. The dicarbonyl cation 1a was dissolved in CH_2Cl_2 and stirred with an excess of saturated aqueous LiOH. Within a few minutes the CH_2Cl_2 layer became orange-yellow. It was separated from the colorless aqueous layer by pipet and the solvent removed to give the product as a yellow solid (soluble in water and insoluble in hexane) in quantitative yield.

Treatment of 1a with an excess NaOD in D_2O produced a yellow solution of the carboxylate anion with ^1H NMR parameters δ 2.00 (15H, Cp*), 3.79 (3H, OMe), 7.00 d (2H, C_6H_4), 7.26 d (2H, C_6H_4) virtually identical with that of the lithium salt.

Preparation of $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(CONH_2)$ (6a)

Solid 1a (50 mg, 0.083 mmol) was added to 5 mL of liquid NH_3 at -50°C. A fast reaction ensued, and the yellow solid that precipitated was washed twice with liquid NH_3 to remove NH_4BF_4.

Yield: 43 mg (98%); m.p. 78–80°C (with decomposition). The compound is stable at room temperature under nitrogen but is extremely hygroscopic, and it was difficult to entirely prevent this when performing microanalysis. The best analysis corresponded to the presence of approximately one H_2O per mole. IR (CH_2Cl_2): 1929 s, ν(CO); 1624 s, ν(NN); 1584 m, ν($CONH_2$) cm^{-1}, weak absorptions for 1a at 2053, 1996 and 1738 cm^{-1} are also visible in this solvent. ^1H NMR ($CDCl_3$): δ 2.10 s (15H, Cp^*), 3.82 s (3H, OMe), 6.93 d (2H, C_6H_4), 7.26 d (2H, C_6H_4); weak resonances from 1a were also observed, δ (NH) was unobserved. MS (FAB, xenon, sulfolane): m/z 513 $(M-NH_2)^+$. Anal. Calcd. for 6a·H_2O: C, 41.75; H, 4.76; N, 7.69. Found: C, 41.63; H, 4.95; N, 7.47. Addition of HCl transformed the IR and NMR entirely to that of the parent dicarbonyl cation 1a.

Preparation of $Cp^*Re(CO)(p-N_2C_6H_4OMe)(CONHMe)$ (6b)

A solution of $MeNH_2$ in CH_2Cl_2 was prepared by extracting aqueous $MeNH_2$ with CH_2Cl_2 and drying over Na_2SO_4. Addition of solid 1a (60 mg, 0.10 mmol) instantaneously resulted in reaction to give, after filtering to remove insoluble $[MeNH_3][BF_4]$ and pumping off solvent, an orange oil which solidified on further pumping to yield the product as a yellow-orange solid. Yield: 50 mg (92%). M.p. 57–59°C (with decomposition). IR (CH_2Cl_2): 1925 br, s ν(CO); 1621 s, ν(NN); 1568 br, m ν(CONHMe) cm^{-1}; weak absorptions from 1a were visible. ^1H NMR ($CDCl_3$): δ 2.09 s (15H, Cp^*), 2.84 d (3H, NMe), 3.82 s (3H, OMe), 5.35 br, s (1H, NH), 6.93 d

(2H, C_6H_4), 7.30 d (2H, C_6H_4). Anal. Calcd. for <u>6b</u>: C, 44.28; H, 4.80; N, 7.75. Found: C, 44.01; H, 5.01; N, 7.99.

Preparation of $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(CONMe_2)$ (<u>6c</u>)

Liquid Me_2NH was condensed at -50°C (5 mL), and solid <u>1a</u> (60 mg, 0.10 mmol) was added. The reaction mixture was stirred for 1 h and then the orange solution filtered under N_2 and pumped until an orange solid formed. The elemental analysis at this stage was correct for 1:1 mixture of <u>6c</u> and $[Me_2NH_2][BF_4]$. Anal. Calcd.: C, 39.94; H, 5.20; N, 8.10. Found: C, 39.68; H, 5.22; N, 8.00. The mixture was repeatedly extracted with ether and precipitated with pentane to give a yellow-orange solid that gave the expected IR and ^1H NMR spectra for <u>6c</u> but unaccountably low carbon analysis. IR (CH_2Cl_2): 1925 vs, $\nu(CO)$; 1621 s, $\nu(NN)$ cm^{-1}. ^1H NMR ($CDCl_3$, 40°C): δ 2.05 s (15H, Cp^*), 3.08 s, br (6H, NMe_2), 3.82 s (3H, OMe), 6.93 d (2H, C_6H_4), 7.35 d (2H, C_6H_4). At 0°C, the resonance was split into two peaks of similar intensity at δ 3.00 and 3.16.

Preparation of $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(COOMe)$ (<u>7a</u>)

<u>Method 1</u>. To a solution of <u>1a</u> (50 mg, 0.083 mmol) in methanol (10 mL) was added solid NaOMe (6 mg, 0.11 mmol), and the mixture was stirred at room temperature for 15 min. The color changed from red to yellow, and the IR spectrum of this solution showed the presence of the new methoxycarbonyl complex <u>7a</u>. The solvent was removed under vacuum, CH_2Cl_2 was added, and the

solution was filtered through Celite. Addition of hexane gave the product as a golden-yellow solid (43 mg) in 95% yield. M.p.: slow decomposition above 105°C. IR (hexane): 1944 vs, ν(CO); 1643 m, 1624 s, ν(NN) and ν(COOMe), cm^{-1}; THF 1930 vs, 1638 s, 1620 s, cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 s (15H, Cp*), 3.65 s (3H, COOMe), 3.81 s (3H, OMe), 6.91 d (2H, C_6H_4), 7.44 d (2H, C_6H_4). MS (FAB, xenon, sulfolane): m/z 513 $(M-OMe)^+$. Anal. Calcd. for 7a: C, 44.20; H, 4.60; N, 5.15. Found: C, 43.91; H, 4.64; N, 5.25.

Method 2. Complex 1a (50 mg, 0.083 mmol) in methanol (10 mL) at -78°C was treated with $K[HB(OCHMe_2)_3]$ (0.10 mL, 0.10 mmol) by syringe. IR monitoring showed the reaction to be complete in 15 min. The solvent was removed at room temperature under vacuum. The orange oily residue was extracted with hexane-THF (9:1) and filtered through celite. Precipitation of a golden-yellow solid occurred when the solution was concentrated under vacuum and was completed by cooling to -78°C. Yield: 44 mg (98%) of 7a characterized as above.

Method 3. To a solution of 1a (20 mg, 0.03 mmol) in methanol (5 mL), 0.5 mL of 0.1 M aqueous NaOH (0.05 mmol) was added or NEt_3 (0.1 mL). Within 10 min the color changed from red to yellow. Evaporation of the solvent and extraction with hexane gave the methoxycarbonyl complex 7a in quantitative yield. It was characterized as above.

Preparation of $Cp^*Re(CO)(p\text{-}N_2C_6H_4OMe)(COOCHMe_2)$ (7b)

An analogous synthesis to that described for the preparation of <u>7a</u>, <u>method 2</u> conducted in THF yielded instead the isopropoxycarbonyl complex <u>7b</u> as a yellow solid. M.p. 107-109°C (with decomposition). IR (hexane): 1944 vs, ν(CO); 1640 m, 1619 s, ν(NN) + ν($COOCHMe_2$), cm^{-1}; (THF): 1930 vs, 1618 br s, cm^{-1}. ^1H NMR (C_6D_6): δ 1.29 d (3H, $CHMe_2$), 1.36 d (3H, $CHMe_2$), 1.85 s (15H, Cp*), 3.24 s (3H, OMe), 5.52 (app.septet, 1H, $CHMe_2$), 6.83 d (2H, C_6H_4), 7.92 d (2H, C_6H_4).

Preparation of $Cp^*Re(CO)(\underline{p}-N_2C_6H_4OMe)(NCO)$ (<u>8</u>)

<u>Method 1</u>. The cationic complex <u>1a</u> (40 mg, 0.06 mmol) was stirred in acetone with excess of KNCO (10 mg, 0.12 mmol) for 30 h. Acetone was pumped off and the residue dissolved in CH_2Cl_2 and filtered through Celite. The filtered red solution was chromatographed on silica gel, and the product eluted with CH_2Cl_2-hexane (1:1) as an orange fraction. Removal of solvent gave a red solid (40 mg) in 90% yield. M.p.: 40°C. IR (CH_2Cl_2): 2240 vs, ν(CO); 1926 vs, ν(CO); 1626 s, ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 s (15H, Cp*), 3.83 s (3H, OMe), 6.94 d (2H, C_6H_4), 7.25 d (2H, C_6H_4). MS (EI): m/z 527 (M^+), 499 $(M-CO)^+$. Anal. Calcd. for <u>8</u>: C, 43.34; H, 4.18; N, 7.98. Found: C, 43.27; H, 4.05; N, 7.80.

<u>Method 2</u>. The cationic complex <u>1a</u> (50 mg, 0.083 mmol) in acetone (15 mL) was stirred with excess solid NaN_3 (15 mg, 0.23 mmol) for 1 h. The color changed quickly from maroon to brown. Acetone was removed by pumping and the residue dissolved in CH_2Cl_2. The filtered solution was chromatographed as above to yield the product as a red solid in 90% yield (40 mg).

Method 3. Excess of N_2H_4 (ca. 0.5 mL) was added to a solution of **1a** (50 mg, 0.083 mmol) in CH_2Cl_2 (ca. 8 mL) at -78°C. The color changed from maroon to yellow-orange. The solution was slowly warmed to room temperature and the product separated by chromatography as above in 95% yield (42 mg).

CHAPTER IV

Substitution of CO in [Cp*Re(CO)$_2$(p-$N_2C_6H_4$OMe)]$^+$ by Two-electron Donor Ligands

4.1. Introduction

In the preceding chapter the transformation of the carbon monoxide ligand in the cationic dicarbonyl complex 1a was demonstrated. As an extension of the remarkable reactivity of this cationic complex 1a toward nucleophiles, reactions leading to the substitution of one of the CO ligands will be considered in this chapter.

Traditionally, substitution reactions of metal carbonyl complexes have been carried out under thermal and/or photochemical conditions. In addition, a number of methods have been devised that facilitate certain metal carbonyl substitution reactions. These methods have been recently reviewed by Alberts and Coville.[128]

The pentamethylcyclopentadienyldicarbonylrhenium aryldiazenido complex 1a, undergoes substitution of one carbonyl group by other two-electron donor ligands. In reactions of 1a with halide ions (X^-), the neutral monocarbonylhalide complexes Cp*ReX(CO)(p-$N_2C_6H_4$OMe) 9 (9a X= Cl, 9b X= Br and 9c X= I) were obtained. In reactions with iodosobenzene (PhIO) in the presence of nitriles (NCR) the monocarbonylnitrile complexes [Cp*Re(CO)(NCR)(p-$N_2C_6H_4$OMe)]$^+$ 11, (11a R= Me, 11b R= n-Pr and 11c R= i-Pr) were produced. The synthesis, characterization and some mechanistic aspects related to the above compounds will be discussed. Also in this chapter are included reactions of the monocarbonylchloro complex 9a with arylcopper reagents leading to the arylmonocarbonyl aryldiazenido complexes $Cp^*Re(Ar)(CO)(p\text{-}N_2C_6H_4OMe)$ 10 (10a Ar= phenyl and 10b Ar= tolyl), and reactions of the acetonitrile complex 11a with some phosphorus-containing ligands leading to the new cationic monocarbonyl phosphine complexes $[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)]^+$ 12 (12a R= Me, 12b R= n-Bu, 12c R= Cy (Cy= cyclohexyl), 12d R= Ph and 12e R= OMe).

4.2. Synthesis and Characterization

(a) Monocarbonylhalide Complexes 9

These compounds were first observed as products of a remarkable solid-state reaction between the dicarbonyl cation complex 1a and finely ground KCl, KBr or KI. These reactions occur very slowly at room temperature, but they are accelerated at 95°C. In each instance, the new monocarbonylhalide complex 9 was produced. In the reaction with solid KBr and KI, some of the dicarbonyldihalide complexes cis-$Cp^*Re(CO)_2X_2$ (X= Br and I) were also formed but, in spite of this, it is possible to isolate the products using this synthetic route, although the overall yield is poor (18-30%). Subsequently, we found the reaction in THF-water to be a convenient solution procedure for the synthesis and isolation of these complexes, i.e., using this method the yield was considerably increased (over 80%). In the case of KI, the dicarbonyldiiodide complex cis-$Cp^{*}Re(CO)_2I_2$ was also produced but neither the dichloride nor the dibromide analogues were observed using KCl or KBr. Interestingly, in the three cases a small amount of the trioxo complex $Cp^{*}ReO_3$ was formed but no IR evidence for the formation of the dinitrogen complex $Cp^{*}Re(CO)_2(N_2)$ was observed.

The dichloride (<u>9a</u>) and bromide (<u>9b</u>) compounds could also be prepared by reaction of the hydride complex <u>4</u> with $CHCl_3$ or $CHBr_3$ respectively (see Chapter III, section 3.2.). In addition, compound <u>9a</u> was also obtained in good yield by reaction of the acetonitrile complex <u>11a</u> with KCl in acetone.

In all cases the monocarbonylhalide complexes <u>9</u> were obtained as red solids and were fully characterized by analysis and spectroscopy. They are air-stable as solids or in solution in organic solvents. In the IR, ν(CO) and ν(NN) occur at ~ 1925 and 1630 cm^{-1} respectively. The electron-impact mass spectra show them to be mononuclear in the vapor phase and to fragment by the loss of a single CO group and the aryldiazenido ligand at an early stage.

(b) Arylmonocarbonyl Complexes <u>10</u>

These complexes were synthesized in good yield following the procedure used by Sweet and Graham in the synthesis of CpRe(Ar)(CO)(NO).[129] This involves the reaction of <u>9a</u> with an excess of arylcopper (prepared from the Grignard reagent and CuBr) in dry THF. In both cases (<u>10a</u> and <u>10b</u>) the compounds were obtained as orange-red solids analytically and spectroscopically pure. They showed in the IR spectra a very strong ν(CO) absorption near 1922 cm^{-1} in hexane and ν(NN) occured at about 1620 cm^{-1}. The electron-impact mass spectra at 16 eV exhibited peaks for the molecular ion M^{+} and for the loss of CO, i.e., (M-CO)$^{+}$. As expected, the ^{1}H NMR spectra showed clearly the presence of the coordinated aryl groups. In the case of the phenyl complex 10a, the aromatic region at 400 MHz showed a typical AA'BB' pattern for the protons contained in the p-methoxyphenyldiazenido group, i.e., two doublets at δ 6.88 and 7.24 with J= 8.9 Hz. Also in this region a triplet was observed at δ 6.99, J= 7.27 Hz, which integrated for 1H and is therefore assigned to the phenyl ligand para proton, a triplet at δ 7.09, J= 7.27 Hz (integral 2H), assigned to phenyl meta protons, and a low field doublet at δ 7.55, J= 6.90 Hz (integral 2H) assigned to the ortho protons of the phenyl ligand. On the other hand the tolyl complex 10b showed AA'BB' resonances for two sets of p-substituted aryl groups. The two doublets at δ 6.88 and 7.24 with J= 8.8 Hz were assigned to the protons of the aryl group of the diazenido ligand (by comparison with 10a), and the remaining two doublets at δ 6.93 and 7.43, J= 7.60 Hz are due to the protons of the tolyl ligand. The high field doublet was assigned to the protons ortho to the rhenium. The assignment of the lower field resonance to protons ortho to a transition metal has been established previously in CpRe(CO)(NO)(aryl) by Sweet and Graham[129,130] using NOE and decoupling experiments.

(c) Monocarbonylnitrile Complexes **11**

These complexes were synthesized in a similar manner to [Cp Re(CO)(NCMe)(NO)]$^+$ (Cp= Cp and Cp*) reported by Gladysz and coworkers.[96,111] This procedure involves the direct reaction of the dicarbonyl cation **1a** with iodosobenzene (PhIO) using the respective nitrile as a solvent; no substitution was observed in a similar reaction using Me_3NO instead of PhIO. In the three cases, the nitrile complexes were obtained as red-orange solids in good to excellent yield. As ionic species, they are insoluble in non-polar organic solvents such as hexane, benzene and ether but they dissolve completely in CH_2Cl_2 and acetone. In the IR spectra (CH_2Cl_2), ν(CO) appeared as a broad and very strong absorption near 1960 cm^{-1}, and a broad and strong absorption near 1660 cm^{-1} was observed for ν(NN). The latter assignment was confirmed by ^{15}N isotopic substitution at N_α of the diazenido ligand in the acetonitrile complex [Cp*Re(CO)(NCMe)(**p**-$^{15}NNC_6H_4OMe$)]$^+$ (**11a**-$^{15}N_\alpha$). A shift to lower wavenumber by 20 cm^{-1} was then observed. Notably, ν(C≡N) for the nitrile ligand, expected to occur strongly in the IR of η^1-bonded nitrile complexes near 2300 cm^{-1} in no instance could be observed, either in CH_2Cl_2 solution or Nujol emulsion.

In addition to the typical resonances for the Cp* and aryldiazenido groups, the presence of the nitrile ligands was clearly observed in the ^1H NMR spectra of these compounds. A singlet at δ 3.10 was observed for the acetonitrile in **11a**; a triplet, multiplet and triplet at δ 1.11, 1.76 and 3.46 for the n-butyronitrile in 11b and a doublet and broad multiplet at δ 2.19 and 3.60 respectively for the i-butyronitrile in 11c. In all the cases the FAB mass spectra showed the unfragmented cations as molecular ions M^+, and fragments corresponding to the loss of the nitrile ligand $(M-NCR)^+$. No fragments corresponding to the loss of CO, $(M-CO)^+$, or loss of CO and nitrile, $(M-CO-NCR)^+$, were observed above the background.

In addition to the above characterization, the acetonitrile complex 11a was studied by nitrogen-NMR spectroscopy. First, the ^{15}N NMR spectrum of 11a-$^{15}N_\alpha$ exhibited a single resonance for $^{15}N_\alpha$ at δ -6.09 (relative to CH_3NO_2). As in the case of the dicarbonyl aryldiazenido complexes 1, we were interested in utilizing ^{14}N NMR for the identification of the nitrogen nuclei in 11a. Interestingly, three broad resonances were observed at δ -6.9, -135.0 and -256.4 assignable to the three distinct nitrogen atoms. The one at δ -6.9 was immediately assigned to N_α, in good agreement with δ -6.09 observed in the ^{15}N NMR spectrum of 11a-$^{15}N_\alpha$. Furthermore this resonance is in the region expected for N_α in a singly-bent diazenido ligand (see Table II, Chapter II). The resonance at δ -135.0 was assigned to N_β. Although this was not confirmed using ^{15}N NMR and $^{15}N_\beta$ enriched 11a, it appears exactly in the region expected for N_β in this type of diazenido ligand (see 1a and 1e in Table II). The third resonance at much higher field (δ -256.4) has no precedent in the literature for cationic complexes and can be tentatively assigned to the nitrogen nucleus of the coordinated acetonitrile ligand. The ^{13}C NMR spectrum of 11a also showed the presence of the acetonitrile ligand. The two singlets observed at δ 142.77 and 5.00 in the proton decoupled ^{13}C NMR spectrum were assigned to the carbons of the cyano and methyl groups respectively.

(d) Monocarbonylphosphine Complexes 12

Good yields of the cationic phosphine complexes $[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)]^+$ 12 were obtained by reaction of the acetonitrile complex 11a with the respective phosphine 12a-d or with trimethylphosphite 12e in acetone at room temperature. In all the cases the compounds were isolated as orange-red solids and were fully characterized by analysis and spectroscopic techniques. They are soluble in the majority of polar organic solvents and insoluble in hexane and ether. All 12a-e exhibited in the IR spectrum in CH_2Cl_2 a very strong terminal $\nu(CO)$ band in the 1965-1940 cm^{-1} region and one strong and broad band at about 1680 cm^{-1} which corresponds to $\nu(NN)$ (see Table III). The $\nu(NN)$ absorption showed the expected isotopic shift to lower wavenumber in going from 12a to 12a-$^{15}N_\alpha$ [$\Delta\nu(NN)$= 35 cm^{-1}] and from 12e to 12e-$^{15}N_\alpha$ [$\Delta\nu(NN)$= 39 cm^{-1}] in CH_2Cl_2 solution. The ^1H NMR spectra of these complexes are exactly those expected by the presence of the phosphine or phosphite ligands (see Experimental Section). Similarly, the ^{31}P NMR spectra showed a single resonance (Table III) in the normal region for a coordinated phosphine.[131] FAB mass spectra showed the unfragmented cation as the molecular

Table III. IR, ^{31}P NMR and FAB Mass Spectra of Monocarbonylphosphinearyldiazenido Complexes (Ar= p-C_6H_4OMe).

$[Cp^*Re(CO)(PR_3)(N_2Ar)][BF_4]$	IR (CH_2Cl_2) cm^{-1}	^{31}P NMR ($CDCl_3$)[a]	FAB-MS[b]
R = Me, 12a	1949 ν(CO)[e], 1677 ν(NN)[f]	-30.39	561
12a-$^{15}N_\alpha$	1949 ν(CO), 1642 ν(^{15}NN)	-	562
R = n-Bu, 12b	1949 ν(CO), 1679 ν(NN)	-2.52	687
R = Cy[c], 12c	1940 ν(CO), 1677 ν(NN)	22.03	n/o[d]
R = Ph, 12d	1954 ν(CO), 1685 ν(NN)	13.9	747
R = OMe, 12e	1965 ν(CO), 1689 ν(NN)	108.79	609
12e-$^{15}N_\alpha$	1965 ν(CO), 1650 ν(^{15}NN)	-	610

[a] 85% H_3PO_4 as reference δ, downfield positive, proton decoupled. [b] m/z based on ^{187}Re. [c] Cy = cyclohexyl. [d] n/o = not observed. [e] very strong. [f] strong.

peak (Table III) except for the cyclohexylphosphine complex 12c for which the FAB MS could not be observed. The fragments corresponding to loss of CO and PR_3 were not observable above the background.

Nitrogen NMR was also used for the characterization of complexes 12a and 12e. The ^{15}N NMR spectra of 12a-$^{15}N_{\alpha}$ and 12e-$^{15}N_{\alpha}$ showed a doublet with small coupling to phosphorus, at a slightly higher field than CH_3NO_2 (see Table IV). The value of the coupling constants to phosphorus ($^2J_{PN}$) 3.5 and 3.0 for 12-$^{15}N_{\alpha}$ and 12e-$^{15}N_{\alpha}$ respectively are in good agreement with those observed in other phosphine complexes with dinitrogen containing ligands i.e., cis-$Mo(PMe_2Ph)_4(^{15}N_2)_2$ $^2J_{PN}$= 5.2,[51] trans-$W(^{15}N_2)(dppe)_2$ $^2J_{PN}$= 2.0[51] and trans-$[WBr(^{15}N_2(Et)H)(dppe)_2]Br$ $^2J_{PN}$= 5.0.[45] On the other hand, the ^{14}N NMR spectrum of the trimethylphosphine complex 12a allowed us to observe also the resonance due to the N_{β} at δ -126. In addition, a second resonance observed at much lower field (δ -1.9) was assigned to N_{α}. This agrees well with that observed in the ^{15}N NMR spectrum of 12a-$^{15}N_{\alpha}$. Both resonances in 12a and the doublets observed in 12a-$^{15}N_{\alpha}$ and 12e-$^{15}N_{\alpha}$ are within the range expected for N_{α} and N_{β} of a singly-bent diazenido ligand.[45,51]

Table IV. ^{13}C of carbonyl and $^{15}N_{\alpha}$ of N_2Ar resonances in $[Cp^*Re(CO)(L)(p\text{-}N_2C_6H_4OMe)]^+$ Complexes

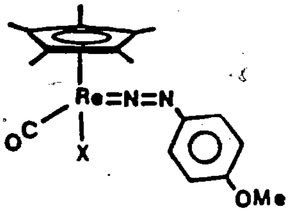
$[Cp^*Re(CO)(L)(p\text{-}N_2C_6H_4OMe)]^+$	$\delta\ (^{13}CO)^a$	$\delta\ (^{15}N_{\alpha})^b$
L= CO, <u>1a</u>	190.65	-7.32
L= $P(OMe)_3$, <u>12e</u>	199.01	-1.97
L= PMe_3, <u>12a</u>	201.24	-0.64

[a] in $CDCl_3$. [b] in acetone/acetone-d_6.

4.3. Discussion

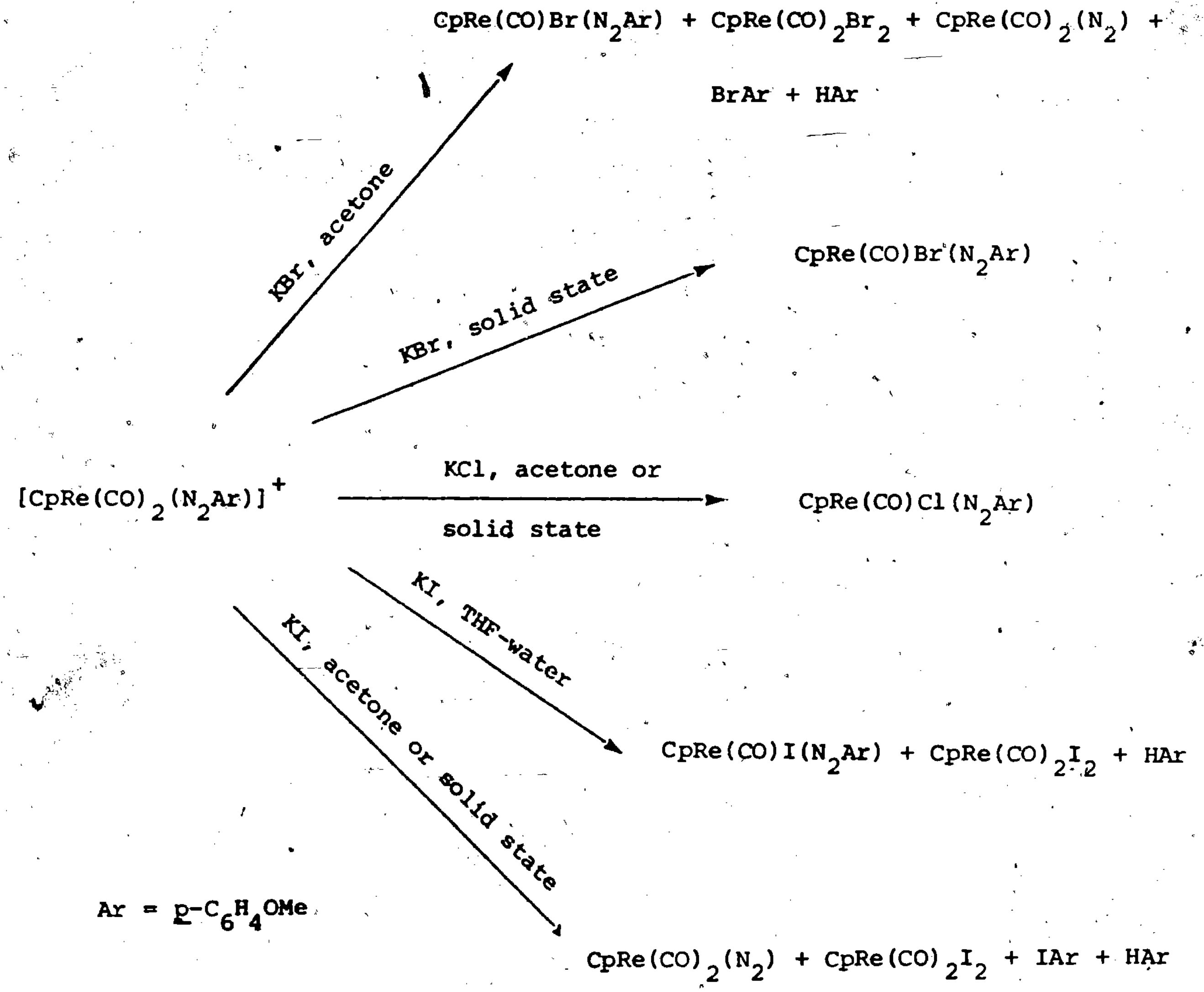
(a) Monocarbonylhalide Complexes

The reaction of the dicarbonyl cation <u>1a</u> with potassium halide (solid state or THF-water solution) has allowed the isolation of the new monocarbonylhalide derivatives $Cp^*ReX(CO)(p\text{-}N_2C_6H_4OMe)$ <u>9</u>, <u>9a</u> X= Cl, <u>9b</u> X= Br and <u>9c</u> X= I. On the basis of spectroscopy these complexes retain the aryldiazenido ligand bound to the metal in a singly-bent three-electron donor fashion, as expected for a 18-electron configuration as shown below.



<u>9</u>

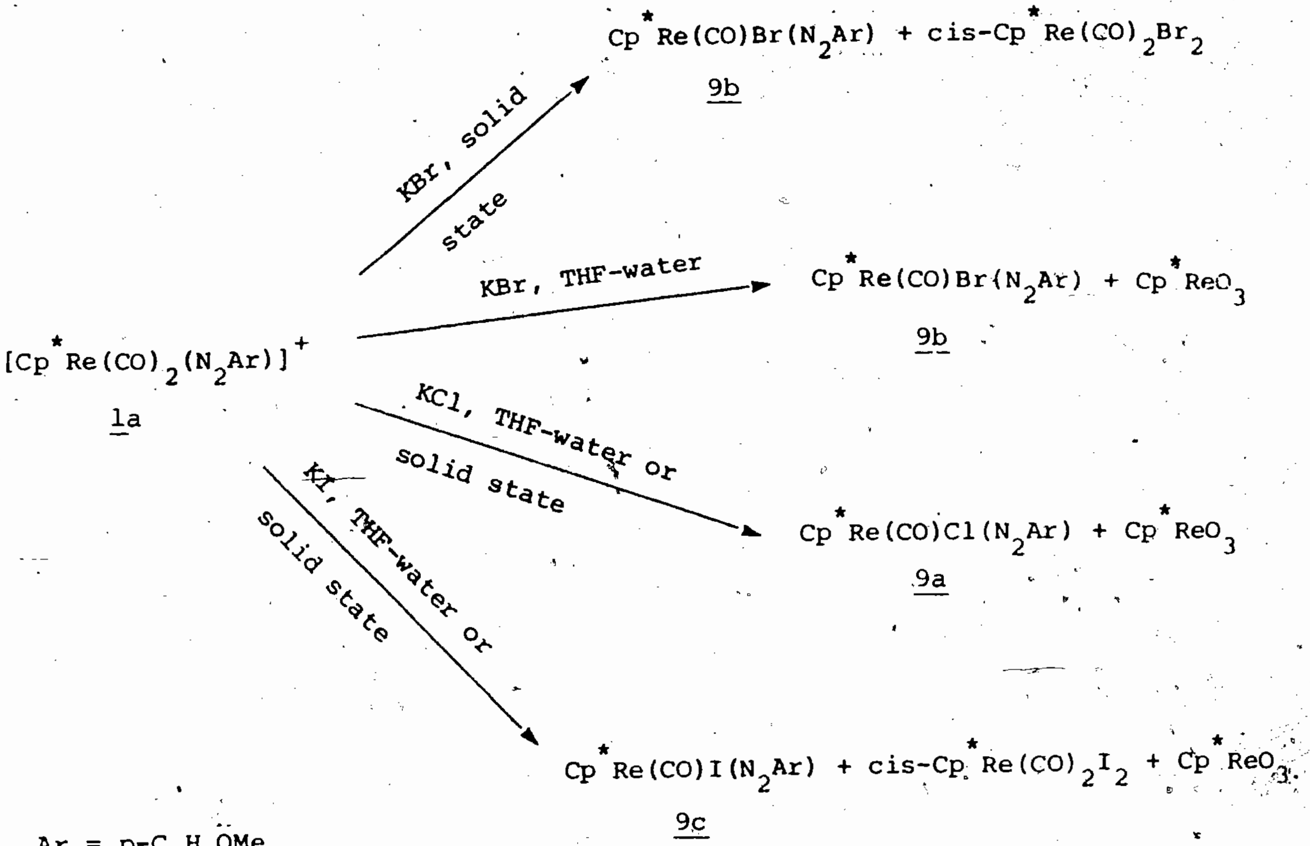
The formation of these derivatives contrasts with the reaction of $[(C_5H_4Me)Mn(CO)_2(N_2Ar)]^+$ with halides X^- where an apparent nucleophilic attack at the ipso carbon occurs to produce the dinitrogen complex $(C_5H_4Me)Mn(CO)_2(N_2)$[9] (see Eq.4 and Scheme III). Also differences are observed from the analogous reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with halides.[27] The products of these reactions are shown in Scheme VI.



Scheme VI

As can be observed in Scheme VI, reactions of $[CpRe(CO)_2(N_2Ar)]^+$ with potassium halides are complex and very dependent on the nature of the solvent and the halide.

Using the pentamethylcyclopentadienylrhenium analogue <u>1a</u>, reactions with KX in THF-water, or even in the solid state, are apparently much simpler, since the production of the dinitrogen complex was never observed (see Scheme VII).



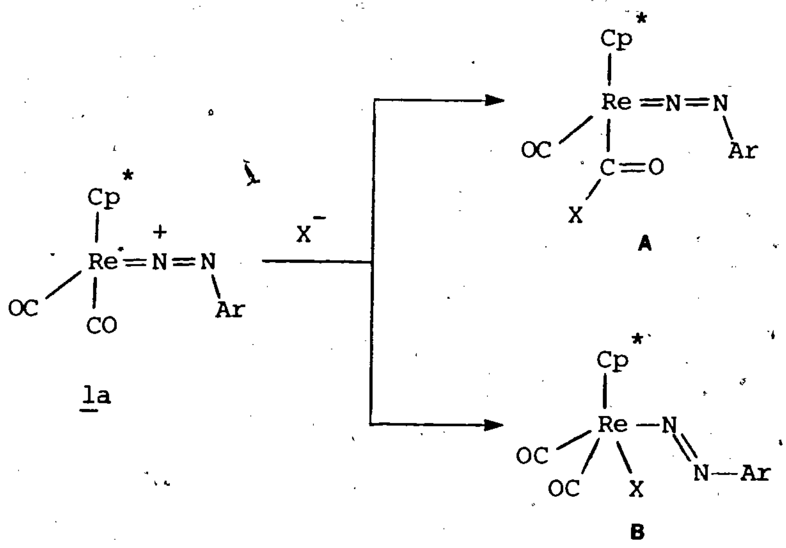
Ar = p-C_6H_4OMe

Cp^*ReO_3 was produced only in THF-water reactions

Scheme VII

The small amount (less than 5%) of the trioxo complex $Cp^{*}ReO_3$ observed in THF-water reactions could result from oxidation of the starting material <u>1a</u> or the products by oxygen contained in the solvent (see Appendix I).

Two possible neutral intermediates that might be formed as a first step of the nucleophilic attack of the halide ion X^- to the dicarbonyl cation are shown in Scheme VIII. However, no evidence for the formation of these, or any other intermediate species, has been obtained.



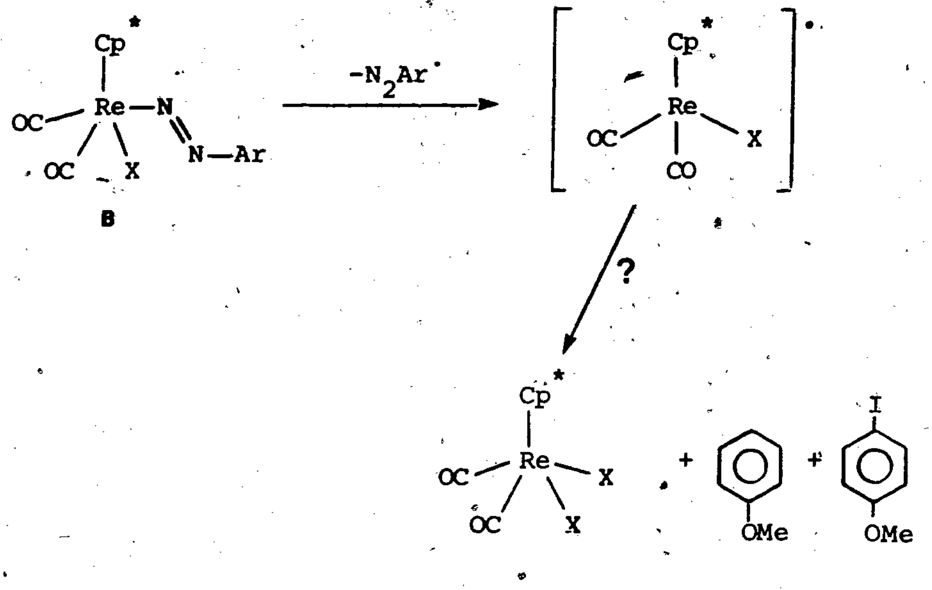
Scheme VIII

The acyl halide intermediate A could result from nucleophilic attack on a CO group. This type of intermediate has been suggested in analogous reactions but never observed as a stable product.[132,133] The monocarbonylhalide complex <u>9</u> could be formed by an internal displacement mechanism analogous to that suggested for the decarbonylation of $RCOMn(CO)_5$.[134]

On the other hand, nucleophilic attack of the halide ion could occur at the metal center to produce the neutral intermediate $Cp^*Re(CO)_2X(N_2Ar)$ B with a doubly-bent aryldiazenido ligand. This type of isomerization of a diazenido ligand in reactions with halides has been observed previously[13] and has already been discussed in Chapter I, Section 1.2.3(b). Intermediate B could lose a CO ligand with concomitant rearrangement of the one-electron doubly-bent ligand back to the three-electron donor singly-bent ligand to give the observed 18-electron species 9.

Both intermediates A and B can explain equally well the formation of compound 9. However, the formation of the dicarbonyldihalide complexes $Cp^*Re(CO)_2X_2$ in reaction of 1a with KBr and KI is a matter of speculation. Here a radical mechanism similar to that proposed for the reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with halides[27] may occur (see Scheme IX).

In Scheme IX it is assumed that the intermediate B loses the aryldiazenido group to generate the $N_2Ar\cdot$ radical and the seventeen- electron organometallic radical $[Cp^*Re(CO)_2X]\cdot$. The diazo radical would decompose to give N_2 the and aryl radical which can abstract a hydrogen atom from the solvent to form anisole or an iodine atom to form p-iodoanisole. The exact mechanism of formation of cis-$Cp^*Re(CO)_2X_2$ is not known at the present time.



Scheme IX

It is possible that both mechanisms (associative and radical) are involved in the reaction at the same time but the high yields of the monocarbonylhalide 9 indicates that the associative one is preferred. The major dependence of the products on the solvent and on the oxidizability of the halide are important factors yet to be determined.

(b) Arylmonocarbonyl Complexes 10

As was mentioned before, the two aryl derivatives 10a and 10b were synthesized using the chloro complex 9a and the respective arylcopper reagent (RCu). The choice of this route to prepare such compounds was stimulated by a recent report by Sweet and Graham using the isoelectronic complex CpRe(CO)(NO)(X) (X= Cl, Br and I) in reactions with Grignard, organolithium and arylcopper reagents.[129] They found that the latter is the most efficient reagent to obtain the desired substitution products. Using Grignard or organolithium they found that the corresponding benzoylmetalate products $[CpRe(NO)(COAr)I]^-$ were almost exclusively formed. This anionic compound would result from carbanion attack on the carbonyl group without subsequent loss of the halide. They also found that the variation of X in CpRe(CO)(NO)X increased the yield of the aryl derivative in the order I < Br < Cl.

In the pentamethylcyclopentadienyl system a similar trend in reactivity of the chloro derivative 9a toward PhMgBr and arylcopper was observed. For instance, a slow reaction took place when complex 9a in THF was treated with PhMgBr. However, the benzoylmetalate complex $[Cp^*ReCl(N_2Ar)(COPh)]^-$ could not be detected by IR and no aryl complex was formed. Instead, only decomposition of the rhenium complex was observed. No attempts were made to identify the decomposition products. Probably, carbanion attack at the carbonyl group occurred and the benzoylmetalate intermediate then formed readily decomposed. Another possible reaction could also occur. This involves nucleophilic attack of the PhMgBr at the aryldiazenido ligand to produce the hydrazido (2-) complex $[Cp^*Re(CO)Cl(NN(Ph)Ar)]^-$ and/or the dinitrogen complex $[Cp^*Re(CO)Cl(N_2)]^-$ which are probably unstable. Neutral analogues of these complexes (benzoyl, hydrazido (2-) and dinitrogen) have been isolated from reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with PhLi.[10]

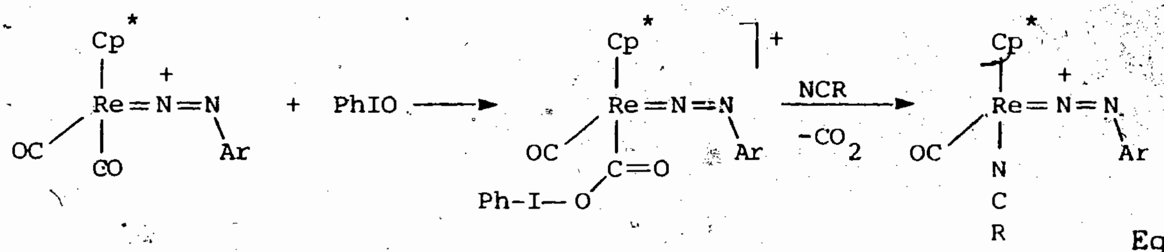
Reaction of 9a with arylcopper (RCu, R= phenyl or tolyl) occurred cleanly to effect the desired substitution. In general, both arylrheniumdiazenido compounds 10a and 10b exhibit very similar spectroscopic properties, comparable to those observed in the arylrheniumnitrosyl species. Substitution of hydrogen by methyl in the *para*-position of the aryl ligand does not significantly change ν(CO) and ν(NN) in the IR spectra of these compounds or the resonances of the Cp^* and methoxy group of the $Cp^*Re(CO)(N_2Ar)$ fragment, in the ^1H NMR spectra.

(c) Monocarbonylnitrile Complexes 11

The substitution of carbonyl by nitrile ligands in the dicarbonyl cationic complex 1a could be achieved by two different routes. First, photochemically, which involved the UV-irradiation of a dilute solution of 1a in acetonitrile. Although it was possible to obtain the nitrile complex 11a by this route there were several problems associated with this reaction. For instance, long irradiation periods ca. 2-3 h resulted in total disappearance of 1a with formation of the acetonitrile complex 11a, but only in low yield. This was probably due to subsequent decomposition of the product under continued irradiation. Using shorter irradiation periods, ca. 30 min, only about one-quarter conversion of 1a to the acetonitrile product was evident by IR. However, the separation of these two cationic complexes could not be achieved by routine laboratory techniques. Since complex 11a could be prepared in excellent yields, analytically pure, by an alternative method as described below, no attempts were made to find the optimum conditions for this photochemical reaction.

While we were studying this reaction, a milder reagent for the oxidative removal of coordinated CO was reported by Gladysz and coworkers.[111] They found that the reaction of the dicarbonylnitrosyl cation $[CpRe(CO)_2(NO)]^+$ in acetonitrile with commercially available iodosobenzene (PhIO) resulted in the smooth formation of $[CpRe(CO)(NCMe)(NO)]^+$ in high yield. Subsequently, the synthesis of $[Cp^*Re(CO)(NCMe)(NO)]^+$ was reported by the same group using a similar procedure.[96]

Iodosobenzene, also called iodosylbenzene[96], works equally well with the dicarbonylaryldiazenido complex 1a in different nitriles NCR (R= Me, n-Pr and i-Pr) as solvents (Eq. 20).



1a

11

Eq. 20.

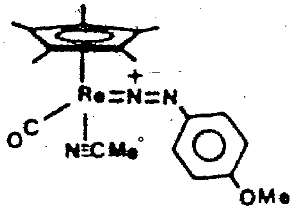
It is believed that the reaction is initiated by nucleophilic attack of PhIO at the carbonyl carbon atom followed by liberation of CO_2 and coordination of a nitrile molecule from the solvent. A similar reaction pathway has been proposed in reactions of $Re_2(CO)_{10}$ with Me_3NO in acetonitrile to give $Re_2(CO)_9(NCCH_3)$.[136]

The labile acetonitrile ligand in 11a can easily be displaced from the metal by other two-electron donor ligands giving complexes of the type $[Cp^*Re(CO)(L)(N_2Ar)]^{n+1}$ (n= 0 or 1) which are normally inaccessible from the dicarbonyl cation 1a. Complex 11a is the second most important species in the work involved in this thesis (the first being complex 1a), since it is the precursor of almost all the chemistry to be described in the rest of this thesis.

The methyl proton resonance of the acetonitrile ligand in 11a (δ 3.10) is in good agreement with those reported for the isoelectronic nitrosyl analogues $[CpRe(CO)(NCMe)(NO)]^+$ δ 2.82 (CD_2Cl_2)[107] and 2.95 (acetone-d_6)[111] and δ 3.05 (acetone-d_6) for $[Cp^*Re(CO)(NCMe)(NO)]^+$.[96] In the latter case the ^{13}C NMR spectrum was also reported. In general, the ^{13}C NMR spectra of 11a and $[Cp^*Re(CO)(NCMe)(NO)]^+$ are comparable, particularly in the resonances attributable to the carbon nuclei of the acetonitrile ligand δ 4.70 and 139.30 (acetone-d_6) in the nitrosyl complex *versus* δ 5.00 and 142.77 ($CDCl_3$) in 11a, for the methyl and cyano carbons respectively.

In both the nitrosyl and aryldiazenido complexes the resonance due to the carbon of the cyano group of acetonitrile ligand (δ ~ 140) was shifted to low field by about 10 ppm by comparison with the cationic complexes $[Re(CO)_5(NCMe)]^+$[137] and $[CpFe(CO)(NCMe)_2]^+$[138,139] which are believed (by IR, ν(C≡N) ~ 2200 cm^{-1}) to contain the acetonitrile coordinated through the nitrogen lone pair (η^1-fashion). Another anomalous result (assuming η^1-coordination of NCMe in <u>11a</u>) was observed in the ^{14}N NMR spectrum of this complex. The value δ -256.4 observed for the nitrogen nucleus of coordinated NCMe is shifted by about 120 ppm upfield by comparison with free NCMe (δ -138.4).[140] This large coordination shift contrasts with those predicted theoretically by Mason[141] and with that observed in $Cr(CO)_5(NCMe)$ (δ -146.0).[142]

In addition, the failure to observe $\nu(C{\equiv}N)$ in complex <u>11a</u> and presumably in Cp and Cp* rheniumnitrosyl analogues (because these were not reported) in the region characteristic of NCMe bound to a metal in a η^1-fashion i.e. 2200-2300 cm^{-1}, suggests that this ligand might instead be π-bonded to the rhenium as shown below.



Coordination of acetonitrile as a π-complex had been previously suspected in $Ru(PPh_3)_4(\eta^2\text{-NCMe})$. This assignment was made on the basis of IR spectroscopy where $\nu(C{\equiv}N)$ appears as a strong absorption at 1912 cm^{-1}.[143] We were unable to observe any other absorption in the 2000-1900 cm^{-1} region in addition to the broad and very strong band due to $\nu(CO)$.

(d) Monocarbonylphosphine Complexes 12

These complexes were easily prepared by thermal substitution of the acetonitrile ligand in 11a by phosphine (12a-d) or trimethylphosphite 12e ligands. Attempts were also made to prepare the triphenylphosphine complex 12d by direct reaction of the dicarbonyl 1a with an excess of PPh_3 in acetone. Unfortunately the only organometallic product isolated was the dicarbonyltriphenylphosphine complex $Cp^*Re(CO)_2(PPh_3)$. This compound had been previously mentioned but without details of its synthesis and characterization.[144] We identified it by IR (ν(CO) 1922 and 1859 cm^{-1} in ether) and mass spectra (m/z 640 M^+, and 584 $(M-2CO)^+$ based on ^{187}Re). A similar reaction was previously observed in $[CpRe(CO)_2(N_2Ar)]^+$ with PPh_3. In this case $CpRe(CO)_2(PPh_3)$ and $[Ph_3P-NNAr][BF_4]$ were positively identified.[27]

In the IR spectra of these complexes, the relative σ-donor (or π-acceptor) abilities of the phosphine ligands are revealed more strongly by changes in ν(CO) than in ν(NN) (see Table III). This can be explained in terms of the better π-acceptor properties of CO compared with the aryldiazenido group.[11]. The greater the σ-donor (or poorer π-acceptor) ability of the phosphorus ligand, the higher will be the degree of delocalization into the carbonyl antibonding orbitals and the lower will be the ν(CO). For example, the order of decreasing ν(CO) $P(OMe)_3 > PPh_3 > P(n\text{-}Bu)_3 \sim PMe_3 > PCy_3$ correlates with increasing σ-donor ability of the phosphorus ligand.[145]

In the ^{13}C NMR spectra of 12a, 12e and 1a some trends were also observed. For example, the replacement of one carbonyl in the parent dicarbonyl cation <u>1a</u> by a phosphorus ligand leads to a deshielding (down field shift) of the carbonyl carbon resonance for the remaining CO ligand (see Table IV). Within the phosphorus containing complex a low field shift of δ (^{13}CO) is observed when the trimethylphosphine <u>12a</u> is compared with the trimethylphosphite <u>12e</u> complex (Table IV). A comparable shift has been observed in several other systems containing carbonyl and phosphorus ligands e.g. $Ni(CO)_3L$[146] and $CpMn(CO)_2L$.[147]

The above trend also occurs in the $^{15}N_\alpha$ resonance of the diazenido ligand in the ^{15}N NMR spectra (Table IV). Indeed, this is the first example where similar periodicities are observed in the ^{13}C resonance of CO, and $^{15}N_\alpha$ resonance of N_2Ar, within the same complex.

The downfield shift observed in δ (^{13}CO) and δ ($^{15}N_\alpha$) of these aryldiazenido complexes as a function of increasing electron-donor ability of ligand L can be explained in terms of the greater metal→carbonyl and metal→diazenido π-backbonding due to an increase of electron density at the metal. It has been suggested[141] that this effect produces a decrease in the magnitude of the separation (ΔE) between the electronic ground state and the lowest lying excited state, which is related to the local paramagnetic term (σ_p) of the screening constant. In the case of ^{13}C and ^{15}N nuclei, σ_p is the main contributor to the chemical shift.[141,146]

4.4. Experimental Section

Synthetic procedures, solvent purification and spectroscopic measurements were done as described in Chapter II. Trimethyl-, tri(n-butyl)-, tricyclohexyl- and triphenylphosphine (Strem Chemical) and trimethylphosphite (Alfa) were used as purchased. Acetonitrile (Fisher Scientific), n-butyronitrile and i-butyronitrile (Aldrich) were distilled from P_4O_{10} prior to use. Phenylmagnesium chloride (Alfa, 1.95 M in THF) and p-tolylmagnesium bromide (Aldrich, 2 M in ether) were used as received. Iodosobenzene was purchased from Pfaltz and Bauer, or prepared from iodosobenzenediacetate (Aldrich) by the method of Saltz and Sharefkin.[148] Electron-impact mass spectral data (m/z) are reported based on ^{187}Re, ^{35}Cl and ^{79}Br.

Preparation of $Cp^*ReCl(CO)(p\text{-}N_2C_6H_4OMe)$ (9a)

(i) Reaction of 1a with KCl in THF-water

The cationic rhenium dicarbonyl 1a (50 mg, 0.083 mmol) was stirred with excess KCl in THF-H_2O (1:1, 10 mL) for 36 h. THF was removed under vacuum, and the slightly yellow aqueous solution remaining was decanted from the insoluble red solid. The latter was dissolved in THF, and placed on a Florisil column (prepared in hexane). A red fraction eluted with THF-hexane (1:4) yielded 9a as a red solid (38 mg, 87%) after evaporation of solvent. A yellow fraction eluted with THF-hexane (2:1) yielded, after precipitation with hexane at low temperature, about 5 mg of Cp^*ReO_3. Compound 9a melted at 125-127°C without decomposition. IR (CH_2Cl_2): 1924 vs

ν(CO), 1624 s ν(NN), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.00 s (15H, Cp*), 3.81 s (3H, OMe), 6.92 d (2H, C_6H_4) and 7.29 d (2H, C_6H_4). MS (EI): m/z 520, (M$^+$), 492, (M-CO)$^+$. Anal. Calcd. for 9a: C, 41.54; H, 4.23; N, 5.38. Found: C, 41.41; H, 4.15; N, 5.19.

(ii) Solid State Reaction

The rhenium complex 1a (100 mg) was finely ground with solid KCl and the mixture heated at 95°C for 12 h, by which time all the starting material had reacted (by IR) and a strong absorption occurred at 1919 and 1627 cm^{-1}. Extraction with CH_2Cl_2 and then chromatography on silica gel with CH_2Cl_2-hexane (7:3) gave an orange-red fraction which contained the product. Recrystallization from CH_2Cl_2-hexane gave 16 mg (19%) of 9a which was characterized as above.

(iii) Reaction of Acetonitrile Complex 11a with KCl

The cationic acetonitrile complex 11a (80 mg, 0.13 mmol) was stirred with finely ground KCl in acetone (8 mL). After 1 h, all 11a had reacted (by IR). Removal of the solvent and purification as in (i) yielded 56 mg (82%) of 9a.

Preparation of Cp*ReBr(CO)(p-$N_2C_6H_4$OMe) (9b)

(i) Reaction of 1a with KBr in THF-water

This was carried out as described for KCl (above). From 50 mg of 1a, 40 mg (80%) of the red solid 9b were obtained. About 7 mg of Cp*ReO$_3$ were also produced. Complex 9b melted at 149-151°C. IR (CH_2Cl_2): 1927 vs ν(CO), 1628 s ν(NN), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.06 s (15H, Cp*), 3.81 s (3H, OMe), 6.90 s (2H, C_6H_4) and 7.27 d

(2H, C_6H_4). MS (EI): m/z 564, (M^+), 536, $(M-CO)^+$. Anal. Calcd. for 9b: C, 38.29; H, 3.90; N, 4.96. Found: C, 38.44; H, 3.89; N, 4.71.

(ii) Solid State Reaction

This was carried out as described for KCl, but the reaction was much faster. It took 4 h at 95°C for complete disappearance of the starting dicarbonyl complex (by IR). From 100 mg of 1a 21 mg (23%) of the bromo complex 9b were obtained after chromatography on a silica gel column eluted with CH_2Cl_2-hexane 7:3. Further elution with CH_2Cl_2 gave a red-orange fraction containing 9b and $Cp^*Re(CO)_2Br_2$ which was identified as the cis-isomer (see Chapter VI).

Preparation of $Cp^*ReI(CO)(p\text{-}N_2C_6H_4OMe)$ (9c)

(i) Reaction with KI in THF-water

This reaction was carried out as described for KCl (above) using 50 mg (0.083 mmol) of 1a, to yield the iodo complex 9c as a red solid in 80% yield. Elution with THF-hexane (7:3) yielded a small amount (ca. 5 mg) of $Cp^*Re(CO)_2I_2$ (cis-isomer, see Chapter VI) as a yellow-orange band. A second yellow compound eluted with THF, was identified as Cp^*ReO_3 (about 5 mg). Compound 9c melted at 175°C. IR (CH_2Cl_2): 1928 vs ν(CO), 1630 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.13 s (15H, Cp^*), 3.81 s (3H, OMe), 6.90 d (2H, C_6H_4) and 7.28 d (2H, C_6H_4). MS (EI): m/z 610 (M^+), 582 $(M-CO)^+$. Anal. Calcd. for 9c: C, 35.35; H, 3.60; N, 4.58. Found: C, 35.37; H, 3.73; N, 4.64.

(ii) Solid State Reaction

This was carried out as described for KCl and KBr, but the reaction was faster and all starting material reacted within 40 min at 95°C. IR showed the presence of 9c (1925 vs, 1628 s cm^{-1}) as major product, and some cis-$Cp^*Re(CO)I_2$ ($\nu(CO)_{sym}$ 2013 cm^{-1}, $\nu(CO)_{asym}$ obscured by 9c). Chromatography on silica gel with CH_2Cl_2-hexane (7:3) first eluted cis-$Cp^*Re(CO)I_2$ and then 9c which was characterized as above. From 100 mg of 1a, 30 mg (31%) of isolated 9c were obtained.

Preparation of $Cp^*Re(CO)(Ph)(p\text{-}N_2C_6H_4OMe)$ (10a)

A solution of phenylmagnesium chloride (0.1 mL, 0.195 mmol) was added dropwise to a stirred suspension of CuBr (55 mg, 0.385 mmol) in 10 mL of THF cooled at 0°C. Solid 9a (30 mg, 0.057 mmol) was added carefully under N_2. The mixture was allowed to warm up to room temperature as stirring continued. After 90 min all the starting complex (9a) reacted (by IR). The mixture was then hydrolyzed with water (0.2 mL) and filtered through Celite under N_2. Solvent was evaporated under vacuum and after overnight drying (under vacuum) the solid residue was extracted with hexane (4 x 8 mL). The combined extracts were filtered through a short neutral alumina column and the solvent removed under vacuum. Recrystallization from hexane at -78°C afforded the product as orange microcrystals. M.p.: 123-125°C. IR (hexane): 1922 vs $\nu(CO)$, 1624 m $\nu(NN)$, cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.90 s (15H, Cp^*), 3.81 s (3H, OMe), 6.88 d (2H, J= 8.90 Hz, C_6H_4), 6.99 t (1H, J= 7.27 Hz, *p*-C_6H_5), 7.09 t (2H, J= 7.27 Hz, *m*-C_6H_5), 7.24 d (2H, J= 8.90 Hz, C_6H_4), 7.55 d (2H, J= 6.90 Hz, *o*-C_6H_5). MS (EI, 16 eV): m/z 562 (M^+), 534 $(M-CO)^+$. Anal. Calcd. for **10a**: C, 51.33; H, 4.81; N, 4.99. Found: C, 51.17; H, 4.78; N, 4.87.

Praparation of $Cp^*Re(CO)$(*p*-tolyl)(*p*-$N_2C_6H_4OMe$) (**10b**)

This compound was prepared following the same procedure used for the preparation of **10a** except that 0.25 mmol of *p*-tolylmagnesium bromide and 0.5 mmol of CuBr in 10 mL of THF were used for reaction with 0.056 mmol of **9a**. Stirring was continued for 4 h before hydrolysis. **10b** was obtained as an orange-yellow microcrystalline solid. M.p. 154-156°C. IR (hexane): 1921 vs ν(CO), 1617 m ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.90 s (15H, Cp^*), 3.81 s (3H, OMe), 6.88 d (2H, J= 8.80 Hz, aryldiazenido), 6.93 d (2H, J= 7.60 Hz, tolyl), 7.24 d (2H, J= 8.80 Hz, aryldiazenido), 7.43 d (2H, J= 7.60 Hz, tolyl). MS (EI, 16 eV): m/z 576 (M^+), 548 $(M-CO)^+$. Anal. Calcd. for **10b**: C, 52.17; H, 5.04; N, 4.87. Found: C, 51.98; H, 5.15; N, 4.99.

Preparation of $Cp^*Re(CO)(NCMe)$(*p*-$N_2C_6H_4OMe$)]$[BF_4]$ (**11a**) and (**11a**-$^{15}N_\alpha$)

An approximate 20% stoichiometric excess of iodosobenzene (PhIO) was added as a solid to a stirred solution of **1a** or **1a**-$^{15}N_\alpha$ (500 mg, 0.835 mmol) in MeCN (40 mL). After 1 h, all of the dicarbonyl cation had reacted (by IR) and no further change occurred. Removal of solvent under vacuum gave a red oily solid which was dissolved in acetone and filtered through Celite. Recrystallization from acetone-ether gave the acetonitrile complex as an orange microcrystalline solid in 91% yield (467 mg). M.p. 65-67°C. IR (CH_2Cl_2): 1962 vs ν(CO), 1659 s ν(NN)(1638 in 11a-$^{15}N_\alpha$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.14 s (15H, Cp*), 3.10 s (3H, MeCN), 3.85 s (3H, OMe), 7.05 d (2H, C_6H_4) and 7.24 d (2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 5.00 (MeCN), 10.03 (C_5Me_5), 55.80 (OMe), 106.31 (C_5Me_5), 115.68 , 121.95, 123.95, 161.79 (C_6H_4), 142.77 (MeCN) and 195.94 (CO) (all resonances appeared as singlets). ^{14}N NMR (acetone/acetone-d_6): δ -256.4 br, s (NCMe); -135.0 br, s (N_β) and -6.9 br, s (N_α). ^{15}N NMR for 11a-$^{15}N_\alpha$ (acetone/acetone-d_6): δ -6.09 s ($^{15}N_\alpha$). MS (FAB, xenon, sulfolane): m/z 526 (527 in 11a-$^{15}N_\alpha$) (M^+ of cation), 485 (486 in 11a-$^{15}N_\alpha$) $(M-NCMe)^+$. Anal. Calcd. for 11a: C, 39.21; H, 4.08; N, 6.86. Found: C, 38.77; H, 4.18; N, 6.63.

Photochemical Reaction of 1a in Acetonitrile

About 20 mg of 1a were dissolved in 20 mL of freshly distilled acetonitrile and irradiated through a quartz tube at room temperature for 30 min. During the photolysis a slow flux of N_2 was maintained. After this time, the IR spectrum of the solution showed a 25% conversion of 1a into the acetonitrile complex 11a. The residual brown solid was dissolved in CH_2Cl_2. Slow addition of ether precipitated a dark red solid which showed in the IR spectrum (in CH_2Cl_2) the same 1a-11a ratio observed in acetonitrile. Crystallization from acetone-ether (5:1) at -78°C or extraction with THF showed (by IR) the same ratio of products.

The remaining 10 mL of the acetonitrile solution were irradiated for an additional 2 h under the same conditions. After this time a dark-brown solution was obtained which showed in the IR spectrum only weak absorptions for 11a. Evaporation of the solvent gave a dark-brown solid from which 11a could not be separated.

Preparation of $[Cp^*Re(CO)(NCPr^n)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (11b)

This compound was synthesized analogously to 11a using n-butyronitrile ($NCPr^n$) as a solvent. From 100 mg (0.167 mmol) of 1a (in 8 mL of $NCPr^n$) 73 mg of 11b (68%) were obtained as a red-orange solid which decomposed above 98°C. IR (CH_2Cl_2): 1962 vs ν(CO), 1660 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 t (3H, $NC(CH_2)_2\underline{Me}$), 1.76 sex. (2H, $NCCH_2\underline{CH_2}Me$), 2.15 s (15H, Cp^*), 3.46 t (2H, $NC\underline{CH_2}CH_2Me$), 3.85 s (3H, OMe), 7.05 d (2H, C_6H_4), 7.27 d (2H, C_6H_4). MS (FAB, xenon, sulfolane): m/z 554 (M^+ of cation), 485 $(M\text{-}NCPr^n)^+$. Anal. Calcd. for 11b: C, 41.75; H, 4.53; N, 6.56. Found: C, 42.03; H, 4.88; N, 6.54.

Preparation of $[Cp^*Re(CO)(NCPr^i)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (11c)

This complex was prepared in a similar manner to 11a using iso-butyronitrile ($NCPr^i$) as a solvent. From 100 mg (0.167 mmol) of 1a, 65 mg (62%) of 11c were obtained as a dark-red solid. M.p. slow decomposition above 80°C. IR (CH_2Cl_2): 1959 vs ν(CO), 1658 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.10 s (15H, Cp^*), 2.19 d (6H, CH<u>Me</u>$_2$), 3.60 br mult. (1H, C<u>H</u>Me$_2$), 3.82 s (3H, OMe), 6.98 d (2H, C_6H_4), 7.22 d (2H, C_6H_4). MS (FAB, xenon, sulfolane): m/z 554 (M^+ of cation), 485 ($M-NCPr^i$)$^+$. Anal. Calcd. for <u>11c</u>: C, 41.25; H, 4.53; N, 6.56. Found: C, 41.48; H, 4.43; N, 6.64.

Preparation of $[Cp^*Re(CO)(PMe_3)(\underline{p}-N_2C_6H_4OMe)][BF_4]$ (<u>12a</u>-$^{15}N_\alpha$)

The acetonitrile complex <u>11a</u> or <u>11a</u>-$^{15}N_\alpha$ (500 mg, 0.816 mmol) in acetone (40 mL) was stirred with an excess of PMe_3 (0.1 mL). The reaction was followed by IR spectroscopy until all the acetonitrile complex reacted (ca. 4 h). Solvent was pumped off, the orange oily solid then obtained was washed three times with ether (30 mL) and dried under vacuum for 2 days. Yield: 475 mg (90%) of the product <u>12a</u> or <u>12a</u>-$^{15}N_\alpha$ as an orange solid. M.p. 169-171°C. IR (CH_2Cl_2): 1949 vs ν(CO), 1677 s (1642 in <u>12a</u>-$^{15}N_\alpha$) ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.88 d (J= 10.69, 9H, PMe_3), 2.19 d (J= 0.52, 15H, Cp^*), 3.86 s (3H, OMe), 7.02 d (2H, C_6H_4) and 7.16 d (2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.72 s ($C_5\underline{Me}_5$), 18.45 d (J= 39.14, P$\underline{Me}_3$), 55.81 s (O<u>Me</u>), 106.24 s ($\underline{C}_5Me_5$), 115.86 s, 119.50 s, 122.63 s, 162.10 s (C_6H_4) and 201.24 d (J= 12.16, CO). ^{14}N NMR (acetone-acetone-d_6): δ -126.0 br, s (N_β), and -1.9 br, s (N_α). ^{15}N NMR for <u>12a</u>-$^{15}N_\alpha$ (acetone/acetone-d_6): δ -0.64 s ($^{15}N_\alpha$). ^{31}P NMR ($CDCl_3$): δ -30.39 s (PMe_3). MS (FAB, xenon, sulfolane): m/z 561 (562 in <u>12a</u>-$^{15}N_\alpha$) (M^+ of cation). Anal. Calcd. for <u>12a</u>: C, 38.95; H, 4.79; N, 4.32. Found: C, 38.37; H, 4.82; N, 4.30.

Preparation of $[Cp^{*}Re(CO)(P(\textit{n}\text{-}Bu)_3)(\textit{p}\text{-}N_2C_6H_4OMe)][BF_4]$ (**12b**)

A procedure similar to that for the preparation of the PMe_3 complex gave the new tri(*n*-butyl)phosphine complex **12b** in 81% yield as an orange solid which melted at 125°C. IR (CH_2Cl_2): 1949 vs ν(CO) and 1679 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.95 t (9H, $P(CH_2(CH_2)_2\underline{Me}_3)$, 1.46 m (12H, $P(CH_2C\underline{H}_2C\underline{H}_2CH_3)_3$), 1.97 m (6H, $P(C\underline{H}_2(CH_2)_2Me_3)_3$), 2.17 s (15H, Cp^{*}), 3.88 s (3H, OMe), 7.03 d (2H, C_6H_4) and 7.19 d (2H, C_6H_4). ^{31}P NMR ($CDCl_3$): δ -2.52 s ($P(\textit{n}\text{-}Bu)_3$). MS (FAB, xenon, sulfolane): m/z 687 (M^+ of cation). Anal. Calcd. for **12b**: C, 46.57; H, 6.34; N, 3.62. Found: C, 46.35; H, 6.47; N, 3.63.

Preparation of $[Cp^{*}Re(CO)(PCy_3)(\textit{p}\text{-}N_2C_6H_4OMe)][BF_4]$ (**12c**)

This complex was synthesized analogously to **12a** as an orange-red solid in 83% yield. M.p.102-104°C. IR (CH_2Cl_2): 1940 vs ν(CO) and 1677 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 and 1.80 both multiplets (~ 30H, $P\underline{Cy}_3$), 2.15 s (15H, Cp^{*}), 3.88 s (3H, OMe), 7.04 d (2H, C_6H_4) and 7.17 d (2H, C_6H_4). ^{31}P NMR ($CDCl_3$): δ 22.03 s (PCy_3). Anal. Calcd. for **12c**: C, 50.10; H, 6.45; N, 3.29. Found: C, 49.70; H, 6.20; N, 3.60.

Preparation of $[Cp^{*}Re(CO)(PPh_3)(\textit{p}\text{-}N_2C_6H_4OMe)][BF_4]$ (**12d**)

This complex was prepared similarly to those previously described. After recrystallization from CH_2Cl_2-ether **12d** was obtained in 70% yield as orange microcrystals which melted at 230°C. IR (CH_2Cl_2): 1954 vs ν(CO) and 1685 s ν(NN), cm^{-1}. ^1H NMR

($CDCl_3$): δ 2.12 s (15H, Cp*), 3.89 s (3H, OMe), 7.08 d (2H, C_6H_4) and 7.30-7.51 m (17H, PPh_3 + C_6H_4). ^{31}P NMR ($CDCl_3$): δ 13.1 s (PPh_3). MS (FAB, xenon, sulfolane): m/z 747 (M^+ of cation). Anal. Calcd. for 12d: C, 51.86; H, 4.44; N, 3.36. Found: C, 51.79; H, 4.74; N, 3.31.

Preparation of $[Cp^*Re(CO)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (12e) and (12e-$^{15}N_\alpha$)

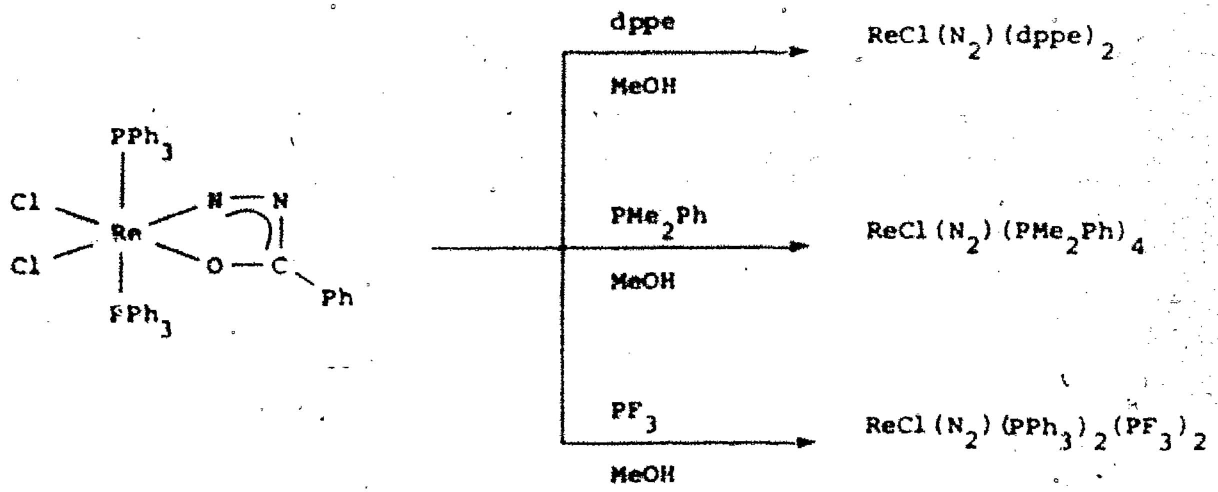
This complex was prepared following the same procedure used for 12a and 12a-$^{15}N_\alpha$ in 75% yield as an orange solid. M.p. 108°C. IR (CH_2Cl_2): 1965 vs ν(CO) and 1689 s (1650 in 12e-$^{15}N_\alpha$), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 d (J= 0.69, 15H, Cp*), 3.78 d (J= 12.18, 9H, $P(OMe)_3$), 3.86 s (3H, OMe), 7.04 d (2H, C_6H_4) and 7.20 d (2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.32 s (C_5Me_5), 54.68 d (J= 6.76, $P(OMe)_3$), 55.90 s (OMe), 106.91 s (C_5Me_5), 115.85 s, 118.64 s, 123.31 s, 162.52 s (C_6H_4) and 199.01 d (J= 19.63, CO). ^{15}N NMR for 12e-$^{15}N_\alpha$ (acetone/acetone-d_6): δ -1.97 s ($^{15}N_\alpha$). ^{31}P NMR ($CDCl_3$): δ 108.79 s ($P(OMe)_3$). MS (FAB, xenon, sulfolane): m/z 609 (610 in 12e-$^{15}N_\alpha$) (M^+ of cation). Anal. Calcd. for 12e: C, 36.26; H, 4.46; N, 4.03. Found: C, 36.39; H, 4.38; N, 4.26.

CHAPTER V

Pentamethylcyclopentadienylrhenium Dinitrogen Complexes

5.1. Introduction

Rhenium dinitrogen complexes have been known since 1969 when Chatt, Dilworth and Leigh[149] first reported the synthesis of a series of six-coordinated rhenium (I) dinitrogen complexes of general formula trans-$ReCl(N_2)(L)_n(L')_{4-n}$ (L= mono or bidentate phosphine, L= L' or CO or PF_3). These complexes were prepared by the degradation of a chelated benzoyldiazenido complex, $ReCl_2(PPh_3)_2(N_2COPh)$. Some of the reactions are shown in Scheme X.



Scheme X

Since methylbenzoate was also a product, a nucleophilic attack of methanol or methoxide ion on the carbonyl carbon was suggested to be one of the steps of these reactions.[71] However, the complete mechanism of the reaction remains unclear.

A different route to prepare analogous complexes involved the reaction of the ammonium salt of enneahydridorhenate(VII) $[NH_4]_2[ReH_9]$ with two equivalents of dppe in 2-propanol under dinitrogen to give the rhenium (I) hydridodinitrogen complex $ReH(N_2)(dppe)_2$.[150]

The compound $CpRe(CO)_2(N_2)$ has been prepared by controlled oxidation of $CpRe(CO)_2(N_2H_4)$ with H_2O_2 in the presence of copper (II) salts[151] or by displacement of the labile THF ligand in $CpRe(CO)_2(THF)$ by dinitrogen under high pressure.[152]

More recently the air-stable cationic complex $[Re(N_2)(PMe_3)_5]^+$ has been synthesized by reaction of $ReCl(PMe_3)_5$ with N_2 in methanol.[59] It has been proposed that $ReCl(PMe_3)_5$ in methanol dissociates to give $[Re(PMe_3)_5]Cl$ which further reacts with dinitrogen at 1 atm to produce $[Re(N_2)(PMe_3)_5]^+$.[59]

As mentioned in Chapter I, $CpRe(CO)_2(N_2)$ has also been prepared in our laboratory by the reaction of the cationic aryldiazenido complex $[CpRe(CO)_2(N_2Ar)]^+$ with some nucleophiles.[9,10]

Using basically the last procedure we have prepared the pentamethylcyclopentadienyl analogue $Cp^*Re(CO)_2(N_2)$ (<u>13a</u>) from the dicarbonyldiazenido complex <u>1a</u> by reaction with $NaBH_4$ or <u>t</u>-BuLi. Furthermore, we have extended this method to the synthesis of a new series of carbonylphosphinedinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$, <u>13b</u> R= Me, <u>13c</u> R= <u>n</u>-Bu, <u>13d</u> R= Cy, <u>13e</u> R= Ph and <u>13f</u> R= OMe. The synthesis and full characterization of these complexes are discussed in this chapter.

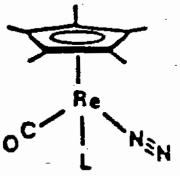
5.2. Synthesis and Characterization

The dinitrogen complexes of general formula $Cp^{*}Re(CO)(L)(N_2)$ with L= CO 13a and L= PR_3 13b-f (R= Me, n-Bu, Cy, Ph and OMe) were synthesized by reaction of the respective cationic aryldiazenido complex $[Cp^{*}Re(CO)(L)(p\text{-}N_2C_6H_4OMe)]^+$ with an excess of reagents such as $NaBH_4$ and t-BuLi for L= CO, and RLi (R= Me and t-Bu) for 13b-f (Method 1). In all cases the dinitrogen complexes were obtained as pale-yellow solids analytically and spectroscopically pure.

BH_4^- could only be used in the formation of $Cp^{*}Re(CO)_2(N_2)$ since, in reaction with the carbonylphosphine diazenido complexes 12a and 12d cleanly gave the hydride complex $Cp^{*}ReH(CO)(N_2Ar)$ with no observable intermediates. In reaction with the dicarbonyl-diazenido complex 1a an intense red color was initially formed that we believe to be the aryldiazene complex $Cp^{*}Re(CO)_2$ $(p\text{-}NHNC_6H_4OMe)$ (IR(acetone): 1914 and 1850 cm^{-1}) which then generates the dinitrogen complex 13a with some $Cp^{*}ReH(CO)(p\text{-}N_2C_6H_4OMe)$ (4). Reaction of $[Cp^{*}Re(CO)(L)(N_2Ar)]^+$ with RLi apparently produces no IR detectable intermediates. However, a second product was formed in competition with the dinitrogen complex $Cp^{*}Re(CO)(L)(N_2)$. We tentatively assign this compound as the hydrazido (2-) complex $Cp^{*}Re(CO)(L)(NN(R)Ar)$. In addition, a second method was used to prepare the dicarbonyl dinitrogen complex 13a. This is similar to that used by Sellmann to prepare $CpRe(CO)_2(N_2)$,[152] and involves direct reaction of $Cp^{*}Re(CO)_2(THF)$ (readily synthesized *in situ* by irradiation of $Cp^{*}Re(CO)_3$ in THF) and dinitrogen under high pressure. One problem associated with this method is the difficulty in separating the dinitrogen complex from the residual tricarbonyl complex, since both species have closely similar molecular weight and properties. However, this method is quick, and is preferred for the preparation of 13a for use in reactions where the $Cp^*Re(CO)_3$ present is inert and can be recovered (see Chapter VI).

The new dinitrogen complexes (13a-f) are very soluble in the majority of organic solvents. As solids, they can be exposed to air for short periods of time without appreciable deterioration and can be stored indefinitely at low temperature (-15°C) under N_2. In solution they are more sensitive to air, especially the phosphine ones. However, solutions under N_2 can be handled for at least one day at room temperature without visible decomposition.

In the IR spectra of these dinitrogen complexes the $\nu(NN)$ of the N_2 ligand is observed as a strong absorption in the 2125-2030 cm^{-1} region (Table V). This region is typical for $\nu(NN)$ of terminal dinitrogen complexes where the N_2 ligand is coordinated in an end-on (η^1) fashion as shown below.



13

The assignment of $\nu(NN)$ has been confirmed by ^{15}N isotopic

Table V. Some Spectroscopic Parameters of the Dinitrogen Complexes Cp*Re(CO)(L)(N_2).

Cp*Re(CO)(L)(N_2)	IR (hex) cm^{-1}	^1H NMR (δ Cp*)[a]	^{31}P NMR ($CDCl_3$)[b]	^{13}C NMR (δ(CO))[a]	MS (EI)[c]
L = CO, <u>13a</u>	2124 ν(NN)[d], 1953, 1901 ν(CO)[f]	2.07 s	-	200.08	406
<u>13a</u>-^{15}N	2091 ν(^{15}NN), 1953, 1901 ν(CO)	-	-	-	407
L = PMe_3, <u>13b</u>	2043 ν(NN), 1864 ν(CO)	1.99 d (J= 0.7)[h]	-29.81	207.16 d (J= 7.0)[h]	454
<u>13b</u>-$^{15}N_{\alpha}$	2010 ν(^{15}NN), 1864 ν(CO)	-	-	-	455
L = P(n-Bu)$_3$, <u>13c</u>	2040 ν(NN), 1863 ν(CO)	1.95 s	-0.21	208.24 d (J= 7.7)	580
L = Cy_3, <u>13d</u>	2030 ν(NN), 1856 ν(CO)	1.92 s	22.03	209.80 d (J= 8.5)	658
L = PPh_3, <u>13e</u>	2058[d], 2045[g] ν(NN), 1866 ν(CO)[i]	1.73 s	32.20	207.41 d (J= 8.8)	640
L = P(OMe)$_3$, <u>13f</u>	2078[g], 2066[d] ν(NN), 1878 ν(CO)[i]	1.99 d (J= 0.8)	139.01	204.90 d (J= 12.4)	502
<u>13f</u>-$^{15}N_{\alpha}$	2045[g], 2033[d] ν(^{15}NN), 1878 ν(CO)[i]	-	-	-	503

Abbreviations: s= singlet, d= doublet. [a] TMS as reference in $CDCl_3$. [b] 85% H_3PO_4 as reference δ, down field positive. [c] m/z based on ^{187}Re (70 eV). [d] strong. [f] very strong. [g] medium. [h] Coupling constants (J) in Hz. [i] Asymmetric Band.

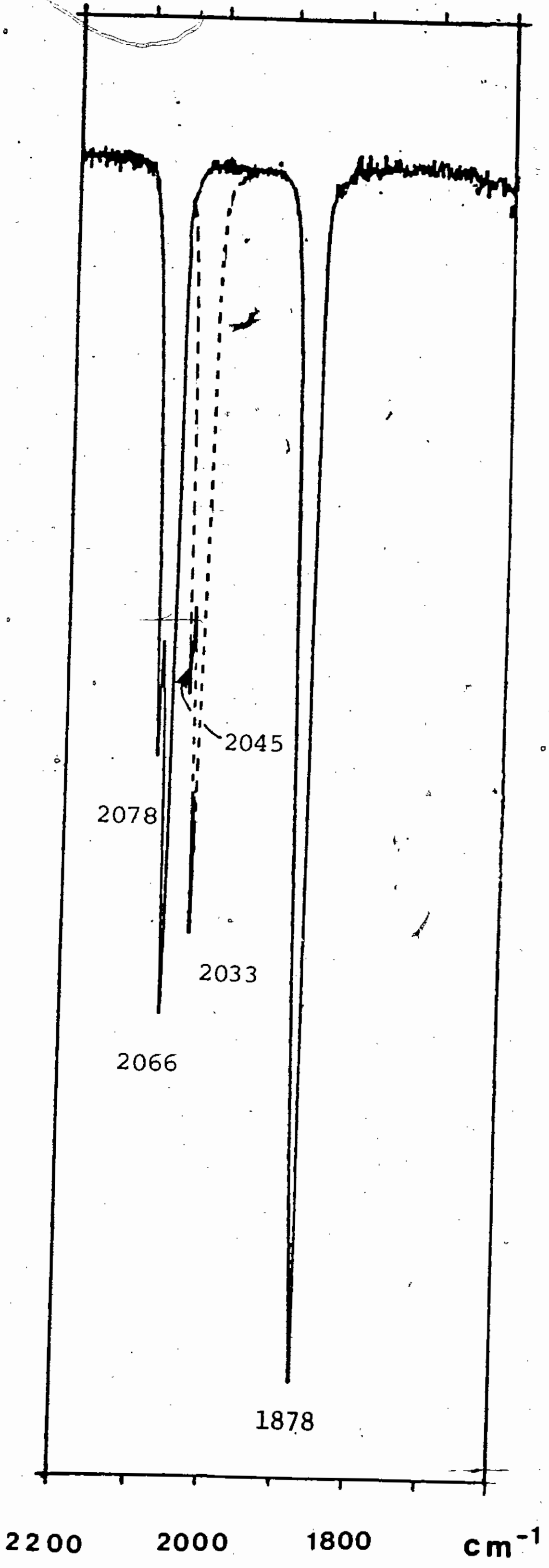
substitution at N_α in 13b and 13f and at both N_α and N_β positions in 13a (see below). In the three cases a shift of ν(NN) by 33 cm^{-1} to lower wavenumber was observed. This shift is similar to those observed in the complexes $RhCl(PPr_3{}^i)_2(N_2)$, $\Delta\nu(NN) = \nu(^{14}N^{14}N) - \nu(^{15}N^{14}N) = 35\ cm^{-1}$ [54] and in $CpRe(CO)_2(N_2)$, where $\Delta\nu(NN) = 33\ cm^{-1}$.[27]

Curiously, the ν(NN) absorption of the triphenylphosphine (13e) and trimethylphosphite (13f) dinitrogen complexes occurs as two closely spaced bands in non-polar organic solvents such as hexane and cyclohexane. In the former case the strong band at 2058 cm^{-1} is accompanied by a medium absorption at lower wavenumber, 2045 cm^{-1}. In the latter the strong band at 2066 cm^{-1} has the medium intensity band occurring at higher wavenumber, 2078 cm^{-1} (Fig.8). Interestingly, exactly the same pattern is observed in 13f-$^{15}N_\alpha$, but shifted by 34 cm^{-1} (see Fig.8). Thus, both absorptions are shifted to lower wavenumber and on this basis both must be assigned to ν(NN). Variable temperature IR studies using solutions of 13f in pentane show that the relative peak heights of these components vary from 0.5:1 at -100°C to 0.73:1 at room temperature. The relative heights in cyclohexane at room temperature and +60°C show no significant change in the ratio. The origin of the additional ν(NN) absorption in these complexes will be considered in the Discussion section.

In the ν(CO) region the carbonylphosphinedinitrogen complexes show a single and very strong absorption between 1878 and 1856 cm^{-1} (Table V). However, 13e and 13f show a second

Fig.8. IR spectra of Trimethylphosphitedinitrogen Complexes: $Cp^*Re(CO)(P(OMe)_3)(N_2)$ (<u>13f</u>) and $Cp^*Re(CO)((P(OMe)_3)(^{15}NN)$ (<u>13f</u>-$^{15}N_\alpha$) (2200-1600 cm^{-1} region; hexane solution). Full line: $Cp^*Re(CO)(P(OMe)_3)(N_2)$ (<u>13f</u>). Dashed line: $Cp^*Re(CO)(P(OMe)_3)(^{15}NN)$ (<u>13f</u>-$^{15}N_\alpha$).

113b

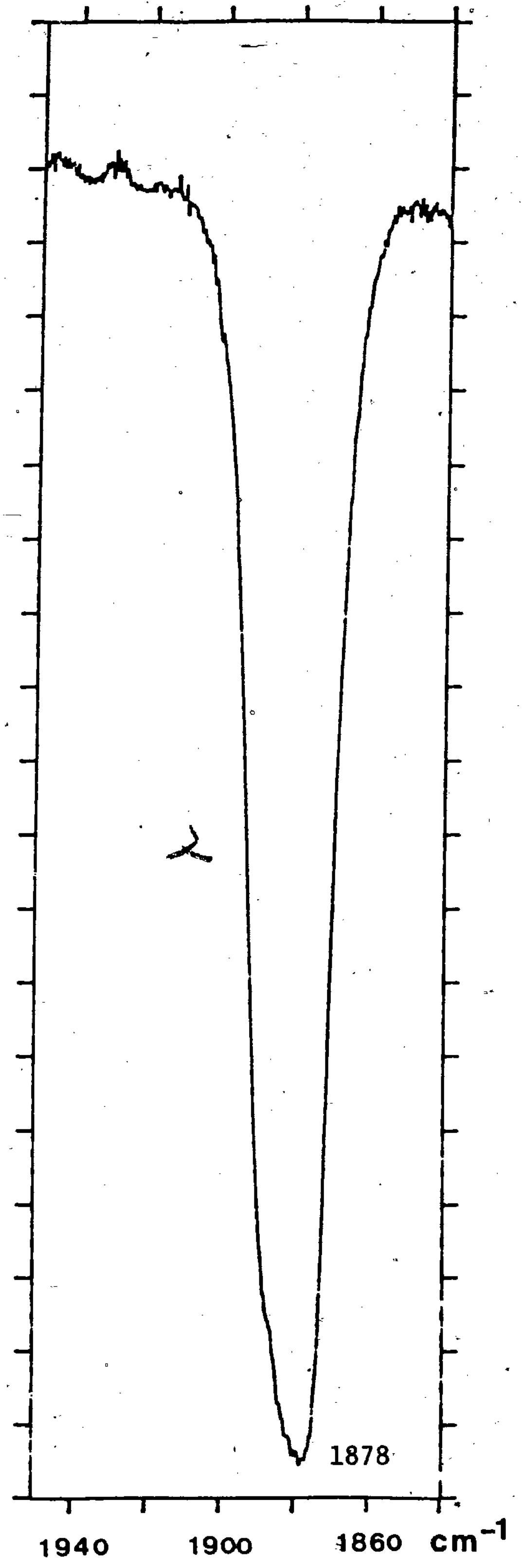


unresolved ν(CO) band which appears as a shoulder. This is illustrated in Fig.9 for 13f. The dicarbonyldinitrogen complex 13a, as expected, exhibits two very strong ν(CO) absorptions at 1953 and 1901 cm^{-1} in hexane solution.

The ^1H NMR spectra of these compounds show no unusual features. In general, a single resonance or doublet with very small coupling to phosphorus ($J_{PH} \approx 0.7$) is observed for the Cp^* groups (see Table V). The presence of the phosphorus ligands in 13b-f is clearly observed not only in the ^1H NMR spectra but also in the ^{31}P NMR spectra where a single resonance is observed in all the cases (Table V). In the $^{13}C\{^1H\}$ NMR spectrum the carbonyl carbon resonance occurs at low field (δ (^{13}CO): 200-210); it is a single line in 13a and a doublet for the phosphine complexes as expected (Table V).

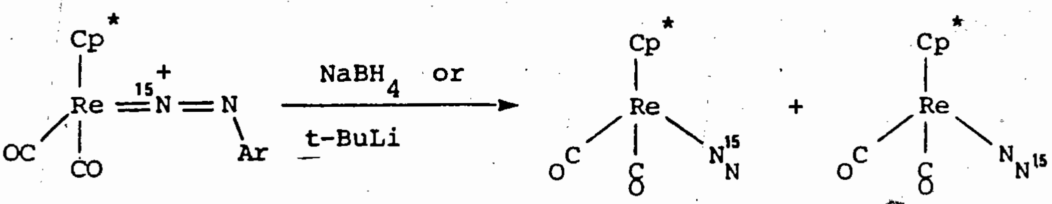
Three of these compounds (13a, 13b and 13f) were also studied by ^{14}N and ^{15}N NMR. In the ^{14}N NMR spectra the dicarbonyl 13a, trimethylphosphine 13b and trimethylphosphite 13f exhibit in each case two broad resonances at about δ -110 to -90 and δ -30 to -28 assigned to N_α and N_β respectively. The former assignment was confirmed by recording the ^{15}N NMR spectra of 13b-$^{15}N_\alpha$ and 13f-$^{15}N_\alpha$ and in both cases a sharp line, with no coupling to phosphorus was observed in almost exactly the same position as the ^{14}N resonances observed for $^{14}N_\alpha$ in the unenriched samples i.e. δ -110 to -90 (see Table VI). Furthermore, the position of N_α and N_β resonances are in the region observed in other studies of dinitrogen complexes by ^{15}N NMR.[27,52,66,76] Some of these

Fig.9. IR spectrum of Trimethylphosphitedinitrogen Complex $Cp^{*}Re(CO)(P(OMe)_3)(N_2)$ (<u>13f</u>) (1950-1840 cm^{-1} region, hexane solution).


1878
1940
1900
1860
cm⁻¹

examples are included for comparison in Table VI.

Unexpectedly the presence of two ^{15}N resonances of equal intensity (corresponding unequivocally to $^{15}N_\alpha$ and $^{15}N_\beta$) was observed in the dicarbonyldinitrogen complex <u>13a</u>-^{15}N but not in the two carbonylphosphine complexes (<u>13b</u>-$^{15}N_\alpha$ and <u>13f</u>-$^{15}N_\alpha$) examined. However, as was mentioned before, all these complexes were prepared by the same procedure from the cationic dicarbonyl- or carbonylphosphine-aryldiazenido complex labelled specifically at N_α i.e. <u>1a</u>-$^{15}N_\alpha$, <u>12a</u>-$^{15}N_\alpha$ and <u>12e</u>-$^{15}N_\alpha$, using <u>t</u>-BuLi. For <u>1a</u>-$^{15}N_\alpha$, $NaBH_4$ was also used with identical results. Evidently, in the case of <u>1a</u>-$^{15}N_\alpha$, the reaction proceeds with scrambling of the ^{15}N label equally between the N_α and N_β sites in the dinitrogen ligand (Eq.21).



Eq.21.

Analogous reaction of the carbonylphosphinearyldiazenido complexes (<u>12a</u>-$^{15}N_\alpha$ and <u>12e</u>-$^{15}N_\alpha$) with <u>t</u>-BuLi gave only the dinitrogen complex labelled at N_α position.

Further characterization of these dinitrogen complexes was obtained by mass spectra. In all the cases the molecular ion was observed as a weak peak and the base peak was the loss of the dinitrogen ligand $(M-28)^+$; this was confirmed by the loss of ^{15}NN i.e. $(M-29)^+$ from <u>13a</u>-^{15}N, <u>13b</u>-$^{15}N_\alpha$ and <u>13e</u>-$^{15}N_\alpha$.

Table VI. Nitrogen-15 Chemical Shifts of Dinitrogen Complexes.[a]

Compound	$\delta(^{15}N_\alpha)$	$\delta(^{15}N_\beta)$	Solvent	Ref.
$Cp^*Re(CO)(L)(N_2)$				
L = CO, (13a)	-110.9 (-110.9)	-28.1 (-26.0)	acet./acet.-d_6	t/w[c]
L = PMe_3, (13b)	-90.7 (-90.2)	(-29.4)	"	t/w
L = $P(OMe)_3$, (13f)	-98.2 (-98.3)	(-30.5)	"	t/w
$CpRe(CO)_2(N_2)$	-121.12	-58.18	"	27
trans-$ReCl(N_2)(PMe_2Ph)_4$	-86.1	-67.6	THF	66
trans-$ReCl(N_2)(dmtpe)_2$	-91.4	-69.1	CH_2Cl_2	52
$ReCl(N_2)(CO)(C(OH)Me)(PPh_3)_2$	-111.2	n/o[b]	THF	52
trans-$[FeH(N_2)(dppe)_2]^+$	-61.1	-37.9	"	66
mer-$OsBr_2(N_2)(PMe_2Ph)$	-120.3	-66.8	"	66
trans-$W(N_2)(L)(dppe)_2$				
L = N_2	-60.1	-48.6	"	76
L = NCMe	-42.3	-55.5	"	76
L = NCPh	-28.1	-56.3	"	76
trans-$Mo(N_2)(L)(dppe)_2$				
L = N_2	-43.1	-42.8	"	52
L = NCMe	-31.2	-34.0	"	76
L = NCPh	-24.0	-33.0	"	76

[a] Chemical shifts relative to external CH_3NO_2. [b] n/o= not observed. [c] This work.

The N_2-ligand in these pentamethylcyclopentadienyl complexes appears to be inert to ligand exchange. Thus, hexane solutions of 13a-^{15}N and 13b-$^{15}N_\alpha$ saturated with $^{14}N_2$ at room temperature show no observable $\nu(^{14}N^{14}N)$ IR absorptions for 13a and 13b respectively, even when pressurized to 2000 psi of $^{14}N_2$ for 24 h; similar behaviour is observed in the cyclopentadienyl complex $CpRe(CO)_2(N_2)$. The dinitrogen ligand is not displaced by PPh_3 in 13a, 13b and 13f even after stirring for one day at room temperature in ether solution, whereas in $CpRe(CO)_2(N_2)$ the N_2-ligand is completely displaced in 6 h under similar conditions.

5.3. Discussion

The synthetic method used for the preparation of the cyclopentadienyldicarbonylrhenium dinitrogen complex $CpRe(CO)_2(N_2)$ by reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with some nucleophiles,[9] has allowed us to synthesize not only the pentamethylcyclopentadienyldicarbonyl analogue (13a) but also the new carbonylphosphinedinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$ (13b R= Me, 13c R= n-Bu, 13d R= Cy, 13e R= Ph and 13f R= OMe) using the corresponding aryldiazenido complex in reaction with alkyllithiums. The synthesis of the phosphinedinitrogen complexes 13b-f by this method is remarkable as we do not expect these types of dinitrogen complexes to be prepared by conventional carbonyl substitution in $Cp^*Re(CO)_2(N_2)$ under thermal or photochemical conditions, since the N_2 ligand ought to be preferentially substituted.

The new dinitrogen complexes 13a-f provide, in addition, a very convenient starting point for the synthesis of other compounds containing the Cp*Re(CO)(L) fragment as will be see in the following chapters.

In general, these complexes exhibit spectroscopic properties (especially IR and nitrogen-NMR parameters) comparable to those observed in a large number of mononuclear dinitrogen complexes of transition metals.[1,5] For example, the IR spectrum of the dicarbonyl dinitrogen complex 13a can be compared with the known cyclopentadienyl analogue $CpRe(CO)_2(N_2)$. As expected, the ν(NN) and ν(CO) values of 13a (see Table V) are consistently lower than those observed for the $CpRe(CO)_2(N_2)$ (2141 ν(NN), 1970, 1915 ν(CO), cm^{-1}, in hexane)[9,151] and are indicative of the greater electron releasing ability of the Cp* ligand. A similar trend has been observed for the complexes (η-aryl)$Cr(CO)_2(N_2)$, aryl= C_6H_6, $C_6H_3Me_3$ and C_6Me_6.[153] Unfortunately, there are not at present Cp analogues of the Cp* carbonylphosphine dinitrogen complexes (13b-f) to use for a more general comparison. However, the relative order of σ-donor (or π-acceptor) abilities of the phosphorus ligands are revealed in the decrease in both ν(NN) and ν(CO) as the phosphine is varied from $P(OMe)_3$, PPh_3, $P(n\text{-}Bu)_3$, PMe_3 to PCy_3 (Table V). According to the electron-richness and -poorness criterion used by Chatt et al.,[63-65] the dicarbonyl complex 13a is the most electron poor (ν(NN)= 2124 cm^{-1}) whereas the cyclohexylphosphine 13d is the most electron-rich (ν(NN)= 2030 cm^{-1}).

It was pointed out in the characterization section that two resolved ν(NN) absorptions occur in the IR spectra of the triphenylphosphine 13e and triphenylphosphite 13f (along with an unresolved shoulder in ν(CO)), whereas the spectra of the PMe_3, $P(\underline{n}\text{-}Bu)_3$ and PCy_3 complexes (13b, 13c and 13d) show no such complication. These secondary ν(NN) absorptions might be expected to occur as a result of (a) the presence of an impurity having ν(NN) in the region similar to the phosphine complex, perhaps $Cp^*Re(PR_3)_2(N_2)$ or $Cp^*Re(PR_3)(N_2)_2$ or (b) the presence of a second isomer, or conformer. The presence of an impurity can be eliminated since repeated crystallization of both complexes does not alter their IR spectra. Furthermore, the ^1H, ^{13}C and ^{31}P NMR spectra of these complexes show only the presence of a single compound.

These results lead us to postulate that isomers or conformers are present in solution for these dinitrogen complexes.

An examination of the literature on carbonylphosphine and carbonylphosphite metal complexes revealed numerous examples of the occurrence of secondary ν(CO) absorptions.[154-157] These have been attributed to the presence of two conformational isomers in solutions. It appears virtually definite that we are observing a similar effect in the ν(NN) absorption in our complexes. The complexes 13e and 13f therefore appear to provide the first documented examples where conformational effects are observed in ν(NN) of dinitrogen complexes, though it should be mentioned that two ν(NN) absorptions were cited to occur for the complex trans-$[ReCl(N_2)(PMe_2Ph)_4]^+$ (2040 and 2010 cm^{-1}, in $CHCl_3$), but without comment.[71]

The most closely comparable carbonyl complexes in the literature exhibiting this effect (ie., examples containing the CpM(CO) fragment with $P(OMe)_3$ or PPh_3 coligands) are $(C_5H_4Me)Fe(CO)(P(OMe)_3)I$ and $(C_5H_4Me)Fe(CO)(PPh_3)I$.[157] The former exhibits ν(CO) absorptions at 1978 and 1966 cm^{-1} in n-heptane solution with an intensity ratio of 0.49:1. On cooling to −80°C a 0.29:1 ratio was then observed.[157] Similarly, in the $(C_5H_4Me)Fe(CO)(PPh_3)I$ complex the ν(CO) absorption is split in n-heptane solution (1961, 1955 cm^{-1} in a ratio 1:0.8.[157] Furthermore, $CpFe(CO)(CN)(PPh_3)$ shows an asymmetric ν(CO) at 1969 cm^{-1} in $CHCl_3$ solution.[156] Another related system where comparable effects have been observed is $(1,6\text{-}C_7H_8)Mo(CO)_2(P(OPh)_3)$.[158]

Considering first the $P(OMe)_3$ case, it has been commonly found by crystallography that the $P(OMe)_3$ ligand can adopt a "two down-one up" arrangement of the methyl groups.[154a] The asymmetry observed in the solid state for $Ru(CO)_4(P(OMe)_3)$ is also maintained (on the IR time scale) in solution since, the equatorial CO groups give rise to two ν(CO) absorptions.[154a] On the other hand, the reverse arrangement, e.g., "two up-one down", has also been observed, in the solid state, in crowded molecules such as $Ni(P(OMe)_3)_4Br$.[154b] In addition, in both arrangements the oxygen atoms are commonly disordered (but usually not the methyl groups).

In the case of the trimethylphosphite complex **13f**, considering steric hindrance of the Cp* group with the methyl groups of the $P(OMe)_3$ a "two up-one down" arrangement seems the more plausible. Coupled with oxygen disorder, this would give the two conformers, which are shown in Newman projection in Fig.10.

Fig.10. Conformational isomers of the trimethylphosphitedinitrogen complex Cp*Re(CO)(P(OMe)$_3$)(N$_2$) (<u>13f</u>). The positions of the Cp*, N$_2$, CO, and methyls are identical but the oxygen positions are disordered with respect to the P-Me vectors.

If the two different conformational isomers for complex <u>13f</u> (Fig.10) are present in solution, two different ν(NN) absorptions would be generated as is observed. The presence of a second conformer is also revealed in the shoulder in the ν(CO) band of this complex (see Fig.9). Upon cooling to -110°C in pentane solution this shoulder disappeared and at the same time the intensities of the ν(NN) absorption at 2066 cm^{-1} and ν(CO) at 1878 cm^{-1} were increased by about 25%, indicating the preferential population of one conformer at low temperature.

Turning to the PPh$_3$ ligand, as was anticipated conformational effects have also been observed in other triphenylphosphine-containing complexes.[156,157] In these cases restricted rotation about the phosphorus-carbon bond (ring flip) has been proposed to generate different conformers in solution.[156,159] The phenyl rings of the PPh_3 ligand, can adopt a "propeller-like" conformation which may be that of a right- or a left-handed helix as shown in Fig.11 for $Cp^*Re(CO)(PPh_3)(N_2)$. These two conformers are believed to be responsible for the observed two ν(NN) absorptions and the asymmetry observed in ν(CO).

Fig.11. Conformational isomers of the triphenylphosphinedinitrogen complex $Cp^*Re(CO)(PPh_3)N_2)$ (<u>13e</u>).

In the ^{13}C NMR spectra of these dinitrogen complexes (<u>13</u>a-f) the replacement of one carbonyl in <u>13a</u> by a phosphorus ligand produces a low-field shift of the carbon resonance of the remaining CO group (see Table V). This trend is similar to that observed in the aryldiazenido precursors which was discussed in the preceding chapter. A similar effect is also observed in the N_α (^{15}N or ^{14}N) resonance of the N_2-ligand in the ^{14}N or ^{15}N NMR spectra (see Table VII). In contrast, the resonance for N_β remains unchanged. Therefore, varying the electron density on the metal produces smaller changes in δ (N_β) than those observed in δ (N_α). This is consistent with previous results covering a wide range of dinitrogen complexes so far studied by ^{15}N NMR

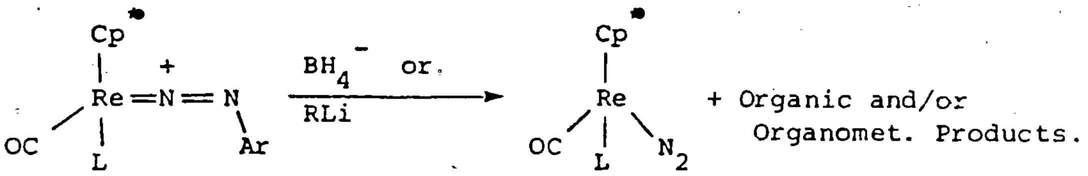
Table VII. Chemical Shifts of the Carbonyl Carbon Resonance and N_α N_β Nitrogen Resonances of the Dinitrogen Complexes.

$Cp^*Re(CO)(L)(N_2)$	δ (^{13}CO)[a]	δ (N_α)[b]	δ (N_β)[b]
L = CO	200.08	-110.9 (-110.9)[c]	-28.1 (-26.0)
L = $P(OMe)_3$	204.90	-98.2 (-98.3)	(-30.5)
L = PMe_3	207.16	-90.7 (-90.2)	(-29.4)

[a] In $CDCl_3$ solution. [b] In acetone/acetone-d_6 solution. [c] Data in parentheses is from ^{14}N NMR.

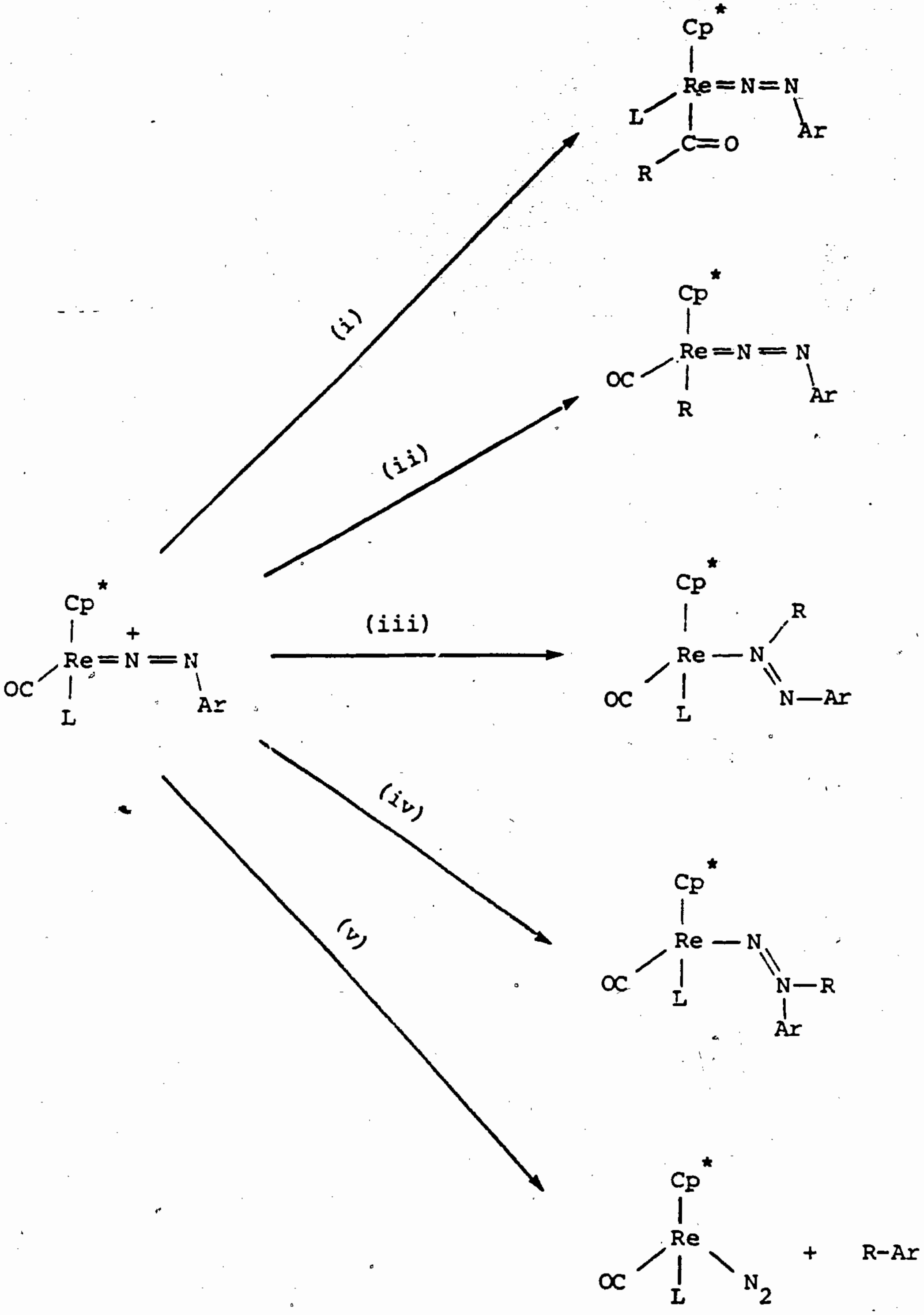
spectroscopy.[52,76] Some of these complexes are listed in Table VI.

The mechanism of the reaction of the cationic aryldiazenido complexes with BH_4^- or RLi to produce the dinitrogen complexes (Eq.22) is not yet understood, but some preliminary suggestions can be made.



Eq.22.

First, we will consider that nucleophilic attack on the cationic aryldiazenido complex occurs as a first step, which may be followed by some type of rearrangement to give the N_2-complex. If that is the case, several sites of possible attack can be considered (Scheme XI).



Scheme XI

In (i), attack at the CO group to form the acyl or formyl complex, and in (ii) attack at the metal, with substitution of ligand L, produces a monocarbonyl alkyl or hydride complex. Alternatively, if attack occurs at the aryldiazenido group, there are three potential sites for nucleophilic attack: (iii) at N_α to give the diazene complex; (iv) at N_β to form the hydrazido (2-) complex, and (v) at the ipso carbon of the aromatic ring to give the N_2-complex and the substituted anisole.

Obviously, reaction (v) is the simplest mechanism to consider for the formation of the dinitrogen complex. Indeed, this type of mechanism was suggested by Chatt et al. to occur in the only other example that we know of, in which a diazenido ligand is transformed into dinitrogen.[71] This is the reaction of the aryldiazenido complex $ReCl_2(PPh_3)_2(N_2COPh)$ with phosphines in methanol, previously illustrated in Scheme X. It was suggested that this reaction is initiated by nucleophilic attack of methanol or methoxide ion on the carbonyl carbon since methylbenzoate was also produced. Using methyllithium as nucleophile only a small amount of the dinitrogen complex was formed, together with decomposition products. The efficiency of the reaction is very dependent on the nature of the nucleophile, and on the phosphine ligands.[71] How these factors influence the production of the dinitrogen complex is unclear and so is the mechanism of the reaction.

In our case, comparable factors determine the capacity of the aryldiazenido complexes to produce the dinitrogen complexes. On the basis of IR data and isolated products, it is clearly evident that the course of the reaction is very dependent upon the ligand L and on the nucleophile used. For a better understanding, the reactions with BH_4^- and alkyllithiums will be considered separately.

(a) Reactions using BH_4^-

Reactions of BH_4^- with cationic aryldiazenido complexes were carried out with the dicarbonyl 1a and with two of the phosphine complexes: PMe_3 complex 12a and the PPh_3 complex 12d. Complex 1a shows a very different course of reaction from that of the phosphines 13a and 13d.

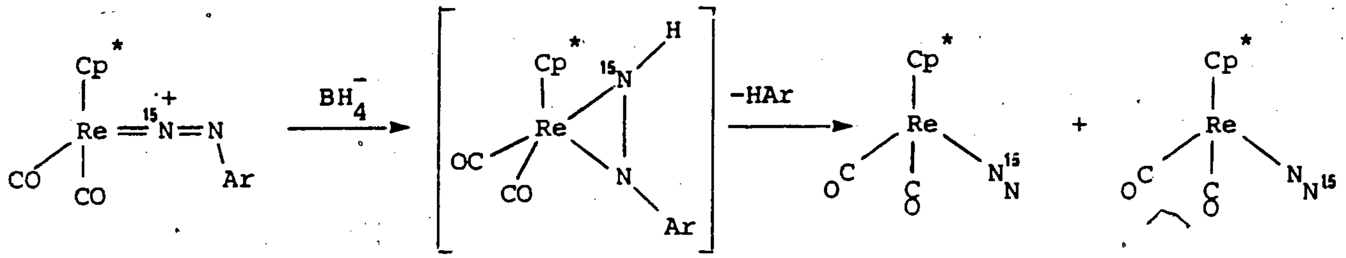
The phosphinearyldiazenido complexes 12a and 12d react cleanly to give yellow solutions from which the hydrido complex $Cp^*ReH(CO)(N_2Ar)$ 4 is formed by displacement of the phosphine ligand. These reactions therefore seem to proceed by route (ii) in Scheme XI. The dicarbonyl 1a, on the other hand, reacts with BH_4^- in acetone to give a red solution having IR bands at 1850 and 1914 cm^{-1} that we assign to the aryldiazene complex $Cp^*Re(CO)_2(NHNAr)$ by comparison with a similar red intermediate $CpRe(CO)_2(NHNAr)$ formed in the reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with BH_4^-.[10] The reaction proceeds further, with loss of the red intermediate and the formation of the dinitrogen complex 13a and the hydrido complex 4. The latter can be synthesized by alternative routes (see Chapter III) and has been shown not to convert to the dinitrogen complex 13a in the presence or absence of BH_4^-; so it cannot be precursor to the dinitrogen complex in this reaction. In agreement, IR evidence shows that both 13a and 4 are formed competitively. It is possible that the diazene complex is formed by route (iii). However, attempts to isolate this compound were unsuccessful due to its low thermal stability. Likewise, we had no success in characterizing this complex by ^{1}H NMR.

What is perhaps surprising is that the dicarbonyl and phosphine aryldiazenido cations show no evidence of undergoing reactions analogous to those of the closely related nitrosyl complexes $[CpRe(CO)_2(NO)]^+$ and $[Cp^*Re(CO)(PPh_3)(NO)]^+$ with BH_4^-. The former has been shown to be capable of stepwise reduction of the CO group by BH_4^- to HCO, CH_2OH and CH_3 ligands.[95] The methyl derivative of the latter compound was prepared in a similar manner.[96] We observe no unaccountable ν(CO) or ν(NN) IR absorptions, and furthermore we have synthesized, by an alternative procedure, the methyl complex $Cp^*Re(CO)(Me)(p\text{-}N_2C_6H_4OMe)$ to demonstrate that it is not a product of the BH_4^- reaction with 1a. Pathway (i) therefore does not appear to be followed.

Assuming that the reaction of 1a is analogous to the reaction of $[CpRe(CO)_2(N_2Ar)]^+$ with BH_4^- to give the diazene complex then pathway (iv) can be ruled out. This constrasts with the reaction with MeLi where the hydrazido (2-) complex $Cp^*Re(CO)_2(NN(Me)Ar)$ could be isolated (see below).

Although the simplest nucleophilic mechanism for the formation of the dinitrogen complex with BH_4^- is route (v), the above evidence does not support such a mechanism. Rather, the decay of the IR of the diazene complex into that of 13a suggests that the diazene complex is an intermediate in this reaction. GC analysis of this reaction mixture indicated that anisole is formed among other unidentified organic products.

At present we do not know whether the elimination of anisole is intermolecular or intramolecular. When the $^{15}N_\alpha$ labelled diazenido complex, 1a-$^{15}N_\alpha$ was used the label was scrambled in the dinitrogen product equally between the α and β positions (13a-^{15}N). If the elimination of anisole from the diazene complex is intramolecular this suggests the possibility of elimination from an η^2-coordinated diazene ligand (see Eq.23).



Eq.23.

An η^2-coordination mode of the diazene ligand has never been observed. All previously reported aryldiazene complexes have been shown, or are believed to be, η^1-bonded to the metal. In the case of $CpRe(CO)_2(NHNAr)$ a η^2-coordination mode was suspected but it could not be confirmed from the spectroscopic data.

The additional possibility that the label is scrambled in the dinitrogen complex itself by a dissociative mechanism can be ruled out since there is no observable exchange of the $^{15}N^{14}N$ complex (13a-^{15}N) with $^{14}N_2$.

(b) Reactions with Alkyllithiums

Tert-butyllithium was used in reactions with all the cationic aryldiazenido complexes (1a and 12a-e). In addition, reactions using methyllithium were carried out with the dicarbonyl cation 1a and the trimethyl and triphenylphosphine cations 12a and 12d. Here there is a much closer correspondence between the dicarbonyl and the carbonylphosphine in the products that are formed.

Acyl derivatives of the type $Cp^*Re(L)(COR)(N_2Ar)$ L= CO and phosphine, R= Me or t-Bu, were never observed in reactions of the cationic aryldiazenido complexes (1a, 12a-f) with alkyllithiums, under any of the conditions used (pathway (i) in Scheme XI). This contrasts with the reaction between $[CpRe(CO)_2(N_2Ar)]^+$ and RLi (R= Me, n-Bu and Ph) where the corresponding acyl derivatives were formed in competition with the hydrazido (2-) complex $CpRe(CO)_2(NN(R)Ar)$ and the dinitrogen complex $CpRe(CO)_2(N_2)$.[10]

Next, route (ii) in Scheme XI can be discarded since no evidence was found for the formation of alkylmonocarbonyl complexes $Cp^*Re(CO)(R)(N_2Ar)$ in reactions with 1a, nor for alkylmonocarbonyl or alkylphosphine complexes $Cp^*Re(L)(R)(N_2Ar)$ (L= CO or phosphine) in reactions with the carbonylphosphine cations. Furthermore, as mentioned previously we know that the methyl complex $Cp^*Re(CO)(Me)(N_2Ar)$ synthesized separately, is stable.

From the reaction of the dicarbonyl cation 1a with MeLi in hexane at room temperature the hydrazido (2-) complex $Cp^*Re(CO)_2[NN(Me)(p\text{-}C_6H_4OMe)]$ was isolated in low yield and characterized by IR, ^1H NMR and MS (see Experimental Section). IR evidence for a similar complex using t-BuLi was obtained (1935, 1861 cm^{-1}, in hexane) using the same conditions. Therefore, the reaction under these conditions seems to proceed according to route (iv) in Scheme XI. In both cases a small amount of the dinitrogen complex 13a was also formed. When the reaction of 1a with t-BuLi was carried out in THF at 60°C only a small amount of the hydrazido (2-) complex was observed (by IR). The major product was the dinitrogen complex 13a, which was isolated in 31% yield. To demonstrate that the formation of 13a does not occur through decomposition of the hydrazido (2-) complex, the complex $Cp^*Re(CO)_2(NN(Me)Ar)$ was boiled in THF in the presence and in the absence of t-BuLi; in neither case was the dinitrogen complex observed. This clearly indicates that the formation of the dinitrogen complex and the hydrazido (2-) complexes from the reaction of 1a with alkyllithiums occur independently, and the ratio dinitrogen:hydrazido (2-) formed depends on the solvent and temperature.

Reactions of the cationic carbonylphosphinediazenido complexes 12 with alkyllithiums seem to follow the same behaviour. For example, with t-BuLi at 60°C in THF solution the corresponding dinitrogen complex $Cp^*Re(CO)(PR_3)(N_2)$ was always the major product. However, the IR spectrum of the crude shows, in addition to ν(NN) and ν(CO) of the dinitrogen complex, a weak or medium absorption at about 1800 cm^{-1} which we believe is due to ν(CO) of the corresponding hydrazido (2-) complexes $Cp^*ReCO(PR_3)(NN(R)Ar)$. These species could not be isolated since they decomposed in the process of purification of the dinitrogen complex by column chromatography. Reactions of the trimethyl or triphenylphosphine diazenido complexes (12a or 12d) with MeLi in THF, but at room temperature, produced a red solution which contained the "hydrazido (2-)" species in about 80% conversion (by IR), with the rest being the dinitrogen complex. However, these products were too unstable to isolate. A partially purified sample derived from 12d (by extraction in hexane) gave no satisfactory MS or ^{1}H NMR. Decomposition of these hydrazido (2-) complexes in hexane or $CDCl_3$ solution did not increase the amount of dinitrogen complex initially present. This again indicates that the behaviour already observed in the dicarbonyl system with alkyllithiums is independent of the CO or phosphine ligand in the precursor cationic aryldiazenido complex, and in no case is the hydrazido (2-) complex a precursor to the dinitrogen complex. GC and GC-MS analyses of the reaction of the trimethylphosphine complex 12a with *t*-BuLi in THF at 60°C, indicated the presence of several organic products. Only anisole has been positively identified from the analyses. None of the remaining products correspond to *para*-*t*-butylanisole, which is the expected product if nucleophilic attack occurred at the ipso carbon of the aromatic ring. Therefore, pathway (v) in Scheme XI can be ruled out.

In summary, the limited evidence presently available seems to suggest that when BH_4^- is used, the reaction with $[Cp^*Re(CO)_2(N_2Ar)]^+$ (1a) proceeds by route (iii) with the formation of the diazene complex $Cp^*Re(CO)_2(NHNAr)$ which subsequently decomposes to the dinitrogen complex **13a** and anisole. Remarkably, the substitution of one CO by a phosphine ligand appears to block this reaction, as none of either the corresponding diazene or dinitrogen complex is observed, and instead the reaction proceeds cleanly by route (ii) to form the hydrido complex $Cp^{*}Re(CO)(H)(N_2Ar)$ (**4**) by displacement of the phosphine.

When *t*-BuLi is used the evidence indicates that a hydrazido (2-) ligand is capable of being formed, presumably by route (iv), but that this is not an intermediate in the formation of the dinitrogen complex. The mechanism of this reaction is still far from being understood and since anisole is observed in the reaction also, it seems likely that a radical mechanism is involved.

5.4. Experimental Section

Manipulations, solvent purification, and spectroscopic measurements were done as described in Chapter II. Variable temperature infrared experiments were performed on a Bruker IFS-85 FT-IR instrument (internally calibrated with a He/Ne laser) using a Specac variable temperature IR cell. Methyllithium (2.4 M in ether) and *t*-butyllithium (1.95 M in pentane) were purchased from Aldrich and used as received.

Preparation of $Cp^{*}Re(CO)_2(N_2)$ (**13a**) and (**13a**-^{15}N)

Method 1. An excess of solid $NaBH_4$ (15 mg, 0.395 mmol) was added to a solution of **1a** or **1a**-$^{15}N_\alpha$ (100 mg, 0.167 mmol) in acetone or acetonitrile (15 mL). An immediate intense red color formed (IR, acetone: 1914 s, 1850 s, cm^{-1}), which gradually decreased in intensity during 1 h of stirring at room tenperature. Hexane (30 mL) was then added, stirring was continued until the red color disappeared, and the supernatant was yellow. IR showed that this was mainly the dinitrogen complex with some $Cp^*ReH(CO)(N_2Ar)$ (4). Chromatography on a silica gel column prepared in hexane with hexane elution moved the dinitrogen complex (13a) and the organic side-products. A GC-MS analysis at this stage showed the presence of 13a, anisole and other unidentified organic products. Recrystallization from hexane-pentane (1:1) at -20°C gave the product as pale-yellow crystals in 44% yield (45 mg). M.p. 106-108°C. IR (hexane): 2124 s (2091 in 13a-^{15}N) $\nu(NN)$, 1953 vs, 1901 vs, $\nu(CO)$ cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.07 s, Cp^*. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.36 ($C_5\underline{Me}_5$), 96.23 ($\underline{C}_5Me_5$), 200.08 ($\underline{C}O$). ^{14}N NMR (acetone/acetone-d_6): δ -110.9 br, s (N_α), -26.0 br,s (N_β). ^{15}N NMR for 13a-^{15}N (acetone/acetone-d_6): δ -110.9 s ($^{15}N_\alpha$), -28.1 s ($^{15}N_\beta$). MS (EI): m/z 406 (407 in 13a-^{15}N) M^+, 378 $(M-^{14}N_2)^+$ in 13a or $(M-^{15}N^{14}N)^+$ in 13a-^{15}N. Anal. Calcd. for 13a: C, 35.55; H, 3.70; N, 6.91. Found: C, 35.62; H, 3.79; N, 6.58.

Method 2. $Cp^*Re(CO)_3$ (600 mg, 1.48 mmol) was irradiated in 300 mL of fresh distilled THF for 120 min at 0°C under N_2 purge. (This time is sufficient to provide a reasonable conversion to the $Cp^*Re(CO)_2(THF)$ complex without too much ensuing decomposition.) The volume was reduced to one-third under vacuum (rotavap), and then the solution was pressurized to 1500 psi using U.S.P.

grade nitrogen (Linde-Union Carbide) in a Parr bomb at room temperature for 24 h. An IR spectrum showed the disappearance of all the $Cp^*Re(CO)_2(THF)$ complex and $\nu(CO)$ absorption from only $Cp^*Re(CO)_2(N_2)$ and residual $Cp^*Re(CO)_3$. The brown solution was evaporated under vacuum and the residue redissolved in CH_2Cl_2 and chromatographed on a silica gel column prepared in hexane. Hexane eluted a pale-yellow band from which was recovered 320 mg (53.3%) of a pale-yellow solid mixture of <u>13a</u> and $Cp^*Re(CO)_3$ in about 3:2 ratio (by IR). Next, hexane-diethylether (1:1) eluted a golden yellow band of Cp^*ReO_3 (formed as a result of O_2 impurity in the N_2, see Appendix I) and then an orange band containing $Cp^*_2Re_2(CO)_3$ and $Cp^*Re_2(CO)_5$.[144] Finally, an unidentified purple band was eluted by using diethylether. The mixture of dinitrogen and tricarbonyl complexes could not easily be separated by column chromatography and was used as such in further reactions.

Preparation of $Cp^*Re(CO)(PMe_3)(N_2)$ (<u>13b</u>) and (<u>13b</u>-$^{15}N_\alpha$)

The trimethylphosphine cationic complex <u>12a</u> or <u>12a</u>-$^{15}N_\alpha$ (150 mg, 0.232 mmol) was dissolved in freshly distilled THF (50 mL) and heated at 60°C, then an excess of <u>t</u>-butyllithium (0.5 mL, 0.975 mmol) was added by syringe. A fast reaction took place and the color of the solution changed from orange-red to light brown. The IR spectrum of this mixture showed the total disappearance of the cationic complex and the presence of absorptions due to the dinitrogen complex. In addition a third medium intensity absorption was observed at 1850 cm^{-1} (in THF) believed to be the $\nu(CO)$

of the hydrazido (2−) complex $Cp^*Re(CO)(PMe)(NN(\underline{t}\text{-}Bu)(\underline{p}\text{-}N_2C_6H_4OMe))$. After 15 min of stirring at room temperature the volume was reduced to one-tenth under vacuum. Then one drop of water was added to hydrolyse the unreacted *t*-butyllithium and the mixture stirred for 5 min. Diethylether (50 mL) was added, stirred for 30 min and the solution filtered through a short column of Celite-neutral alumina. Evaporation of the solvent under reduced pressure gave a pale-brown oily solid which was chromatographed on a neutral alumina column (prepared in hexane). Hexane elution moved the dinitrogen complex and the organic side-products. Recrystallization from pentane at −78°C gave the product as pale-yellow microcrystals in 51% yield (54 mg). M.p. 99-101°C with decomposition. IR (hexane): 2043 s (2010 in *13b*-$^{15}N_\alpha$) ν(NN), 1864 vs, ν(CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.56 d, (J= 8.76, 9H, PMe_3), 1.99 d (J= 0.68, 15H, Cp^*). $^{13}\{^1H\}$ NMR ($CDCl_3$): δ 10.74 s ($C_5\underline{Me}_5$), 20.64 d (J= 33.16, $P\underline{Me}_3$), 93.26 s ($\underline{C}_5Me_5$) and 207.16 d (J= 7.04, $\underline{C}O$). ^{14}N NMR (acetone/acetone-d_6): δ −90.2 br,s (N_α), −29.4 br, s (N_β). ^{15}N NMR for *13b*-$^{15}N_\alpha$ (acetone/acetone-d_6): δ −90.7 s ($^{15}N_\alpha$). ^{31}P NMR ($CDCl_3$): δ −29.81 s ($\underline{P}Me_3$). MS (EI): m/z 454 (455 in *13b*-$^{15}N_\alpha$) M^+, 426 $(M-{}^{14}N_2)^+$ in *13b* or $(M-{}^{15}N{}^{14}N)^+$ in *13b*-$^{15}N_\alpha$.

Preparation of $Cp^*Re(CO)(P(\underline{n}\text{-}Bu)_3)(N_2)$ (*13c*)

A procedure similar to that described for the preparation of *13b* was used for the synthesis of this dinitrogen complex. It was obtained in 44.5% yield as a pale-yellow microcrystalline solid. M.p. 73°C. IR (hexane): 2040 s, ν(NN), 1863 vs ν(CO) cm^{-1}. ^1H NMR

(CDCl$_3$): δ 0.93 t (9H, P(CH$_2$(CH$_2$)$_2$(C$\underline{H}_3$)$_3$), 1.38 m (12H) and 1.71 m (6H, P(C$\underline{H}_2$)$_3$CH$_3$), 1.95 s (15H, Cp*). ^{13}{^{1}H} NMR (CDCl$_3$): δ 10.60 s ((C$_5\underline{Me}_5$), 13.86 s (P(CH$_2$)$_3\underline{C}$H$_3$), 24.33 d (J= 13.1, PCH$_2\underline{C}$H$_2$ CH$_2$CH$_3$), 25.97 s (PCH$_2$CH$_2\underline{C}$H$_2$CH$_3$), 29.06 d (J= 29.9 P$\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 92.72 s ($\underline{C}_5$Me$_5$), 208.24 d (J= 7.7, CO). ^{31}P NMR (CDCl$_3$): δ -0.21. MS(EI): m/z 580 M$^+$, 552 (M-N$_2$)$^+$. Anal. Calcd. for 13c: C, 46.57; H, 6.34; N, 3.62. Found: C, 46.35; H, 6.47; N, 3.63.

Preparation of Cp*Re(CO)(PCy$_3$)(N$_2$) (13d)

This complex was synthesized analogously to 13b as a pale-yellow solid in 38% yield. M.p. 129°C with decomposition. IR (hexane): 2030 s ν(NN), 1856 vs ν(CO), cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.25 m, 1.70 m (33H, P(C$_6$H$_{11}$)$_3$) 1.93 s (15H, Cp*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 10.75 s (C$_5\underline{Me}_5$), 26.67 s, 27.74 d (J= 7.05), 30.09 d (J= 37.07), 38.74 d (J= 24.40, P(C$_6$H$_{11}$)$_3$), 92.63 s ($\underline{C}_5$Me$_5$), 209.81 d (J= 8.47, $\underline{C}$O). ^{31}P NMR (CDCl$_3$): δ 27.48 s (PCy$_3$). MS (EI): m/z 658 M$^+$, 630 (M-N$_2$)$^+$. Anal. Cald. for 13d: C, 53.00; H, 7.31; N, 4.26. Found: C, 53.90; H, 7.77; N, 4.15.

Preparation of Cp*Re(CO)(PPh$_3$)(N$_2$) (13e)

This complex was synthesized analogously to 13b as a pale-yellow microcrystalline solid in 39% yield. M.p. 133°C with decomposition. IR (hexane): 2058 s, 2045 m ν(NN), 1866 unsymmetricalvs ν(CO), cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.73 s (15H, Cp*), 7.37 m (15H, PPh$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.94 s (C$_5\underline{Me}_5$), 93.22

s ($\underline{C}_5$Me$_5$), 127.84 d (J= 9.79), 129.19 s, 133.53 d (J= 11.83), 137.84 d (J= 47.20, P$\underline{Ph}$), 207.41 d (J= 8.76, $\underline{C}$O). ^{31}P NMR (CDCl$_3$): δ 32.20 s ($\underline{P}$Ph$_3$). MS (EI): m/z 640 M$^+$, 612 (M-N$_2$)$^+$. Anal. Calcd. for **13e**: C, 54.45; H, 4.70; N, 4.38. Found: C, 54.63; H, 4.81; N, 4.60.

Preparation of Cp*Re(CO){P(OMe)$_3$}(N$_2$) (**13f**) and (**13f**-^{15}N$_\alpha$)

This complex was prepared following the same procedure used for the synthesis of **13b** and **13b**-^{15}N$_\alpha$ in 48% yield as a pale-yellow micricrystalline solid. M.p. 54°C. IR (hexane): 2078 m, 2066 s ν(NN), 1887 unsymmetricalvs ν(CO), cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.99 d (J= 0.79, 15H, Cp*), 3.50 d (J= 12.10, 9H, P(OMe)$_3$). ^{13}{^{1}H} NMR (CDCl$_3$): δ 10.28 s (C$_5\underline{Me}_5$), 51.22 s (POMe)$_3$, 94.12 d (J= 1.50, $\underline{C}_5$Me$_5$), 204.94 d (J= 12.40, $\underline{C}$O). ^{14}N NMR (acetone/acetone-d$_6$): δ -98.3 br,s (N$_\alpha$), -30.5 br, s (N$_\beta$). ^{15}N NMR (acetone/acetone-d$_6$): δ -98.2 s (^{15}N$_\alpha$). ^{31}P NMR (CDCl$_3$): δ 139.0 s ($\underline{P}$(OMe)$_3$). MS (EI): m/z 502 (503 in **13f**-^{15}N$_\alpha$) M$^+$, 474 (M-^{14}N$_2$)$^+$ in **13f** or (M-^{15}N^{14}N)$^+$ in **13f**-^{15}N$_\alpha$. Anal. Calcd. for **13f**: C, 33.46; H, 4.78; N, 5.57. Found: C, 33.60; H, 4.83; N, 5.66.

Preparation of Cp*Re(CO)$_2$(NN(Me)($\underline{p}$-N$_2$C$_6$H$_4$OMe))

A suspension of the dicarbonyl cation complex (**1a**) (50 mg, 0.083 mmol) in hexane was stirred with an excess of MeLi (0.2 mL, 0.480 mmol) at room temperature. The solution slowly turned red and after 4 h was separated from the red-brown solid by pipette. Evaporation of solvent gave a dark red solid which was crystallized from ether-hexane (1:1) at -78°C as a red microcrystalline solid in 38% yield (18 mg). From the supernatant solution about 4 mg of $Cp^*Re(CO)_2(NN(Me)(\textit{p}\text{-}N_2C_6H_4OMe)$. M.p. decomposed over 160°C. IR (hexane): 1936 s, 1862 s ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.13 s (15H, Cp^*), 3.69 s (3H, *Me*), 3.80 s (3H, O*Me*), 6.82 d (2H, C_6H_4) and 7.34 d (2H, C_6H_4). MS (EI): m/z 528 M^+, 500 $(M-CO)^+$, 472 $(M-2CO)^+$.

By using *t*-BuLi instead of MeLi under identical conditions, the hydrazido (2-) complex $Cp^*Re(CO)_2(NN(\textit{t}\text{-}Bu)(\textit{p}\text{-}C_6H_4OMe)$ and the dinitrogen complex **13a** were formed in approximately 5:1 ratio (by IR). The hydrazido (2-) complex exhibited two strong ν(CO) absorptions at 1935 and 1861 cm^{-1} in hexane solution.

Reaction of $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$ (R= Me 12a and Ph 12d, Ar= $\textit{p}\text{-}C_6H_4OMe$) with Methyllithium in THF

(a) At room temperature

Addition of an excess of MeLi (0.1 mL, 0.240 mmol) to a THF solution of **12d** (20 mg, 0.023 mmol) resulted in a dark-red solution which showed in the IR spectrum an intense absorption at 1805 cm^{-1} (in THF). This absorption occurred at 1795 cm^{-1} in the PMe_3 complex. In both cases about 20% (by IR) of the respective dinitrogen complex was also formed. Attempts to isolate these monocarbonyl species, which we believe are the hydrazido (2-) complexes $Cp^*Re(CO)(PR_3)(NN(Me)Ar)$, were unsuccessful due to their low stability to silica gel column. Partially purified sample derived from **12d** (by extraction with hexane at 0-5°C) gave unsatisfactory ^{1}H NMR and MS. In $CDCl_3$ or hexane solutions these hydrazido (2-) complexes decomposed after about 3 h at room temperature to give green solutions which showed no ν(CO) absorption for the hydrazido (2-) complexes. In both cases the intensity of ν(NN) and ν(CO) absorptions of the dinitrogen complex initially present were not increased.

(b) At 60°C

These reactions were carried out under identical conditions to that described using t-BuLi. In both cases, the dinitrogen complexes were the major products: 13b (39% isolated yield) and 13e (29% isolated yield). The respective hydrazido (2-) were also present in small amounts (by IR).

Reaction of $[Cp^*Re(CO)_2(N_2Ar)]^+$ (1a) with t-BuLi

This reaction was carried out using 100 mg (0.167 mmol) of 1a dissolved in 20 mL of THF at 60°C and treated with 0.1 mL (0.195 mmol) of t-BuLi. Following the same purification procedure to that used for the PMe_3 complex, the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ (13a) was obtained in 31% yield (21 mg). A small amount of the hydrazido (2-) complex$Cp^*Re(CO)_2$(NN(t-Bu)(Ar)) was also formed. (IR (hexane): 1935, 1861 cm^{-1} ν(CO)).

GC, GC-MS Analysis of the Reaction of 12a with t-BuLi

After the addition of t-BuLi to the THF solution of 12a the solvent was evaporated under vacuum and trapped at low temperature (liquid nitrogen) (solution A). The residues were extracted with ether and filtered through Celite (solution B). GC and GC-MS analysis of solution A showed only impurities contained in the commercial t-BuLi (Aldrich), such as benzene, hexane and 2,2',3,3'-tetramethylbutane. This was confirmed by GC-MS of the trapped solvent of t-BuLi. GC-MS of solution B showed the presence of anisole (M^+, 108) among other minor unidentified organic products. This was confirmed by coinjection with an authentic sample of anisole.

Reaction of $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$ (R= Me (12a), R= Ph (12d)) with $NaBH_4$

The phosphinearyldiazenido complex (12a or 12d) (50 mg) was dissolved in 5 mL of acetone at room temperature. An excess of solid $NaBH_4$ (ca. 5 mg) was added. After stirring for 1 h the color changed from orange-red to yellow. Evaporation of the solvent under vacuum at room temperature gave an orange-red solid which was extracted with hexane and characterized as the hydrido complex $Cp^*Re(CO)(H)(p\text{-}N_2C_6H_4OMe)$ (4) by comparison with authentic sample. In both cases over 70% yield of complex 4 were obtained.

Preparation of $Cp^*Re(CO)(Me)(p\text{-}N_2C_6H_4OMe)$

The acetonitrile complex 11a (50 mg, 0.081 mmol) was dissolved in 15 mL of THF at room temperature. To this solution MeLi (0.1 mL, 0.240 mmol) was added by syringe and stirred for 3 h. Evaporation of the solvent under vacuum gave a red oily solid which was extracted with hexane and column chromatographed on neutral alumina. Elution with ether/hexane 2:1 gave the product $Cp^{*}Re(CO)(Me)(\underline{p}\text{-}N_2C_6H_4OMe)$ (13 mg, 32% yield) as a red solid. M.p. 138-140°C. This complex was characterized by IR and ^1H NMR. IR (hexane): 1941 vs ν(CO), 1629 s ν(NN), cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.06 s (3H, Re-Me), 2.06 s (15H, Cp^{*}), 3.81 s (3H, OMe), 6.90 d (2H, C_6H_4), 7.27 d (2H, C_6H_4).

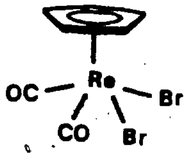
CHAPTER VI

Non-photochemical Reactions of Rhenium Dinitrogen Complexes

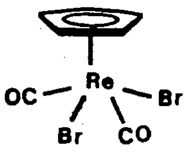
6.1. Introduction

In this chapter we describe some reactions of $Cp^{*}Re(CO)_2(N_2)$ (13a) and $Cp^{*}Re(CO)(PMe_3)(N_2)$ (13b) that were carried out to determine the chemistry of these molecules under non-photochemical conditions. The reactions to be described are with halogens X_2 and hydrogen halides HX (X= Cl, Br, I) and proceed with elimination of N_2 and the formation of the dihalide complexes $Cp^{*}Re(CO)(L)X_2$ (14, L= CO; 15, L= PMe_3) and the hydridohalide complexes $Cp^{*}Re(CO)(L)(H)(X)$ (see Scheme XII).

The first rhenium (III) compound containing cyclopentadienyl dihalide ligands to be synthesized was $CpRe(CO)_2Br_2$. It was prepared from reaction of $CpRe(CO)_3$ with Br_2 in trifluoroacetic acid.[160] Subsequently, the product of this reaction was shown to consist of cis or lateral (I) and trans or diagonal (II) isomers which could be separated.[161]

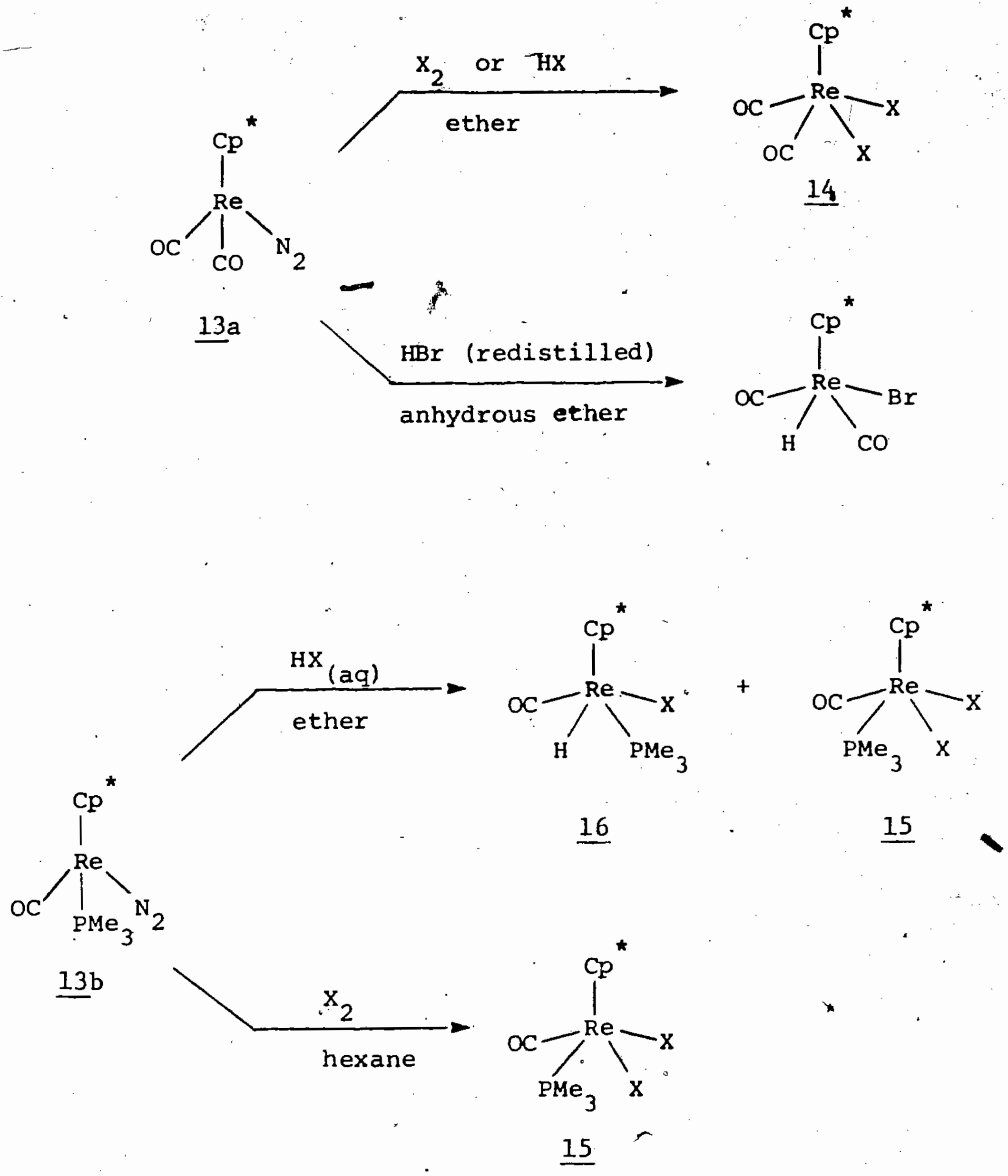


I



II

The iodide $CpRe(CO)_2I_2$ was not reported until 1981,[162,163] and was also prepared in cis and trans forms from the direct



Scheme XII

reaction of $CpRe(CO)_3$ with I_2 in dimethylsulfoxide. The chloride analogue $CpRe(CO)_2Cl_2$ was unknown. Attempts to prepare this compound from $CpRe(CO)_3$ and Cl_2 failed; instead the unstable salt

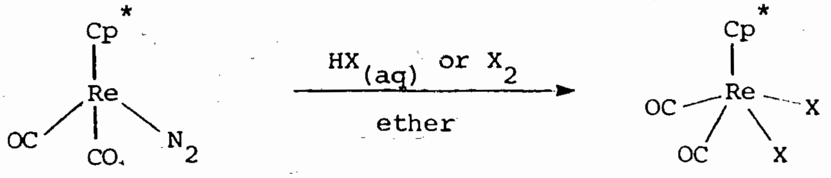
$[CpRe(CO)_3Cl][Cl]$ was proposed to be the product,[162] while reaction with $SbCl_5$ gave the stable, well characterized salt $[CpRe(CO)_3Cl][SbCl_6]$.[164] Of the pentamethylcyclopentadienyl analogues, only $Cp^*Re(CO)_2I_2$ had been mentioned (briefly) but without details of its synthesis, characterization or stereochemistry;[144] the dibromides and dichlorides were unknown. In the cyclopentadienyl monocarbonyldihalides containing phosphorus ligands only the phosphite complexes $CpRe(CO)(P(OR)_3)Br_2$ (R= Me, Et and Ph) were already known. They were synthesized in either the cis or the trans forms by reaction of $CpRe(CO)_2Br_2$ with $P(OR)_3$. The particular isomer obtained depended on the temperature at which the reaction was carried out.[165] Pentamethylcyclopentadienylrhenium dihalides containing a phosphorus ligand were completely unknown.

Part of the work described in this chapter has already been published.[166]

6.2. Synthesis and Characterization

(a) Cis-pentamethylcyclopentadienyldihalides (cis-**14** and cis-**15**)

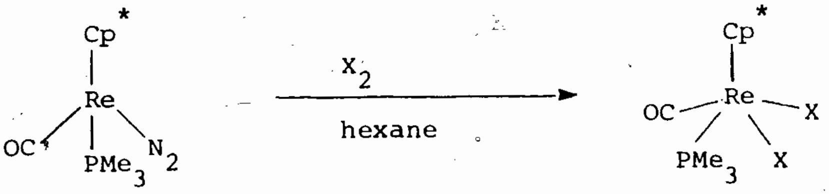
These compounds were easily prepared by reaction of the respective dinitrogen complex in diethylether with HX either as aqueous solution (X= Cl, Br, I) or the unpurified gas (X= Cl, Br), or with X_2 according to Eqs.24 and 25.



Eq. 24.

13a cis-14

cis-14a, X= Cl; cis-14b, X= Br; cis-14c, X= I



Eq. 25.

13b 15

cis-15a, X= Cl; cis-15b, X= Br; cis-15c, X= I

In both cases, cis-14 and cis-15 were obtained as a single compound in good to excellent yields. In the majority of the reactions for the preparation of cis-14, the dinitrogen complex 13a was used in a mixture with $Cp^*Re(CO)_3$ (prepared by method 2, see Chapter V). However, $Cp^*Re(CO)_3$ does not interfere in the reaction with HX and can be recovered (see Experimental Section). This reaction (Eq.24) occurred slowly but in high yield. Much faster reactions were observed using halogens (X_2) instead of HX but these were not so clean, especially when $Cp^*Re(CO)_3$ was present. By contrast, the phosphinedinitrogen complex 13b reacted with HX to produce trans-$Cp^*Re(CO)(PMe_3)(H)(X)$ (16) (see below) in high yields, along with only small amounts (< 10%) of the corresponding dihalide cis-15 (see below). However, reaction of 13b with halogens (Eq.25) occurred instantaneously to give only cis-15 in excellent yield.

All these dihalide compounds (cis-14 and cis-15) were obtained as red or orange-red microcrystalline solids, which are indefinitely stable under N_2 and can be exposed to air for periods of days without visible deterioration. They are very soluble in the majority of polar solvents such as acetone, CH_2Cl_2 and $CHCl_3$ in which they are very stable with regard to thermal isomerization. For example, no isomerization was observed even in boiling benzene or toluene, though the complexes did not survive for long at these temperatures (especially the phosphine ones cis-15). Acetone solutions of cis-14a, cis-14c and cis-15b showed no isomerization over four days at room temperature.

The spectral properties of these cis-dihalides are consistent with their possessing a monomeric four-legged piano stool structure, which in the case of cis-14c was confirmed by an X-ray crystal structure determination, kindly done by Prof. F.W.B. Einstein and Dr K.G. Tyers. A perspective view of this complex is shown in Fig.12. Thus their electron-impact mass spectra display peaks corresponding to the molecular ions M^+, plus $(M-CO)^+$, $(M-2CO)^+$ or $(M-CO-PMe_3)^+$, and $(M-X)^+$ fragments respectively. In the ^1H and ^{13}C NMR spectra they exhibit just the resonances expected for a single isomer (see Table VIII). The IR spectra of the dicarbonyldihalide complexes (cis-14) in each case consist of only two $\nu(CO)$ absorp-

Fig.12 Perspective View of the Complex cis-$Cp^{*}Re(CO)_2I_2$ (cis-<u>**14c**</u>).
The numbering scheme is that used in ref.166.

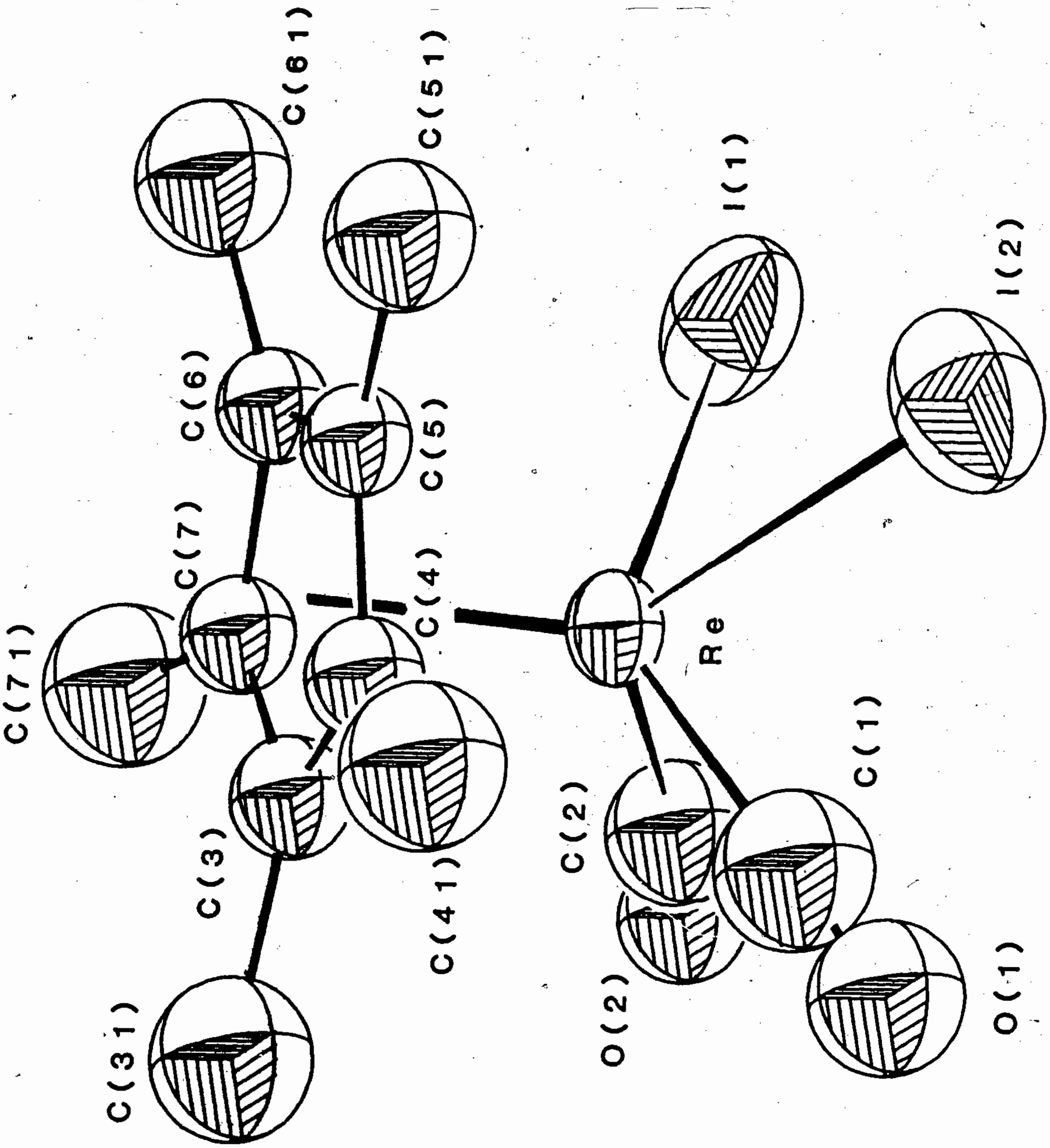

C(61)
C(51)
I(1)
I(2)
C(6)
C(5)
C(7)
C(4)
Re
C(71)
C(1)
C(2)
C(3)
C(41)
O(2)
O(1)
C(31)

Table VIII. Some Spectroscopic Parameters of Cis and Trans Dihalide Complexes.

Compound			IR (CH_2Cl_2) cm^{-1}, $\nu(CO)$		^{13}C NMR ($CDCl_3$), $\delta(CO)$		^{1}H NMR ($CDCl_3$), $\delta(Cp^*)$	
L	X		cis	trans	cis	trans	cis	trans
CO	Cl	14a	2037 vs, 1958 s	2059 s, 1986 vs	203.94	189.74	1.98	1.89
CO	Br	14b	2033 vs, 1958 s	2050 s, 1981 vs	201.52	186.40	2.06	2.00
CO	I	14c	2022 vs, 1953 s	2028 s, 1964 vs	199.52	183.00	2.23	2.21
PMe_3	Cl	15a	1899 vs	-	222.90 (24.6)[b]	-	1.82	-
PMe_3	Br	15b	1902 vs	1937 vs	220.28 (24.9)	205.20 (3.7)	1.89	1.85
PMe_3	I	15c	1902 vs	-	217.25 (26.3)	-	1.95	-
$CpRe(CO)_2Cl_2$			2056 vs, 1976 s[a]	2081 s, 2017 vs	201.85	185.72	6.54[c]	5.69[c]

[a] In $CHCl_3$ solution. [b] Data in parenthesis indicate $^{2}J_{CP}$ in Hz. [c] Chemical shift of the Cp ring protons.

Abbreviations: vs, very strong; s, strong.

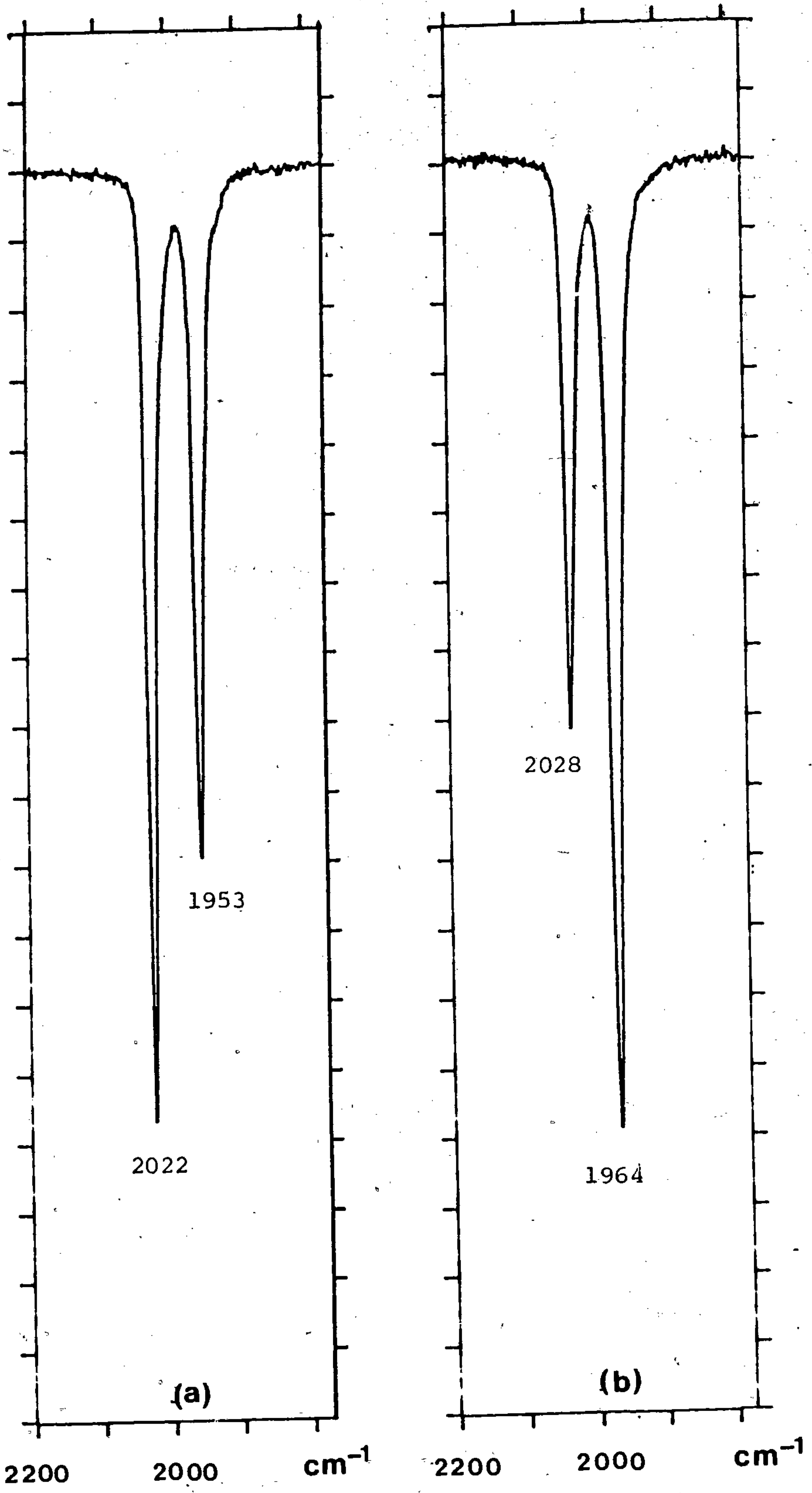
tions in the region 2040-1950 cm-1 (Table VIII) with the higher wavenumber one much more intense (the IR spectrum of cis- 14c is shown in Fig.13a), whereas for the carbonylphosphinedihalide (cis-15) the single ν(CO) absorption is observed very close to 1900 cm^{-1} (see Table VIII).

The intensity patterns, as well as the correspondence between the IR values of our dicarbonyldihalide complexes (cis-14), are in good agreement with those reported for cis-$CpRe(CO)_2Br_2$ [161,165] and cis-$CpRe(CO)_2I_2$.[162] Furthermore, we have used the relative ν(CO) IR intensities to calculate the OC-Re-CO angle (2θ) using the relationship[161]

$$\tan^2\theta = I_{as} / I_s$$

where I_{as} and I_s are the areas under the antisymmetric (lower wavenumber) and symmetric (higher wavenumber) bands respectively. The angles determined by this method are 87° (cis-14a), 84° (cis-14b) and 80° (cis-14c) and accord with their postulated cis structure. The X-ray crystal structure of cis-14c provided a value of 78(1)° for this angle, in excellent agreement. The assignment of cis structure for the carbonylphosphinedihalides (cis-15) is less straightforward than for the dicarbonyl ones in view of the inapplicability of IR ν(CO) relative intensity measurements to the monocarbonyls. However, in the three cases (cis-15a,b,c) the cis stereochemistry was assigned on the basis of $^2J_{CP}$ obtained from the ^{13}C NMR spectra of these compounds. The value $^2J_{CP}\sim$ 25 Hz

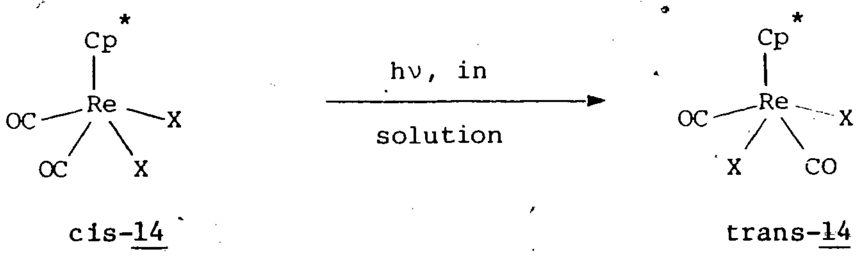
Fig.13. IR Spectra of Dicarbonyldiiodide Complexes (2200-1780 cm^{-1} region, CH_2Cl_2 solution). (a): cis-$Cp^*Re(CO)_2I_2$ (cis-**14c**), (b): trans-$Cp^*Re(CO)_2I_2$ (trans-**14c**).


2022
1953
(a)
2200
2000
cm⁻¹
2028
1964
(b)
2200
2000
cm⁻¹

(Table VIII) is in good agreement with those observed in other related compounds containing a phosphine ligand cis to a carbon monoxide e.g. trans-$CpMo(CO)_2(PPh_3)Cl$ (27.2 Hz)[167] and cis-$CpMo(CO)_2(PPh_3)I$ (28.6 Hz).[168]

(b) Trans-Pentamethylcyclopentadienyldihalides (trans-14 and trans-$Cp^*Re(CO)(PMe_3)Br_2$)

Trans-$Cp^*Re(CO)_2X_2$ trans-14a, X= Cl; trans-14b, X= Br and trans-14c, X= I were prepared by photochemical isomerization of the respective cis-isomer (cis-14) according to Eq.26.



Eq.26.

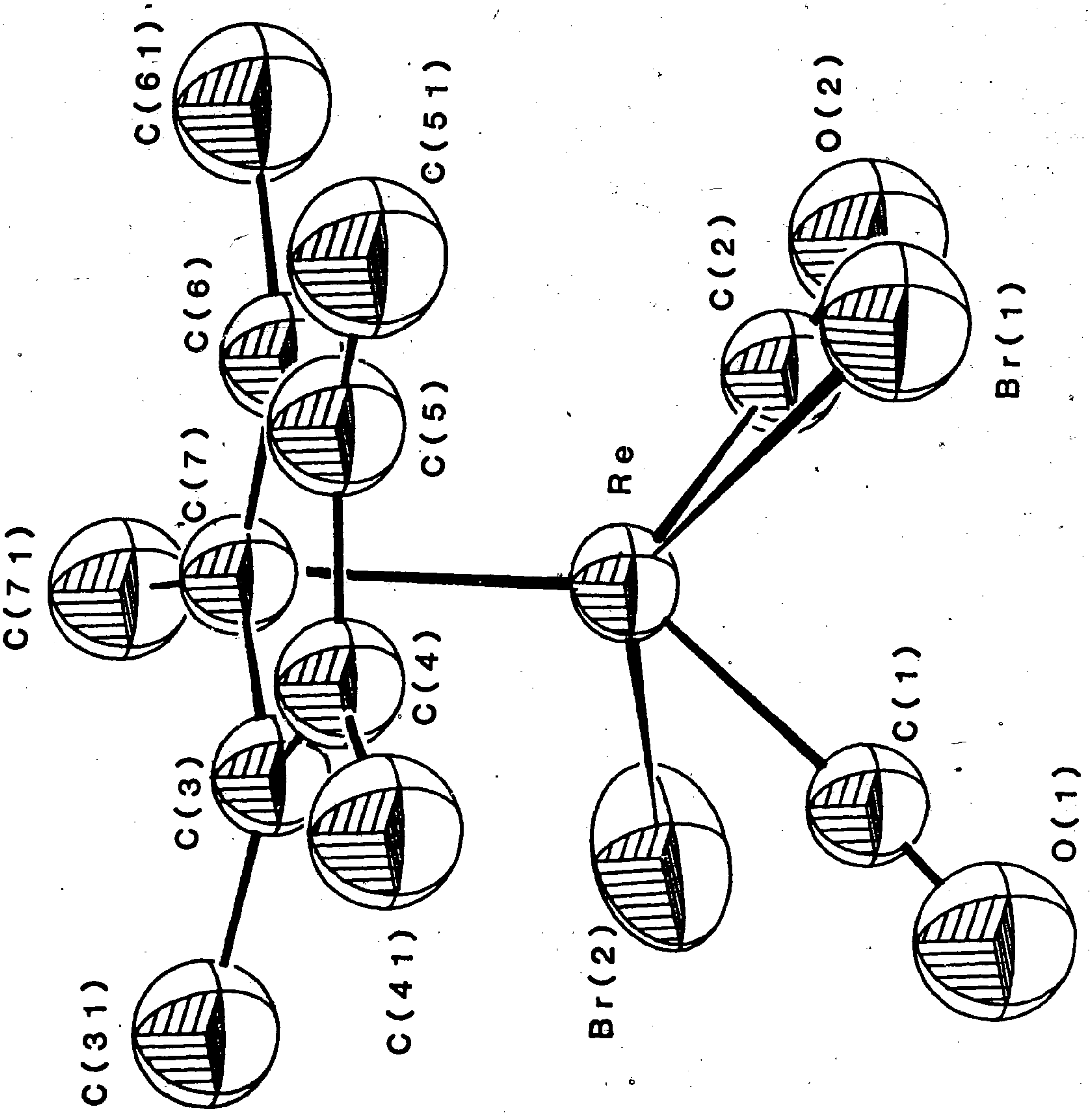
The cis-dichloride or dibromide complexes (cis-14a or cis-14b) were UV-irradiated in $CHCl_3$ solution with formation of the trans isomer (trans-14a or trans-14b) in 60-70% yield after about 30-40 min. However, isomerization of cis diiodide (cis-14c) could not be carried out in $CHCl_3$, because chlorine substitution occurred. Both the trans dichloride (trans-14a) and traces of $Cp^*Re(CO)_2ClI$ were formed instead. No separation of these derivatives was attempted. The latter was identified by MS (m/z 520 (M^+) based on ^{187}Re and ^{35}Cl). Irradiation of a suspension of cis-14c in hexane for 90 min produced the trans-14c in about 20% yield, plus decomposition. Alternatively, trans-14c was obtained in 11% yield by irradiation of a suspension of $[Cp^*Re(CO)_3I][I_3]$ (see below) in hexane. Also cis-14c was produced in this reaction.

As expected, the trans dihalides (trans-14) show considerably greater solubility, especially in hydrocarbon solvents, than do the less symmetrical cis isomers. They also tend to be thermally less stable, and decompose at considerably lower temperatures. As solids or solution they are stable with regard to isomerization. No isomerization of trans-14b and trans-14c was observed in acetone solution after four days.

These compounds are recognizable by having two IR ν(CO) absorptions in the region 2060-1960 cm^{-1} (Table VIII), where the higher wavenumber one (ν(CO) sym) is now the less intense of the pair. The IR spectrum of the diiodide (trans-14c) is shown in Fig. 13b. The OC-Re-CO interbond angles, estimated from the ν(CO) relative intensities were found to be ca. 115°, some 28-35° greater than the angles in the cis compounds, and consistent with the postulated trans stereochemistry. The stereochemistry of the dibromide complex trans-14b was confirmed by X-ray crystallography also kindly carried out by Prof. F.W.B. Einstein and Dr. K.G. Tyers. A perspective view of this complex is shown in Fig.14. From the structural study an OC-Re-CO angle of 104° was determined.

In the MS these complexes exhibit the same fragmentation pattern as observed in their cis analogues. Similarly, the ^1H and ^{13}C NMR spectra are as expected for pure, single compounds and it is observed that Cp^* proton resonances and ^{13}C carbonyl carbon

Fig.14. Perspective View of the Complex trans-$Cp^*Re(CO)_2Br_2$ (trans-14b). The numbering scheme is that used in ref.166.


C(61)
C(51)
O(2)
C(2)
C(6)
Br(1)
C(5)
C(7)
Re
C(71)
C(4)
C(1)
C(3)
O(1)
C(41)
Br(2)
C(31)

resonances are consistently shifted to higher field compared with the same resonances in the cis analogues (see Table VIII).

Turning to the carbonylphosphine complexes, only in one case could the trans-isomer be obtained and this was the dibromide. Attempts to obtain any of the trans compounds using a similar procedure to that used to prepare the trans dicarbonyl complexes was unsuccessful since under the photochemical conditions used all of the cis-15 complexes readily decomposed giving intractable products. Nevertheless, trans-$Cp^*Re(CO)(PMe_3)Br_2$ could be prepared by reaction of trans(H,Br)-$Cp^*Re(CO)(PMe_3)(H)(Br)$ with N-bromosuccinimide (NBS) in THF at 0°C. By contrast, trans(H,Cl)- and trans (H,I)-$Cp^*Re(CO)(PMe_3)(H)(X)$ were recovered unreacted when treated with N-chloro and N-iodosuccinimide, respectively, under similar conditions. At room temperature, in both cases a slow reaction took place and the cis-$Cp^*Re(CO)(PMe_3)X_2$ (X= Cl, I) were produced. Presumably, the trans-isomers were first formed and then they rearrange to the more stable cis isomers, as happened with trans-$Cp^*Re(CO)(PMe_3)Br_2$ (see below).

The trans-$Cp^*Re(CO)(PMe_3)Br_2$ complex was isolated as an orange-red solid in almost quantitative yield. In the IR spectrum, the ν(CO) absorption appears 35 cm^{-1} to higher wavenumber than in the cis isomer. The carbonyl carbon resonance is a doublet with $^2J_{PC}$= 3.7 Hz (compare with 24.9 Hz for the cis isomer) and is shifted upfield by 15.1 ppm with respect to cis-15b. About 80% isomerization of trans to cis-15b occurred in benzene in the dark over five days, at room temperature.

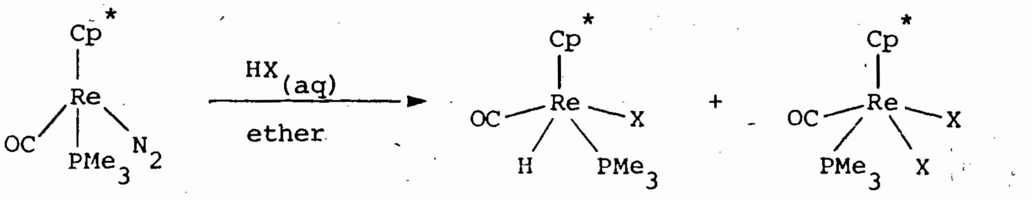
(c) Cis and Trans Cyclopentadienyldicarbonyldichloride

Cis-CpRe$(CO)_2Cl_2$ was prepared from the reaction of Cl_2 with CpRe$(CO)_2(N_2)$ (which also reacts with Br_2 and I_2 to produce only cis-CpRe$(CO)_2X_2$, X= Br and I), but the dinitrogen complex appeared unreactive to gaseous or aqueous HCl. Its spectroscopic properties are comparable to those observed in the cis-14 series and are listed in Table VIII. Analogous with cis-14a, cis-CpRe $(CO)_2Cl_2$ does not isomerize thermally to the trans isomer in acetone at room temperature within 24 h (whereas the diiodide cis-CpRe$(CO)_2I_2$ was isomerized to trans in this solvent in 3 h). However, like cis-14a, when UV-irradiated in acetone, it quickly and cleanly isomerized to trans-CpRe$(CO)_2Cl_2$ (compare Eq.26). In general, this compound resembles, in its spectroscopic properties, the trans-14 analogues with Cp* (see Table VIII).

(d) Trans-Pentamethylcyclopentadienylhydrido Halides

The preparation of some of these derivatives was kindly assisted by Mr. R. Singer, a summer undergraduate student in our laboratory.

In contrast to Cp*Re$(CO)_2(N_2)$, the trimethylphosphinedinitrogen complex 13b reacted with an excess of concentrated aqueous hydrogen halides (HX) to produce primarily trans(H,X)-Cp*Re(CO)(PMe_3)(H)(X) 16, 16a, X= Cl; 16b, X= Br; 16c, X= I in over 80% yield, with only less than 10% of the corresponding cis-dihalide (cis-15) being formed, Eq.27.



13b 16 (>80%) 15 (<10%) Eq. 27.

In all the cases, the complexes trans-16 were isolated as yellow solids which are indefinitely stable under N_2. They are very soluble in the majority of organic solvents including hexane and cyclohexane. They show in the IR spectra a single very strong ν(CO) absorption at about 1922 cm^{-1} in hexane (see Table IX). The presence of the hydride ligand (which could not be observed in the IR spectra) was clearly determined from the ^1H NMR spectra in which there appears a doublet of relative intensity 1H in the high field region at ca. δ -10.0 (Table IX). In the three cases a value of $^2J_{PH} \sim$ 56.0 Hz was observed. This value is in good agreement with those observed in other four-legged piano-stool complexes containing a cis H-M-P moiety ,e.g. $[CpMn(CO)_2(PMe_2Ph)(H)]^+$, 52 Hz;[169] $CpMo(CO)_2(PR_3)H$, 64-67 Hz[170] and $[CpRe(CO)_2(PPh_3)H]^+$, 39 Hz.[171] In a trans H-M-P arrangement, $^2J_{PH}$ is expected, from various precedents to be 2-3 times smaller than that observed in the cis arrangement.[169-171] In the proton coupled ^{13}C NMR spectrum the carbonyl carbon resonance is a doublet with $^2J_{CH} \sim$ 8-11 Hz and a singlet in the proton decoupled spectrum with no observable coupling to ^{31}P. These values of $^2J_{CH}$ are close to that observed in trans-$Cp^*Re(CO)_2(H)(Br)$ (see below) and are

Table IX. Some Spectroscopic Parameters of trans-Hydridohalide Complexes Cp*Re(CO)(L)(H)(X).

Compound L	X		IR (hexane) cm^{-1}, ν(CO)	^{13}C NMR (C_6D_6), δ(CO)	^{1}H NMR (C_6D_6), δ(ReH)
PMe$_3$	Cl	<u>16a</u>	1920	207.80 (10.0)[a]	-9.35 (56.1)[b]
PMe$_3$	Br	<u>16b</u>	1922	206.45 (8.7)	-10.33 (55.7)
PMe$_3$	I	<u>16c</u>	1925	204.32 (10.8)	-11.46 (56.1)
CO	Br		2030 s, 1964 vs	195.75 (13.7)	-9.98

Values in parenthesis indicate coupling constants in Hz. [a] $^2J_{CH}$; [b] $^2J_{PH}$.

a further indication of the correctness of the proposed geometry for 16, with a cis arrangement of CO and hydride ligands.

Although, as already stated, the reaction of $Cp^*Re(CO)_2(N_2)$ (13a) with aqueous HX in ether gave only the dihalides, from the reaction of 13a with redistilled gaseous HBr under anhydrous conditions, the complex trans-$Cp^*Re(CO)_2(H)(Br)$ could be isolated in 42% yield and fully characterized. It exhibits a typical ν(CO) pattern for a trans carbonyl stereochemistry in its IR spectrum i.e. a medium absorption at 2030 cm^{-1} and a strong band at 1964 cm^{-1}, in hexane solution. The hydride resonance in the ^1H NMR spectrum occurs at δ -9.98 and is a singlet, as expected. In the ^{13}C proton-coupled NMR spectrum, δ (^{13}CO) is observed at 195.75 as a doublet with $^2J_{CH}$= 13.7 Hz and as a singlet in the $^{13}C\{^1H\}$ spectrum.In the reaction with excess of aqueous HBr, this complex smoothly produced cis-$Cp^*Re(CO)_2Br_2$ (cis-14b).

(e) Cationic Monoiodide Complexes $[Cp^*Re(CO)_2(L)I]^+$ L= CO and PMe_3

These complexes were prepared by reaction of $Cp^*Re(CO)_3$ in hexane or $Cp^*Re(CO)_2(PMe_3)$ in ether with an excess of I_2 at room temperature. In both cases they were obtained in quantitative yields as dark-red solids.

The presence of the cations $[Cp^*Re(CO)_2(L)I]^+$ (L= CO and PMe_3) in the solids is convincingly demonstrated by the FAB mass spectra, which show as expected, strong isotopic patterns for the unfragmented cations and successive losses of three CO for $[Cp^*Re(CO)_3I]^+$ and two CO and PMe_3 for $[Cp^*Re(CO)_2(PMe_3)I]^+$.

The tricarbonyl cation $[Cp^{*}Re(CO)_3I]^+$ appears to be quite stable as a solid under N_2 at room temperature, but repeated attempts to wash it with hexane (in which it must be scarcely soluble) always resulted in purple washings owing to the partial reformation of I_2 and $Cp^{*}Re(CO)_3$. An IR spectrum in KBr of the freshly washed solid contains ν(CO) absorptions of $[Cp^{*}Re(CO)_3I]^+$ at 2078, 2045 and 2027 cm^{-1} and very weak absorptions at 1994 and 1900 cm^{-1} from the tricarbonyl complex. The spectrum is unchanged after 24 h. In $CHCl_3$ or CH_2Cl_2 solutions the equilibrium shown in Eq.28 is established

$$Cp^{*}Re(CO)_3 + 2\ I_2 \rightleftarrows [Cp^{*}Re(CO)_3I][I_3] \qquad \text{Eq.28.}$$

and the bands for $[Cp^{*}Re(CO)_3I]^+$ (ν(CO) 2099 and 2043 cm^{-1}) and $Cp^{*}Re(CO)_3$ (ν(CO) 2008 and 1914 cm^{-1}) have roughly similar intensity. Even when the $CHCl_3$ solution was saturated with I_2, the absorptions for the latter were only about half as intense. Despite this, an I_2 saturated solution of $[Cp^{*}Re(CO)_3I][I_3]$ in $CDCl_3$ exhibited at room temperature only a sharp single ^1H NMR resonance at δ 2.39 for Cp^{*} and a single set of ^{13}C NMR resonances, two singlets at δ 11.4 and 103.2 for Cp^{*} and a broad singlet for CO at δ 191.0. This can be attributed to a fast interconversion averaging the resonances for $[Cp^{*}Re(CO)_3I][I_3]$ and $Cp^{*}Re(CO)_3$. At -50°C the proton resonance has broadened slightly and shifted to δ 2.47.

By contrast, cis-$[Cp^{*}Re(CO)_2(PMe_3)I][I_3]$ is indefinitely stable as a solid or in solution under N_2. In the IR spectrum, it showed only two ν(CO) absorptions. Furthermore, the relative intensity of these absorptions are typical for a cis arrangement of the two CO groups i.e. the higher wavenumber absorption at 2039 cm^{-1} being much more intense than that observed at 1973 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ of this complex showed no unusual features, a doublet for PMe_3 at δ 2.12 (J= 10.3 Hz) and a doublet for Cp^* at δ 2.37 (J= 0.9 Hz). In the ^{13}C NMR spectrum, in addition to the single resonances for the Cp^* and doublet for the PMe_3 (J= 4.17 Hz) two doublets for the carbonyl carbon resonances were observed. The one at lower field (δ 202.45) with J= 24.8 Hz is tentatively assigned to the CO cis to the PMe_3 by comparison with the J-values observed in cis-<u>15</u> (ca. 25 Hz), and the one at much higher field δ 187.72 with J= 15.3, to the carbonyl trans to the PMe_3. The $^2J_{CP}$ observed for the latter resonance however contrasts with the values of 3.7Hz observed for the trans-$Cp^*Re(CO)(PMe_3)Br_2$ and with 5.0 Hz for the cis-$CpMo(CO)_2(PPh_3)I$.[167]

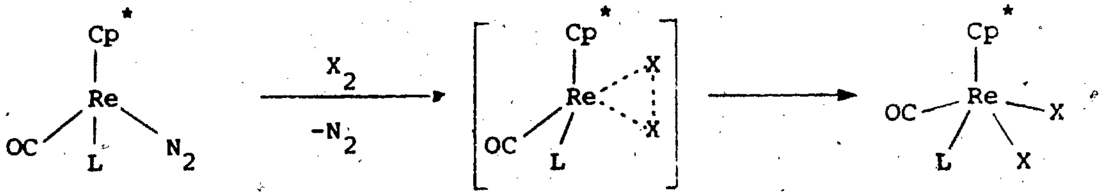
6.3. Discussion

The formation of cis-$Cp^*Re(CO)(L)X_2$ and trans-$Cp^*Re(CO)(PMe_3)(H)(X)$ from the reaction of the dinitrogen complexes <u>13a</u> or <u>13b</u> with halogens or hydrogen halides are typical examples of oxidative addition reactions with loss of the dinitrogen ligand. These types of reactions have been observed in a variety of N_2-complexes and have been described in Chapter I, section 1.3.3(a). Some examples involving halogens or HX are the reactions of (i) trans-

$Mo(N_2)_2(dppe)_2$ with Br_2 to give trans-$[MoBr_2(dppe)_2)]Br_3$,[69] (ii) trans-$ReCl(N_2)(py)(PMe_2Ph)_3$ (py= pyridine) with HCl to yield $ReCl_3(PMe_2Ph)_3$[172] and (iii) trans-$IrCl(N_2)(PPh_3)_2$ with HCl to produce $IrHCl_2(PPh_3)_2$.[173] However, no examples of N_2-complexes possessing a "piano-stool" type structure have been previously known to give oxidative addition products with halogen or hydrogen halides.

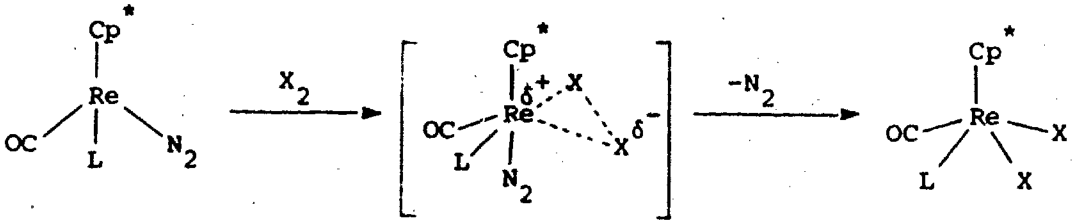
The reactions of the dinitrogen complexes 13a or 13b with halogens, give stereospecifically cis-$Cp^*Re(CO)(L)X_2$ (cis-14 and cis-15). A radical mechanism is therefore unlikely, and two non-radical mechanisms can be considered.

Mechanism I is a concerted mechanism involving first the dissociation of the N_2 ligand followed by the formation of a three-center transition state (Eq.29).



Eq.29.

Mechanism II is a "pseudoionic" mechanism involving nucleophilic attack of the metal complex to the halogen, generating a transition state of considerable polarity (Eq.30).



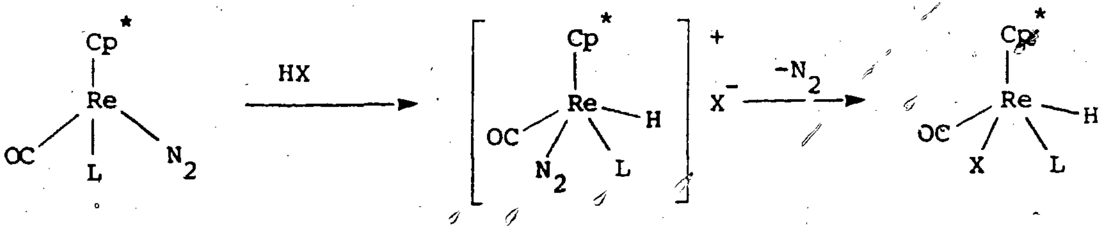
Eq.30.

Mechanism I agrees with the observed cis-addition products. However, it should be noted that the N_2 ligand in the starting complexes appears to be inert to dissociation (see preceding chapter), thus, it does not seem likely that the unsaturated fragment "$Cp^*Re(CO)(L)$" is generated under thermal conditions. On this basis, we are not in favor of this concerted mechanism.

Mechanism II seems to be more plausible, even though we have no direct evidence for the formation of either a "highly polar" or a completely ionic intermediate ($[Cp^*Re(CO)(L)(N_2)X][X]$). Nevertheless, it has been demonstrated in several ways that the rhenium atom in the isoelectronic dicarbonyl analogues, $CpRe(CO)_2(L)$ (L= CO and PPh_3), of these dinitrogen complexes, possesses basic character. First, these complexes can be protonated by CF_3COOH to produce the cationic hydride derivatives $[CpRe(CO)_2(L)(H)]^+$.[171] Also, Ginzburg et al. have suggested on the basis of IR that $CpRe(CO)_2(PR_3)$ (R= Ph, OMe and OPh) reacts with Lewis acids such as $TiCl_4$, $SnCl_4$ and $SnBr_4$ to form adducts of the type $Cp(CO)_2(PR_3)ReMCl_4$.[174] More recently, the reaction of $CpRe(CO)_2(PPh_3)$ with Cl_2 to produce the cationic complex $[CpRe(CO)_2(PPh_3)Cl]^+$ has been reported.[162] It is expected that the presence of the Cp^* ligand in these types of rhenium complexes will increase the basicity of the metal center. In agreement, as reported in this chapter, the carbonyl complexes $Cp^*Re(CO)_2(L)$ (L= CO and PMe_3) react with I_2 to give the corresponding cationic complexes $[Cp^*Re(CO)_2(L)I]^+$.

On the basis of these observations it is expected that the rhenium center in the dinitrogen complexes 13a and 13b should have basic character at least as great as that observed in the Cp and Cp* dicarbonyl analogues. The positive charge created on the rhenium in the "polar" intermediate can be envisaged to labilize the N_2 ligand (by reducing the Re-N_2 backbonding), facilitating the oxidative addition. If the ionic complexes [Cp*Re(CO)(L)(N_2)X][X] were to be formed instead, following loss of N_2 we would expect the addition of the halide (X^-) counter ion to occur stereospecifically trans to the halogen already present, just like the trans addition to the hydride ligand in the intermediate in the reaction of 13a and 13b with HX (see below).

In the reactions of the dinitrogen complex 13a with HBr in anhydrous conditions, and 13b with aqueous HX, the situation is different to that already discussed, since the stereochemistry of the oxidative addition products (16) in this case is trans. Here, an ionic mechanism involving attack of the proton to the metal complex followed by nucleophilic attack of the halide with loss of dinitrogen is more likely to occur (Eq.31).

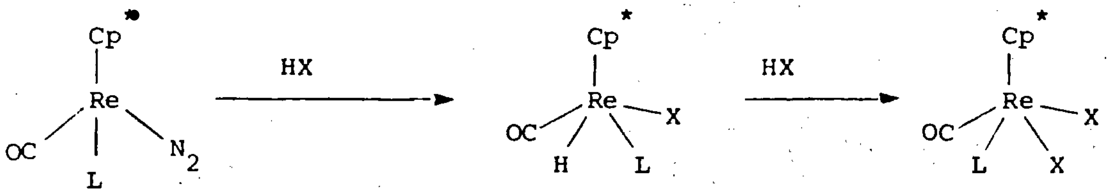


Eq.31.

The trans stereochemistry observed in 16 can be understood in terms of the trans-effect of the hydride ligand. It is a well documented phenomenon that a ligand strongly σ-bonded to a metal (like hydride) has a strong labilizing effect upon the ligand opposite (trans) to it.[175] This effect has been observed in a wide variety of metal complexes, especially in square-planar Pt and Pd complexes.[176]

Although these rhenium systems may represent a rather large departure from the model system based on Pt (II) complexes, comparable effects can be expected to control the stereochemistry of the reaction. Within this context a trans (H,N_2) stereochemistry is assumed for the cationic intermediate $[Cp^*Re(CO)(L)(N_2)H]^+$. Substitution of N_2 by addition of the halide at the trans position, presumably via an associative mechanism, would give the observed trans-16.

The formation of cis-$Cp^*Re(CO)(L)X_2$ (cis-14 and cis-15), and probably H_2, from the reaction of $Cp^*Re(CO)(L)(N_2)$ with HX is not as straightforward as the reactions with halogens which give identical products. This reaction presumably occurs as shown in Eq. 32.

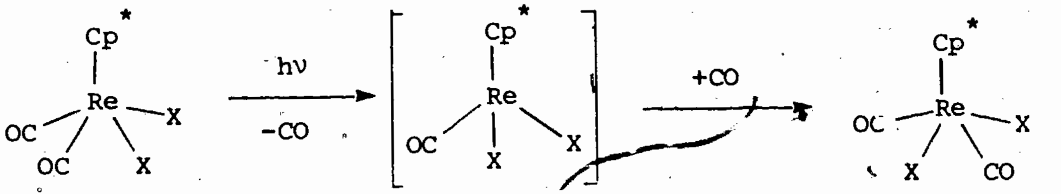


Eq. 32.

The first step has already been discussed. The second step, i.e., hydride substitution from the trans(H,X)-$Cp^*Re(CO)(L)(H)(X)$ by halide to give cis-$Cp^*Re(CO)(L)X_2$, has been confirmed by reaction of trans(H,Br)-$Cp^*Re(CO)_2(H)(Br)$ with aqueous HBr, which gave only cis-$Cp^*Re(CO)_2Br_2$ (cis-14). However, the mechanism of this reaction is not understood at the present time. It apparently depends on the ligand L and whether the hydrogen halide is either anhydrous or aqueous. For example, reaction of the dicarbonyldinitrogen complex <u>13a</u> with aqueous HX (X= Cl, Br, I) gave only cis-$Cp^{*}Re(CO)_2X_2$ in excellent yields. No intermediate such as the hydrido halide complex $Cp^{*}Re(CO)_2(H)(X)$ was observed in either case. The same reaction with stoichiometric or excess of redistilled gaseous HBr did not go to completion and the only isolated products under anhydrous conditions were trans(H,Br)-$Cp^{*}Re(CO)_2(H)(Br)$ and traces of cis-<u>14b</u>. The amount of the latter was increased when the ether solution containing HBr during reaction was exposed to normal atmosphere for short periods of time. Quantitative transformation was observed after overnight exposure to open atmosphere.

Reaction of the phosphinedinitrogen complex <u>13b</u> with aqueous HX however, gave the corresponding hydridohalide derivative <u>16</u> as the major product and about 10% of cis-<u>15</u>. The role of water in these reactions is an important factor to be determined.

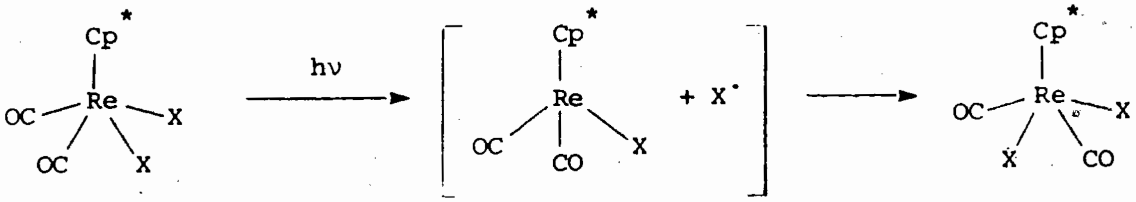
Photochemical cis-trans isomerization was observed to occur in the dicarbonyldihalide complexes $Cp^{*}Re(CO)_2X_2$ (X= Cl, Br, I) and $CpRe(CO)_2Cl_2$, but not in the phosphine ones $Cp^{*}Re(CO)(PMe_3)X_2$. Unfortunately, with the data available at the present time it is not clear if the isomerization occurs via a dissociative, radical or intramolecular mechanism. The former should involve the dissociation of one of the CO ligands from the cis-isomer followed by reassociation into the more sterically favored trans-isomer (see Eq.33).



Eq.33.

The generation of a rhenium (III) unsaturated complex "$Cp^{*}Re(CO)X_2$" can be analogous to the intermediate proposed in the photochemical reaction of $CpRe(PPh_3)_2H_2$, where dissociation of one of the PPh_3 ligands was demonstrated to occur with the generation of "$CpRe(PPh_3)H_2$".[177] The photolysis of cis-$Cp^{*}Re(CO)_2X_2$ in the presence of ^{13}CO could answer this question since incorporation of ^{13}CO into the trans-$Cp^{*}Re(CO)_2X_2$ product would support this mechanism.

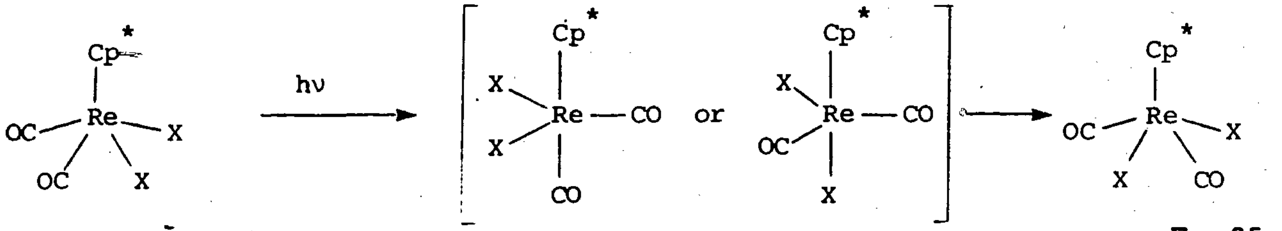
A radical mechanism should involve homolytic cleavage of a Re-X bond with generation of X· and the 17-electron complex $Cp^{*}Re(CO)_2X$ followed by reassociation into the trans-isomer (Eq.34).



Eq.34.

Radicals seem to be involved in the photolysis of cis-$Cp^{*}Re(CO)_2I_2$ conducted in $CHCl_3$ since the products of this reaction were trans-$Cp^{*}Re(CO)_2Cl_2$ and traces of $Cp^{*}Re(CO)_2ClI$. When the photolysis was carried out in hexane only 20% conversion into the trans isomer was observed; the rest was decomposition. No attempts were made to detect the presence of iodine which could be formed in this reactions.

A third possibility is an intramolecular mechanism involving a trigonal-bipyramidal intermediate or transition state with the Cp^* ligand always occupying one axial position (Faller-Anderson Model).[170] (Eq.35).



Eq.35.

This model has been postulated for the thermal cis-trans isomerizations of the square-pyramidal complexes $CpMo(CO)_2(L)X$ (L= phosphine or phosphite and X= halide). However, in the case of our rhenium complexes, these are thermally stable towards isomerization. Nevertheless, these trigonal-bipyramidal species could be expected to occur under photochemical conditions.

The irradiation of the dibromide complex cis-<u>14b</u> in $CHCl_3$ apparently did not involve a radical mechanism since no formation of $Cp^*Re(CO)_2Cl_2$ or $Cp^*Re(CO)_2BrCl$ was observed. This result suggests that CO dissociation or intramolecular rearrangement are more likely to occur in complexes possessing much stronger M-X bonds, i.e. cis-$Cp^*Re(CO)_2X_2$ (X= Cl, Br) and $CpRe(CO)_2Cl_2$.

It is evident that more work needs to be done in order to gain more insight into the mechanism of the reactions involved in this chapter. Nevertheless, the reactions of the dicarbonyl- and monocarbonyltrimethylphosphinedinitrogen complexes with halogens (X_2) or hydrogen halides (HX) to produce dihalide and hydridohalide derivatives are further illustrations of the synthetic potential of dinitrogen complexes. They can be regarded as a source of reactive low-valent metal centers by ready loss of the dinitrogen ligand from the intermediate produced under non-photochemical conditions.

6.4. Experimental Section

All manipulations, solvent purification and spectroscopic measurements were performed as described in the preceding chapters. The m/z values reported for the MS are referred to the more abundant isotopes i.e., ^{187}Re, ^{35}Cl and ^{79}Br. Photochemical reactions were carried out using quartz tubes. Gaseous HCl and HBr (Matheson) were used without purification, except for the anhydrous reaction. Coupling constants (J) are reported in Hz.

Preparation of cis-$Cp^*Re(CO)_2Cl_2$ (cis-**14a**)

The mixture of $Cp^*Re(CO)_2(N_2)$ (**13a**) and $Cp^*Re(CO)_3$ (Method 2; 80 mg) was dissolved in diethylether (10 mL) at room temperature and aqueous conc. HCl (2 mL) was added with stirring or HCl(g) was bubbled through the solution for 3-4 min. After 10 min the yellow color began to change to red and the mixture was stirred overnight. Solvent was pumped off and the residue washed with hexane to remove the $Cp^*Re(CO)_3$ (32 mg). The red-orange residue was dissolved in CH_2Cl_2 and chromatographed on a Florisil column (prepared in hexane). Hexane was first used to elute any traces of $Cp^*Re(CO)_3$ then the product was eluted as an orange-red band using acetone (42 mg; 79% yield) and recrystallized from CH_2Cl_2 as orange microcrystals which decomposed above 180°C without melting. IR (CH_2Cl_2): 2037 vs, 1958 s ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.98 s (Cp^*). ^{13}C NMR ($CDCl_3$): δ 10.20 q (J= 129.6 Hz, $C_5\underline{Me}_5$), 108.03 ($\underline{C}_5Me_5$), 203.94 (CO). MS (EI): m/z 448 (M^+), 420 $(M-CO)^+$, 392 $(M-2CO)^+$, 413 $(M-Cl)^+$. Anal. Calcd. for cis-14a: C, 32.14; H, 3.34. Found: C, 31.90; H, 3.17.

Preparation of trans-$Cp^*Re(CO)_2Cl_2$ (trans-14a)

Cis-$Cp^*Re(CO)_2Cl_2$ (19 mg) was dissolved in $CHCl_3$ (15 mL) and irradiated for 25 min in a quartz tube. The color of the solution changed from orange to yellow. Chromatography on a Florisil column (prepared in hexane) using 1:1 CH_2Cl_2-hexane moved an orange band from which the trans isomer was obtained as yellow-orange needles (12 mg, 64%) after recrystallization from CH_2Cl_2-hexane (4:1) at -20°C. It decomposed without melting above 85°C. Acetone moved residual cis isomer. IR (CH_2Cl_2): 2059 s, 1986 vs ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.89 s (Cp^*). ^{13}C {^1H} NMR ($CDCl_3$): δ 9.48 s ($C_5\underline{Me}_5$), 106.15 s ($\underline{C}_5Me_5$), 189.74 (CO). MS (EI): m/z 448 (M^+), 420 $(M-CO)^+$, 392 $(M-2CO)^+$, 413 $(M-Cl)^+$. Anal. Calcd. for trans-14a: C, 32.14; H, 3.34. Found: 31.66; H, 3.44.

Preparation of cis-$Cp^*Re(CO)_2Br_2$ (cis-14b)

Hydrogen bromide was bubbled through diethylether (15 mL) for 5 min at room temperature, then the mixture of 13a and $Cp^*Re(CO)_3$ (Method 2; 110 mg) was added. Alternatively, 2 mL of 48% aqueous HBr were used. The mixture was stirred overnight and changed color slowly from yellow to red. A red solid precipitated. Solvent was removed and the solid was washed twice with 10 mL portions of hexane to remove $Cp^*Re(CO)_3$ (47 mg) then redissolved in CH_2Cl_2 and chromatographed on Florisil. Elution with CH_2Cl_2-hexane (1:1) moved a red band which gave 76 mg (91%) of the cis isomer. Recrystallization from CH_2Cl_2-hexane gave red microcrystals which decomposed above 190°C without melting. IR (CH_2Cl_2): 2033 vs, 1958 s ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.06 s (Cp^*). ^{13}C NMR ($CDCl_3$): δ 10.42 q (J= 129.6, $C_5\underline{Me}_5$), 106.88 s ($\underline{C}_5Me_5$), 201.52 s (CO). MS (EI): m/z 536 (M^+), 508 $(M-CO)^+$, 480 $(M-2CO)^+$, 457 $(M-Br)^+$. Anal. Calcd. for cis-14b: C, 26.77; H, 2.78. Found: C, 26.83; H, 2.56.

Preparation of trans-$Cp^*Re(CO)_2Br_2$ (trans-14b)

Cis-$Cp^*Re(CO)_2Br_2$ (24 mg) was dissolved in $CHCl_3$ (15 mL) and irradiated for 35 min in a quartz tube. The color changed from red to orange-yellow. Solvent was pumped off and the orange solid was dissolved in CH_2Cl_2 and chromatographed on a Florisil column prepared in hexane. Elution with CH_2Cl_2-hexane (2:3) moved an orange band which yielded the trans isomer as an orange solid. Recrystallization twice from CH_2Cl_2-heptane gave orange crystals

(15 mg, 63%) which decomposed above 115°C without melting. IR (CH_2Cl_2): 2050 s, 1981 vs ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.00 s (Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.33 s ($C_5\underline{Me}_5$), 105.04 s ($\underline{C_5}Me_5$), 186.40 s (CO). MS (EI): m/z 536 (M^+), 508 $(M-CO)^+$, 480 $(M-2CO)^+$, 457 $(M-Br)^+$. Anal. Calcd. for trans-14b: C, 26.77; H, 2.78. Found: C, 26.73; H, 2.88.

Preparation of cis-$Cp^*Re(CO)_2I_2$ (cis-14c)

The mixture of 13a and $Cp^*Re(CO)_3$ (Method 2; 80 mg) was dissolved in diethylether (15 mL). Hydrogen iodide (2 mL of a freshly opened, colorless 47% aqueous solution, Eastman Kodak was added and the two phase mixture was stirred vigorously overnight. Ether was pumped off and the residual aqueous HI was removed by syringe to leave a red solid which was washed with water (2 x 2 mL) and vacuum dried. Washing with pentane removed the $Cp^*Re(CO)_3$ component (36 mg) and the remaining red solid was dissolved in CH_2Cl_2 and chromatographed on a Florisil column eluting with CH_2Cl_2-hexane (3:2). Recrystallization from CH_2Cl_2-hexane gave red needles (67 mg; 98%) which decomposed above 210°C without melting. IR (CH_2Cl_2): 2022 vs, 1953 s ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.23 s (Cp^*). ^{13}C NMR ($CDCl_3$): δ 11.13 q (J=129.9, $C_5\underline{Me}_5$), 104.63 s ($\underline{C_5}Me_5$), 199.52 s (CO). MS (EI): m/z 632 (M^+), 604 $(M-CO)^+$, 576 $(M-2CO)^+$, 505 $(M-I)^+$. Anal. Calcd. for cis-14c: C, 22.82; H, 2.37. Found: C, 22.95; H, 2.46.

Preparation of trans-$Cp^*Re(CO)_2I_2$ (trans-14c)

The cis isomer (25 mg) suspended in hexane (in which it is slightly soluble) was irradiated in a quartz tube for 2 h. The resulting brown-red solution was chromatographed on Florisil column using 3:2 CH_2Cl_2-hexane as eluant and removed a red-orange band which contained the product (ca. 20% conversion). Then, acetone removed a brown band which did not show IR absorptions in the 2200-1800 cm^{-1} region. The trans isomer was identified by comparison with that formed from $Cp^*Re(CO)_3$ and I_2 (see below). Irradiation in $CHCl_3$ did not result in formation of diiodo compounds; trans-14a and a trace of $Cp^*Re(CO)_2ClI$ (identified by its MS) were formed instead.

Reaction of $Cp^*Re(CO)_3$ with I_2

$Cp^*Re(CO)_3$ (200 mg) was dissolved in hexane (100 mL) and an excess of I_2 in hexane was added to give an immediate dark red precipitate of $[Cp^*Re(CO)_3I][I_3]$ (see below). The suspension was rapidly stirred and irradiated for 1 h in a quartz tube. Solvent was pumped off and the red solid residue which was a mixture of cis-14c and trans-14c was chromatographed on a Florisil column prepared in hexane. A hexane wash first removed traces of unreacted $Cp^*Re(CO)_3$, then red-orange trans-14c (35 mg; 11%; decomposed without melting above 170°C) was recovered from an orange band which was eluted using CH_2Cl_2-hexane (1:1). IR (CH_2Cl_2): 2028 s, 1964 vs ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.21 s (Cp^*). ^{13}C NMR ($CDCl_3$): δ 12.12 q (J= 129.3, C_5Me_5), 102.94 s (C_5Me_5), 183.00 s

(CO). MS (EI): m/z 632 (M^+), 604 $(M-CO)^+$, 576 $(M-2CO)^+$, 505 $(M-I)^+$. Anal. Calcd. for trans-14c: C, 22.82; H, 2.37. Found: C, 22.94; H, 2.34.

A red band was next eluted using CH_2Cl_2-hexane (4:1) which yielded cis-14c (160 mg; 51%) as a red solid.

The precipitate of $[Cp^*Re(CO)_3I][I_3]$ was identified as follows: IR (KBr) 2087 vs, 2045 m, 2027 vs ν(CO) cm^{-1}. MS (FAB): m/z for cation $[Cp^*Re(CO)_3)I]^+$ 553 (M^+), 505 $(M-CO)^+$, 447 $(M-2CO)^+$, 405 $(M-3CO)^+$, 406 $(M-I)^+$. Anal. Calcd. for $[Cp^*Re(CO)_3I][I_3]$: C, 17.60; H, 1.69. Found: C, 17.20; H, 1.70. When stirred with hexane, the suspended solid partly redissociated to give a violet solution containing I_2 and $Cp^*Re(CO)_3$ (IR). Freshly prepared solutions in $CHCl_3$ exhibited IR bands of $[Cp^*Re(CO)_3I][I_3]$ (2099 s, 2043 s ν(CO) cm^{-1}) and $Cp^*Re(CO)_3$ (2007 s, 1914 s ν(CO) cm^{-1}) having comparable intensities. Addition of I_2 to saturation increased the relative intensity of the former but those of $Cp^*Re(CO)_3$ were still present (though about half as intense). ^1H NMR ($CDCl_3$): δ 2.39 s (Cp^*) (at -50°C δ 2.48 s). $^{13}C\{^1H\}$ NMR δ 11.4 s ($C_5\underline{Me}_5$), 103.2 s ($\underline{C}_5Me_5$), 191 br (CO). Spectra are assigned to fast exchange of $[Cp^*Re(CO)_3I][I_3]$ and $Cp^*Re(CO)_3$. M.p. 128°C.

Preparation of cis-$CpRe(CO)_2Cl_2$

The dinitrogen complex $CpRe(CO)_2(N_2)$ (prepared by reacting $[CpRe(CO)_2(\underline{p}-N_2C_6H_4OMe)][BF_4]$ (100 mg) in acetone with KI) was dissolved without further purification in hexane and a dilute solution of Cl_2 in hexane was added dropwise until all of the dinitrogen complex was reacted (by IR). The brown precipitate formed was removed, washed twice with hexane and with ether, and then recrystallized in good yield from acetone-ether (10:1) at -10°C as red microcrystals which decomposed slowly above 170°C without melting. IR (acetone): 2056 vs, 1976 s ν(CO), cm^{-1}. IR ($CHCl_3$): 2061 vs, 1988 s ν(CO), cm^{-1}. ^1H NMR (acetone-d_6): δ 6.54 s ((C_5H_5). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 98.55 s (C_5H_5), 201.85 s (CO). MS (EI): m/z 378 (M^+), 350 $(M-CO)^+$, 322 $(M-2CO)^+$, 343 $(M-Cl)^+$. Anal. Calcd. for cis-$CpRe(CO)_2Cl_2$: C, 22.28; H, 1.32. Found: C, 22.50; H, 1.40.

Preparation of trans-$CpRe(CO)_2Cl_2$

Cis-$CpRe(CO)_2Cl_2$ was dissolved in a large excess of $CHCl_3$ (in which it is poorly soluble) and irradiated for 40 min in a quartz tube. The IR spectrum now showed only the trans isomer to be present. The red solid remaining after pumping off the solvent was chromatographed on Florisil with CH_2Cl_2 as eluant. Recrystallization from CH_2Cl_2-ether (3:1) gave red microcrystals in approximate 70% yield which decomposed without melting above 135°C. IR (CH_2Cl_2): 2078 s, 2012 vs ν(CO), cm^{-1}. IR ($CHCl_3$): 2081 s, 2017 vs ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.69 s (C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 95.32 s (C_5H_5), 185.72 s (CO). MS (EI): m/z 378 (M^+), 350 $(M-CO)^+$, 343 $(M-Cl)^+$. Anal. Calcd. for trans-$CpRe(CO)_2Cl_2$: C, 22.28; H, 1.32. Found: C, 22.42; H, 1.19.

Preparation of cis-$Cp^*Re(CO)(PMe_3)Cl_2$ (cis-15a)

This complex was prepared following the same procedure to prepare cis-15b (see below) using dilute hexane solution of Cl_2 (prepared by bubbling Cl_2 gas into hexane for few minutes). Cis-15a was obtained as a red solid in 88% yield. It melted at 183oC with decomposition. IR (CH_2Cl_2): 1899 vs ν(CO), cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.76 d (J= 10.41, 9H, PMe_3), 1.82 d (J= 0.4, 15H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$: δ 10.46 s ($C_5\underline{Me}_5$), 17.89 d (J= 41.2, $P\underline{Me}_3$), 103.69 s ($\underline{C}_5Me_5$), 222.90 d (J= 24.6, CO). MS (EI): m/z 496 (M^+), 468 $(M-CO)^+$, 433 $(M-CO-Cl)^+$, 392 $(M-CO-PMe_3)^+$. Anal. Calcd. for cis-15a: C, 33.87; H, 4.84. Found: C, 33.73; H, 4.77.

Preparation of cis-$Cp^*Re(CO)(PMe_3)Br_2$ (cis-15b)

To a stirred solution of the dinitrogen complex 13b (50 mg, 0.110 mmol) in hexane a dilute hexane solution of Br_2 was added dropwise until all the starting material disappeared (by IR). Upon addition of the bromine solution, a red precipitate was formed. Hexane was pipetted off and the precipitate dried under vacuum. The resulting red-brown solid was chromatographed on a neutral alumina column. The column was washed with hexane and the product then eluted with acetone. Removal of the acetone under vacuum, resulted in a red-brown solid. Recrystallization from CH_2Cl_2/hexane at -15°C gave cis-15b (6.2 mg) as dark red microcrystals in 97% yield. M.p. decomposed above 210oC. IR (CH_2Cl_2): 1902 vs ν(CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.84 d (J= 10.2, 9H, PMe_3), 1.89 d (J= 0.4, 15H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.83 s ($C_5\underline{Me}_5$), 19.20 d (J= 41.5, PMe_3), 102.67 s ($\underline{C}_5Me_5$), 220.28 d (J= 24.9, CO). MS (EI): m/z 584 (M^+), 556 $(M-CO)^+$, 480 $(M-CO-PMe_3)^+$. Anal. Calcd. for cis-15b: C, 28.72; H, 4.10. Found: C, 28.88; H, 4.11.

Preparation of trans-$Cp^*Re(CO)(PMe_3)Br_2$ (trans-15b)

$Cp^*Re(CO)(PMe_3)(H)(Br)$ (40 mg, 0.079 mmol) was dissolved in 10 mL of freshly distilled THF. To this yellow solution at 0°C was added 16 mg of solid NBS. The color changed immediately to orange-red and the ν(CO) absorption in the IR spectrum was replaced by one ~ 40 cm^{-1} to higher wavenumber. Evaporation of THF, extraction with hexane and recrystallization from hexane at -78°C gave 42.5 mg (95% yield) of trans-15b as an orange-red solid. M.p. slow decomposition above 185°C. IR (CH_2Cl_2): 1937 vs ν(CO) cm^{-1}. IR (THF): 1943 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.63 d (J= 9.6, 9H, PMe_3), 1.85 s (15H, Cp^*). ^{13}C NMR ($CDCl_3$): δ 10.33 q (J= 128.1, $C_5\underline{Me}_5$), 16.13 q of d ($^1J_{CH}$= 130.3, $^1J_{CP}$= 36.0, PMe_3), 101.25 s ($\underline{C}_5Me_5$), 205.20 d ($^2J_{CP}$= 3.7, CO). MS (EI): m/z 584 (M^+), 556 $(M-CO)^+$, 480 $(M-CO-PMe_3)^+$. Anal. Calcd. for trans-15b: C, 28.72; H, 4.10. Found: C, 28.99; H, 4.06.

Other Properties of trans-$Cp^*Re(CO)(PMe_3)Br_2$

Isomerization trans→cis is observed in C_6H_6 (dark) after 1 day ~ 10% (by IR); after 5 days ~ 80% (room temperature). After 1 day in $CDCl_3$ at room temperature in presence of daylight ~ 25% (by IR).

Preparation of cis-Cp*Re(CO)(PMe$_3$)I$_2$ (cis-15c)

A procedure similar to that used in the synthesis of the cis-15b complex, using hexane solution of I$_2$ gave the product in 90% yield as brown-red microcrystals. M.p. 191°C with decomposition. IR (CH$_2$Cl$_2$): 1902 vs ν(CO) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.95 d (J= 9.8, 9H, PMe$_3$), 2.04 d (J= 0.64, Cp*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 11.77 s (C$_5$Me$_5$), 21.82 d ($^1J_{CP}$= 41.7, PMe$_3$), 100.80 s (C$_5$Me$_5$), 217.25 d $^2J_{CP}$= 26.3, CO). MS (EI): m/z 680 (M$^+$), 652 (M-CO)$^+$, 576 (M-CO-PMe$_3$)$^+$. Anal. Calcd. for cis-15c: C, 24.71; H, 3.53. Found: C, 25.01; H, 3.60.

Preparation of trans-Cp*Re(CO)(PMe$_3$)(H)(Cl) (16a)

In a similar procedure to that described below for 16b, using 37% aqueous HCl solution, this hydridochloride complex 16a was obtained in 85% yield as a yellow solid. Also cis-15a was obtained in about 10% from the aqueous layer. M.p. 75°C. IR (hexane): 1920 vs ν(CO) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ -9.35 d ($^2J_{PH}$= 56.10, 1H, Re-H), 1.58 d (J= 9.6, 9H, PMe$_3$), 1.97 s (15H, Cp*). ^{13}C NMR (C$_6$D$_6$): δ 10.98 q (J= 127.5, C$_5$Me$_5$), 19.33 q of d ($^1J_{CH}$= 130.8, $^1J_{CP}$= 35.4, PMe$_3$), 96.38 s (C$_5$Me$_5$), 207.80 d ($^2J_{CH}$= 10.0 (singlet in ^{13}C{^{1}H} NMR), CO). MS (EI): m/z 462 (M$^+$), 432 (M-CO)$^+$. Anal. Calcd. for 16a: C, 36.36; H, 5.41. Found: C, 36.20; H, 5.38.

Preparation of trans-Cp*Re(CO)(PMe$_3$)(H)(Br) (16b)

The dinitrogen complex 13b (50 mg, 0.110 mmol) in diethylether was stirred with an excess of aqueous HBr solution (0.5 mL, 48%). The reaction was followed by IR spectroscopy until all the dinitrogen complex reacted (ca. 10 min) giving a yellow organic layer and brownish aqueous layer which contained cis-15b in less than 10%. The yellow solution was separated, and the solvent pumped off. The yellow product was then dissolved in hexane and filtered through Celite, resulting in a yellow solid when dried under vacuum. Yield 50 mg (90%). M.p. 120°C. IR (hexane): 1922 vs, ν(CO) cm^{-1}. ^{1}H NMR (C_6D_6): δ -10.33 d ($^2J_{PH}$= 55.74, 1H, Re-H), 1.38 d (J= 9.30, 9H, PMe_3), 1.84 s (15H, Cp*). ^{13}C NMR (C_6D_6): δ 11.23 q (J= 127.5, $C_5\underline{Me}_5$), 20.68 q of d ($^1J_{CH}$= 128.0, $^1J_{CP}$= 36.9, PMe_3), 95.37 s ($\underline{C}_5Me_5$), 206.45 d ($^2J_{CH}$= 8.71 (singlet in $^{13}C\{^1H\}$ NMR), CO). MS (EI): m/z 506 (M^+), 476 $(M-30)^+$. Anal.Calcd. for 16b: C, 32.20; H, 4.94. Found: C, 32.99; H, 4.95.

Preparation of trans-Cp*Re(CO)(PMe_3)(H)(I) (16c)

A procedure similar to that used in the synthesis of the previous hydridohalide complexes, using 47% aqueous HI solution gave the product in 82% yield as a yellow solid. A small amount (ca. 5%) of cis-15c was also contained from the aqueous layer. M.p. 140°C. IR (hexane): 1925 vs, ν(CO) cm^{-1}. ^{1}H NMR (C_6D_6): δ -11.46 d ($^2J_{PH}$= 56.1, 1H, Re-H), 1.45 d (J= 9.1, 9H, PMe_3), 1.89 s (15H, Cp*). ^{13}C NMR (C_6D_6): δ 11.85 q (J= 127.7, $C_5\underline{Me}_5$), 23.05 q of d ($^1J_{CH}$= 130.6, $^1J_{CP}$= 36.5, PMe_3), 95.11 s ($\underline{C}_5Me_5$), 204.32 d ($^2J_{CH}$= 10.8 (singlet in $^{13}C\{^1H\}$ NMR), CO). MS (EI): m/z 554 (M^+), 524 $(M-30)^+$. Anal. Calcd. for 16c: C, 30.32; H, 4.51. Found: C, 30.12; H, 4.46.

Preparation of cis-$[Cp^*Re(CO)_2(PMe_3)I][I_3]$

100 mg (0.220 mmol) of $Cp^*Re(CO)_2(PMe_3)$[190] (prepared from the reaction of $Cp^*Re(CO)_2(THF)$ with PMe_3) were dissolved in 8 mL of diethylether at room temperature ,and saturated ether solution of I_2 was added with stirring until all the carbonylphosphine complex reacted (by IR). The red precipitate then formed was washed three times with ether (5 mL) and dried under vacuum. Yield 209 mg (99%). M.p. VVV Ir (CH_2Cl_2): 2039 vs, 1973 s, ν(CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.12 d (J= 10.3) and 2.37 d (J= 0.9, 15H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.85 s ($C_5\underline{Me}_5$), 19.99 d (J=41.7, $P\underline{Me}_3$), 107.02 s ($\underline{C}_5Me_5$), 187.72 d (J= 15.3, CO), 202.45 d (J= 24.8, CO). MS (FAB, xenon, sulfolane): m/z 581 (M^+), 553 $(M-CO)^+$, 525 $(M-2CO)^+$, 505 $(M-PMe_3)^+$.

Reaction of $Cp^*Re(CO)_2(N_2)$ (13a) with Anhydrous HBr

This reaction was carried out in a vacuum system equipped with a Toepler pump. Compound 13a (prepared according to method 1) (118 mg, 0.291 mmol) was dissolved in 40 mL of ether and degassed twice. To this pale-yellow solution an stoichiometric amount of redistilled gaseous HBr (8.0 mL, 0.291 mmol) was added and stirred overnight at room temperature. After this time the mixture became yellow, and contained a small amount of a bright yellow solid. The amount of gas evolved at this stage was very small, only N_2 was detected by MS. An IR spectrum of the yellow solution indicated that most of 13a remained unreacted, but in addition, a new carbonyl absorption was present at 2031 cm^{-1}. More gaseous HBr was added (ca. 15 mL) and the mixture stirred for four additional days. After this time, the color intensity of the solution increased and about 15 mg of the same bright yellow solid were formed. The solution was taken off by syringe and was allowed to react under undried N_2 for an additional five days. Simultaneously, 3 mL of the same solution were exposed to air and a red solid precipitated out. This productwas analyzed by IR as the bromide complex cis-14b. After five days, ether was evaporated under vacuum and a yellow-brown residuewas extracted with hexane (2 x 10 mL). Some insoluble light-brown material was identified by IR as cis-14b (ca. 4 mg). After successive recrystallization from hexane at -78°C, additional 25 mg of the golden yellow solid were isolated and identified as the hydridobromide complex trans(H,Br)-$Cp^*Re(CO)_2(H)(Br)$. 35 mg of the unreactive dinitrogen complex 13a were also obtained from the supernatant solution. The total isolated yield of the hydridobromide complex was 40 mg (42.6% based on the unreacted dinitrogen). The hydridobromide complex decomposed above 75°C. It is stable in ether solution under nitrogen, however when aqueous HBr was added a slow reaction took place. After one day stirring at room temperature, it quantitatively converted to cis-14b. IR (hexane): 2030 m, 1964 vs, ν(CO) cm^{-1}. ^1H-NMR (C_6D_6): δ -9.98 s (1H, Re-H), 1.64 s (15H, Cp^*). ^{13}C NMR (C_6D_6): δ 10.49 q (J= 128.6, $C_5\underline{Me}_5$), 99.85 s ($\underline{C}_5Me_5$), 195.75 d (J= 13.6, singlet in $^{13}\{^1H\}$ NMR, CO).

MS (EI): m/z 458 (M^+), 430 $(M-CO)^+$. Anal. Calcd. for trans-(H,Br)-Cp*Re(CO)$_2$(H)(Br): C, 31.44; H, 3.49. Found: C, 31.42; H, 3.48.

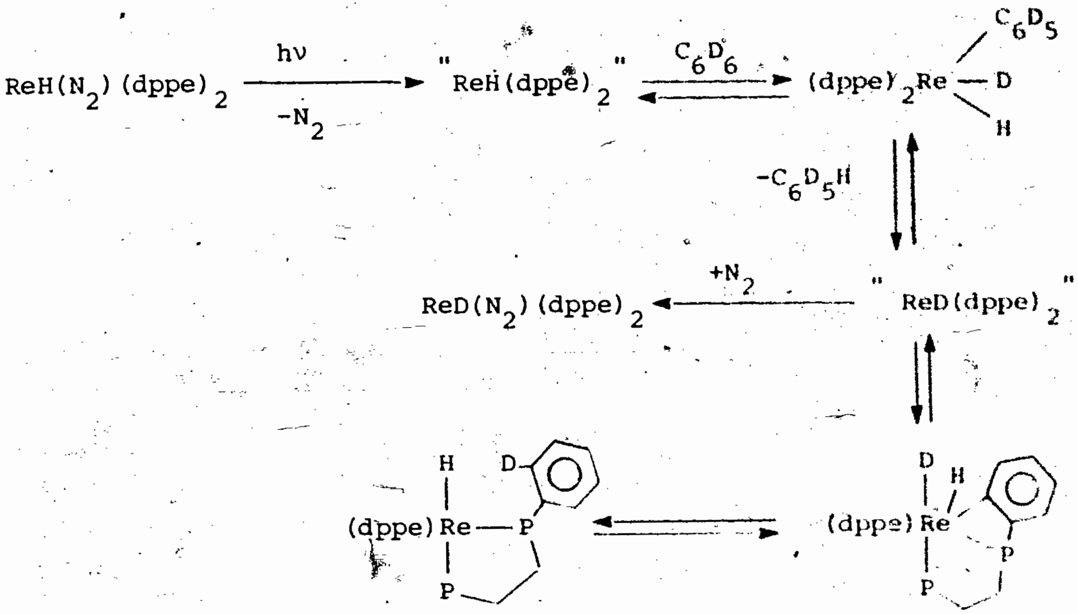
CHAPTER VII

Photochemical Reactions of $Cp^*Re(CO)(L)(N_2)$, L=CO and PMe_3 with Saturated and Unsaturated Hydrocarbons

7.1. Introduction

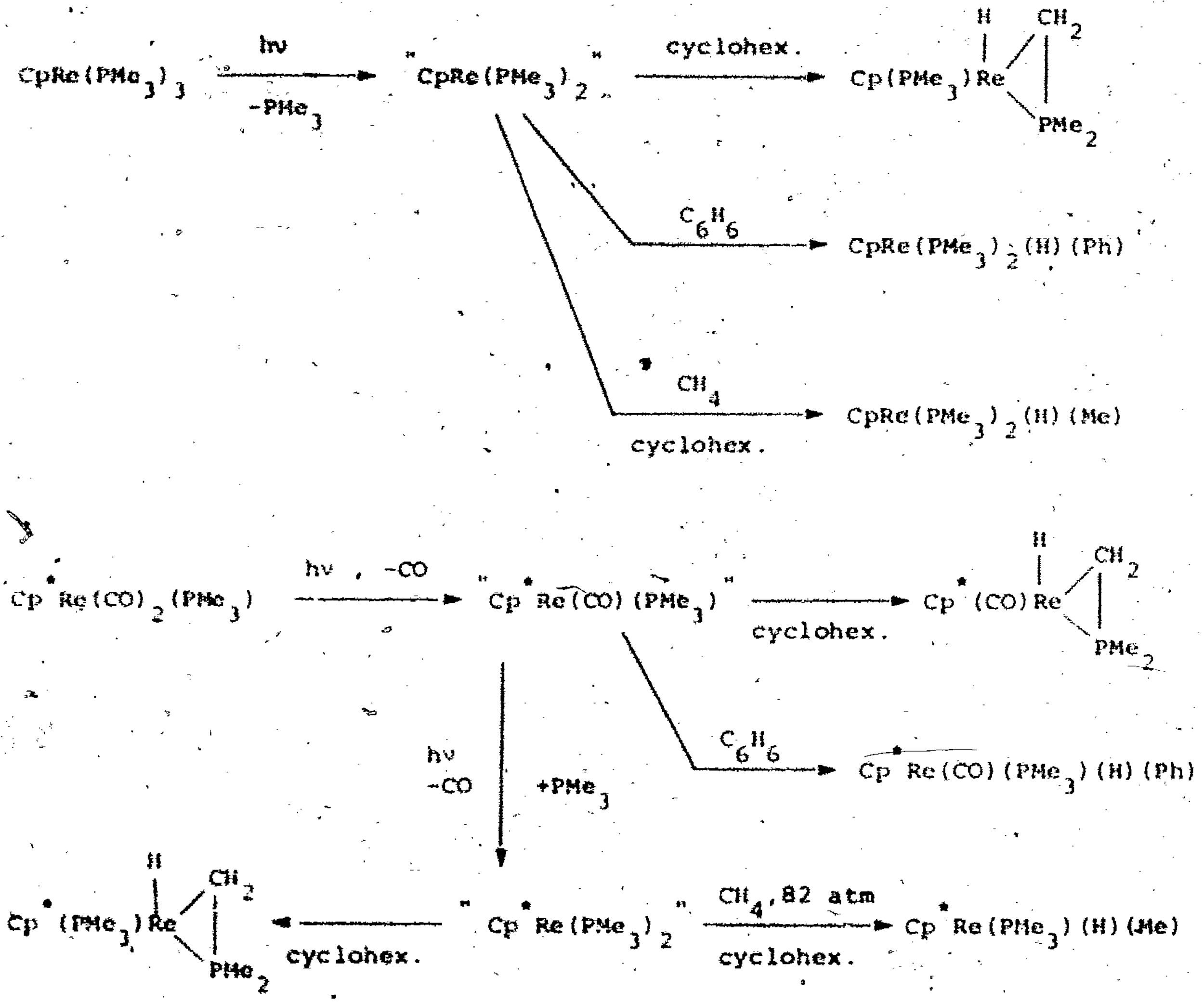
The photoextrusion of N_2 from dinitrogen complexes has been known since 1972 when Darensbourg first reported that N_2 substitution by CO in some Fe, Mo, Re and Os complexes was greatly facilitated by UV irradiation.[178] Since then, several reports have been published involving photochemical reactions of dinitrogen complexes to facilitate substitution[179] or addition reactions[90] at the metal center. In most of these reactions, notably carried out in aromatic solvents such as benzene, the unsaturated fragment formed by photoextrusion of N_2 apparently does not react with the solvent.[180] As far as we know, only one dinitrogen complex $ReH(N_2)(dppe)_2$ has been reported capable of activating aromatic C-H bonds both intramolecularly and intermolecularly by photoelimination of N_2.[181] The sequence of reactions leading to the incorporation of deuterium from C_6D_6 into both the metal and the dppe ligand, with the corresponding hydrogen incorporation into the deuterated solvent, is shown in Scheme XIII.

However, this reaction did not provide isolable inter- or intramolecular C-H activation products.[181]



Scheme XIII

Intermolecular C-H bond activation in unsaturated, and especially in saturated, hydrocarbons by soluble transition metal complexes is today one of the most important topics in organometallic chemistry. The main interest in these reactions is to learn the chemical requirement for causing such stable substances to react and to understand their mechanisms. In recent years, several reports (including some reviews[182,183]) have been published emphasizing the synthesis of metal complexes (or their fragments) which are able to activate hydrocarbon C-H bonds. The most comprehensive studies in this field involving iridium and rhodium complexes are currently being carried out by Bergman,[184,185] Crabtree,[183,186] Graham[187,188] and Jones.[189] In 1985, Bergman and coworkers demonstrated that the rhenium complexes $CpRe(PMe_3)_3$, $Cp^*Re(CO)_2(PMe_3)$ and $Cp^*Re(CO)(PMe_3)_2$ can also be used as photochemical precursors for intra and intermolecular C-H activation products.[190] Some of these reactions are shown in Scheme XIV.



Scheme XIV

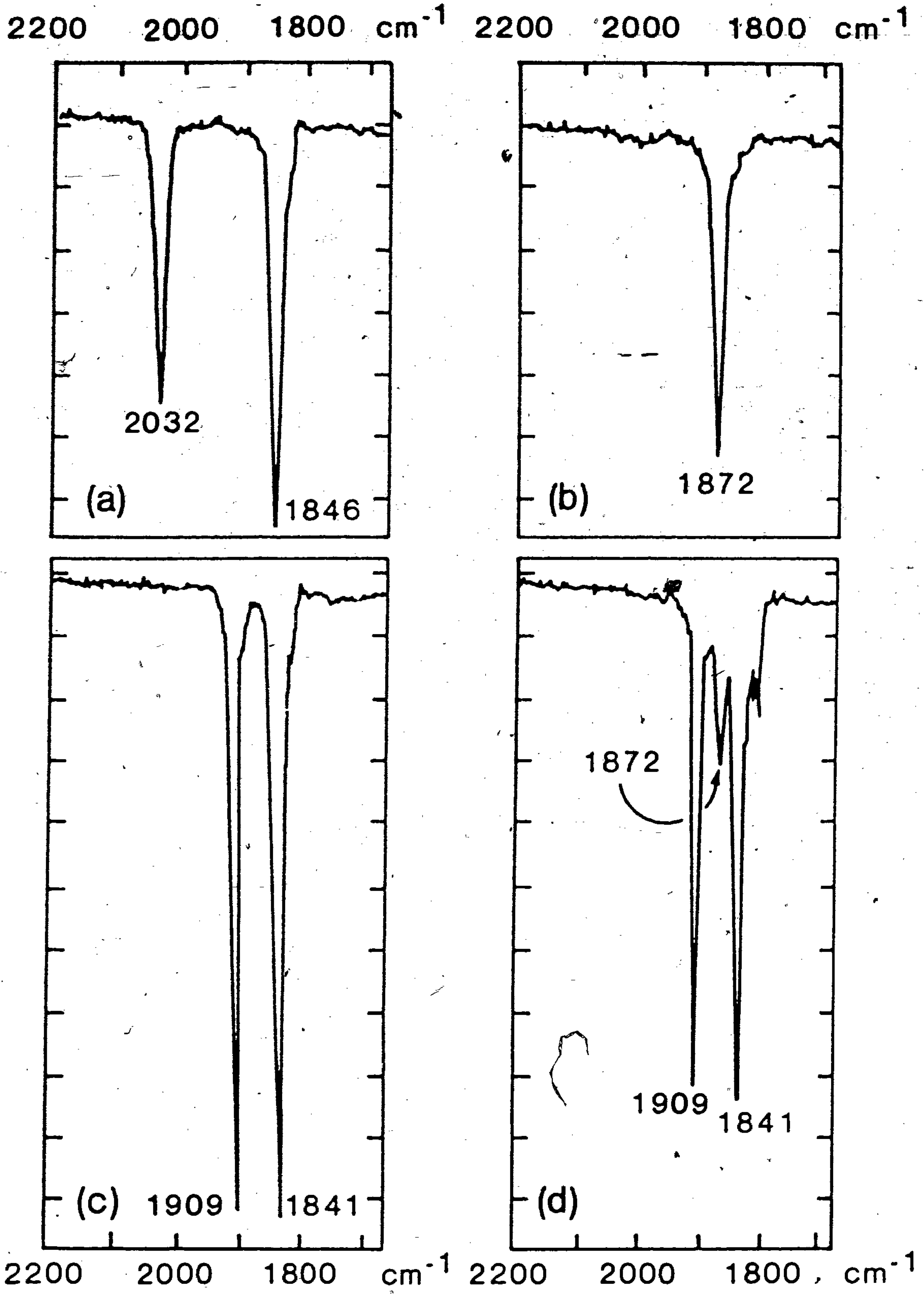
It was found that the best results were obtained in the photolysis of $CpRe(PMe_3)_3$, for which all the insertion products could be isolated and characterized.[190] For the Cp^* systems, particularly those containing the $Cp^*Re(CO)(PMe_3)$ fragment, it was suggested that, due to the instability of the insertion products, these could not be isolated, and therefore they were only partially characterized by IR and ^1H NMR. Very recently in further rhenium work, trans-$CpRe(PPh_3)_2H_2$ has been shown to catalyze H/D exchange between benzene and a variety of alkanes including methane under photochemical conditions.[177] Photodissociation of the phosphine ligand to generate an unsaturated rhenium (III) fragment "$CpRe(PPh_3)H_2$", followed by oxidative addition of the hydrocarbon to produce a rhenium (V) intermediate, has been proposed to be the mechanism.[177]

In this chapter, the potential use of dinitrogen complexes in C-H bond activation is illustrated by the photochemical reactions of the trimethylphosphinedinitrogen complex $Cp^*Re(CO)(PMe_3)(N_2)$ (13b) in saturated and unsaturated hydrocarbons. The effectiveness of 13b by comparison with the Bergman precursor $Cp^*Re(CO)_2(PMe_3)$, in intra and intermolecular C-H activation will be presented. Some preliminary photochemical reactions using the dicarbonyl dinitrogen complex 13a are also included. A preliminary report of this work has been accepted for publication.[191]

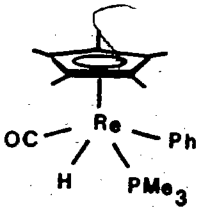
7.2. Synthesis and Characterization

UV-irradiation of the trimethylphosphinedinitrogen complex 13b in benzene solution (Fig.15a) at room temperature for only 10

Fig.15. A comparison of the production of the phenylhydrido complex (17) (ν(CO) 1872 cm^{-1}) from irradiation of Cp*Re(CO)(PMe$_3$)(N$_2$) (13b) or Cp*Re(CO)$_2$(PMe$_3$) in benzene. IR spectra of (a) 13b, (b) 10 min irradiation of 13b, (c) Cp*Re(CO)$_2$(PMe$_3$), (d) 10 min irradiation of Cp*Re(CO)$_2$(PMe$_3$).


2200
2000
1800
cm-1
2032
1846
(a)
1872
(b)
1909
1841
(c)
1872
1909
1841
(d)

min resulted in quantitative conversion to a single carbonyl containing product (Fig.15b). This compound could be isolated from hexane at -78°C as a white solid and was characterized by spectroscopy and analysis as the benzene C-H activation product trans(H,Ph)-$Cp^*Re(CO)(PMe_3)(H)(Ph)$ (17).



17

By way of comparison, we observed (Figs.15c and 15d) that the irradiation of one of Bergman's photoprecursors $Cp^*Re(CO)_2(PMe_3)$[190] under identical conditions gave a low yield of 17. Compound 17 is air-sensitive but stable as a solid and in hexane solution under N_2 at low temperature (-15 to -78°C). Solid samples can be stored at -15°C under N_2 atmosphere (freezer) for several months without visible deterioration. It is very soluble in benzene, hexane and cyclohexane. It also dissolves in $CHCl_3$ and $CHBr_3$ but gives orange-red solutions which have been identified as the corresponding cis-dihalide complexes , cis-15a and cis-15b, respectively. When dissolved in C_6D_6, about 20% exchange of bound C_6H_6 with bulk solvent was determined by ^1H NMR and MS during six days at 8°C. A complete regeneration of the parent dinitrogen complex 13b was observed when 17 in hexane solution was pressurized to 2000 psi with N_2 for 12h.

The IR spectrum of 17 shows a strong and quite broad $\nu(CO)$

absorption at 1872 cm^{-1} in benzene (Fig.15b) and a sharp absorption at 1889 cm^{-1} in hexane. The presence of the hydride and phenyl ligands was clearly observed in the ^1H NMR spectrum. The resonance for the former appears as a doublet at δ -9.18 with $^2J_{PH}$= 66.7 Hz and integrates for 1H. For the latter a multiplet at δ 7.16 with a relative intensity of 3H is tentatively assigned to meta and para protons, and a second multiplet, at much lower field (δ 7.96) and with a relative intensity of 2H, is assigned to the ortho protons by analogy with the phenylcarbonyldiazenido complex 10a, discussed in Chapter IV. The ^{13}C NMR spectrum of complex 17 also demonstrates the presence of the phenyl ligand. The ^{13}C resonances appeared in the 123-147 ppm region and the assignment of each resonance was done on the basis of carbon couplings to phosphorus and protons (see Experimental Section). The carbonyl carbon resonance was observed at δ 209.02 as a doublet in the proton coupled spectrum and as a singlet in the decoupled spectrum.

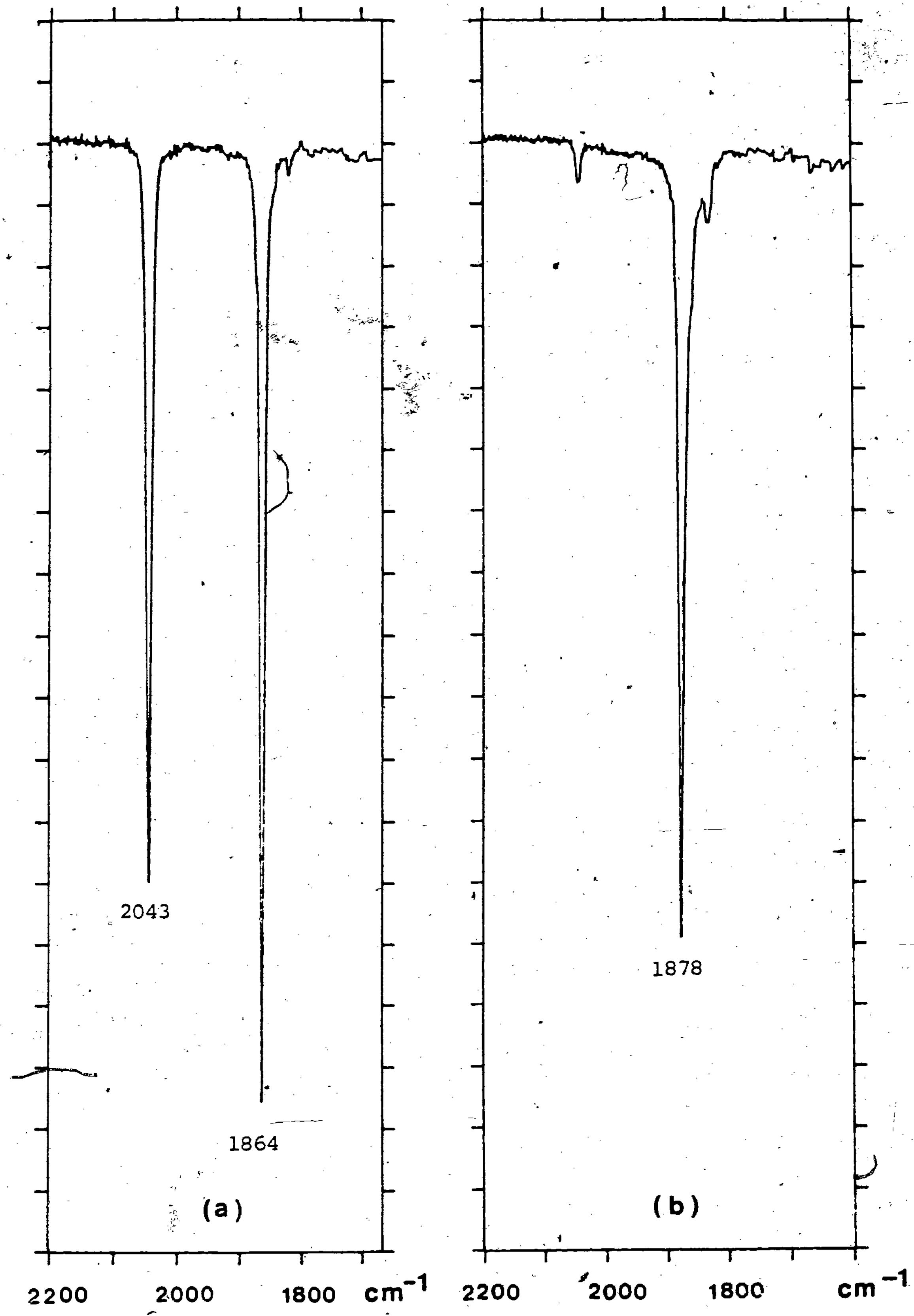
The electron-impact MS at 12 eV clearly confirms the formulation of this compound. It showed the molecular ion at m/z 504, and a base peak at m/z 426 resulting from the loss of benzene. At much higher energy (70 eV) the molecular ion could not be observed. Instead, the MS showed peaks at m/z 502, 474 and 426 which are believed to result from $Cp^*Re(CO)(PMe_3)_2$ formed by decomposition of 17.

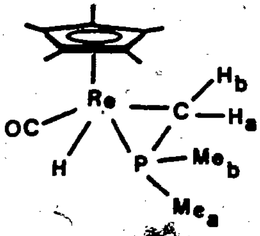
The assignment of mutually trans hydride and phenyl groups in complex 17 was based on the following results. The $^2J_{PH}$ value for the hydride resonance (66.7 Hz) indicates cis-hydride and PMe_3 groups. This value is in good agreement with those observed in the hydridohalide derivatives (16) which also possess a cis H-Re-PMe_3 moiety (see Chapter VI), and in the complexes cis-CpMo$(CO)_2(PR_3)(H)$[170] ($^2J_{PH}$= 64-67 Hz). For the CO group, a value of $^2J_{CH}$= 10.8 Hz was observed in the ^{13}C NMR spectrum and along with no observable coupling to phosphorus, this indicates that the CO is cis to the hydride and trans to the PMe_3 group. The value of $^2J_{CH}$ is in good agreement with that observed in trans(H,Br)-Cp*Re$(CO)_2(H)(Br)$ ($^2J_{CH}$= 13.7 Hz) (see Chapter VI). Furthermore, a strong NOE enhancement of the hydride and phenyl resonances resulted from irradiation of the PMe_3 proton signal.

UV-irradiation of the pure dicarbonyldinitrogen complex 13a in benzene under similar conditions to those used for 13b also resulted in loss of dinitrogen (by IR) and the formation of a clear yellow solution. This solution exhibited two strong ν(CO) absorptions of approximately equal intensity at 1937 and 1872 cm^{-1} (in benzene). A ^1H NMR spectrum of the crude yellow solution (in C_6H_6/C_6D_6, 4:1) showed no hydride resonance in the high field region (-5 to -15 ppm). Instead, two resonances were observed in the Cp* region, at δ 1.45 and 1.64 in a 2:3 ratio and a third at δ 5.98. The ν(CO) absorptions and the two resonances observed at δ 1.64 and 5.98 are comparable to those recently reported by Pasman and coworkers for Cp*Re$(CO)_2(\eta^2\text{-}C_6H_6)$ (IR (benzene): 1938, 1870 ν(CO), cm^{-1}; ^1H NMR (C_6H_6-C_6D_6 , 95:5): δ 1.59 (Cp*), 5.87 (C_6H_6)), and $[\{Cp^*Re(CO)_2\}_2(\mu\text{-}\eta^2,\eta^{2'}\text{-}C_6H_6)]$ (IR (benzene): 1937, 1871 ν(CO), cm^{-1}); ^1H NMR (C_6D_6): δ 1.66 (Cp^*), 2.85, 4.14 and 6.41 (μ-C_6H_6)). The former complex was a primary product of the photochemical reaction of $Cp^*Re(CO)_3$ in benzene, and the latter was formed in a dark reaction following the photolysis.[192] In our particular case, the ^1H NMR data was obtained immediately after photolysis of 13a in benzene. On the basis of these results, we suspect our spectroscopic analysis corresponds to the η^2-benzene complex $Cp^*Re(CO)_2(\eta^2$-$C_6H_6)$. However, we have not yet established the origin of the resonance observed at δ 1.45 in the ^1H NMR spectrum.

Irradiation of the dinitrogen complex 13a in saturated solvents such as hexane or cyclohexane gave the known dimers $Cp^*{}_2Re_2(CO)_3$ and $Cp^*{}_2Re_2(CO)_5$ reported by Hoyano and Graham.[144] However, the photolysis of the phosphinedinitrogen complex 13b in hexane or cyclohexane for 10 min resulted in the complete disappearance of the dinitrogen complex and the formation of a single carbonyl containing product showing a very strong and sharp ν(CO) at 1878 cm^{-1}. The efficiency of this transformation is shown in Fig.16. The carbonyl product was isolated at -78°C as a white solid and was characterized as the cyclometalated complex $Cp^*Re(CO)(\eta^2$-$PMe_2CH_2)(H)$ 18 resulting from the intramolecular C-H activation of a methyl group of the PMe_3 ligand.

Fig.16. Generation of the cyclometalated complex 18 (ν(CO) 1878 cm^{-1}) from irradiation of Cp*Re(CO)(PMe$_3$)(N$_2$) (13b) in cyclohexane. IR spectra of (a) 13b, (b) 8 min irradiation of 13b.


2043
1864
(a)
2200
2000
1800
cm⁻¹
1878
(b)
2200
2000
1800
cm⁻¹



18

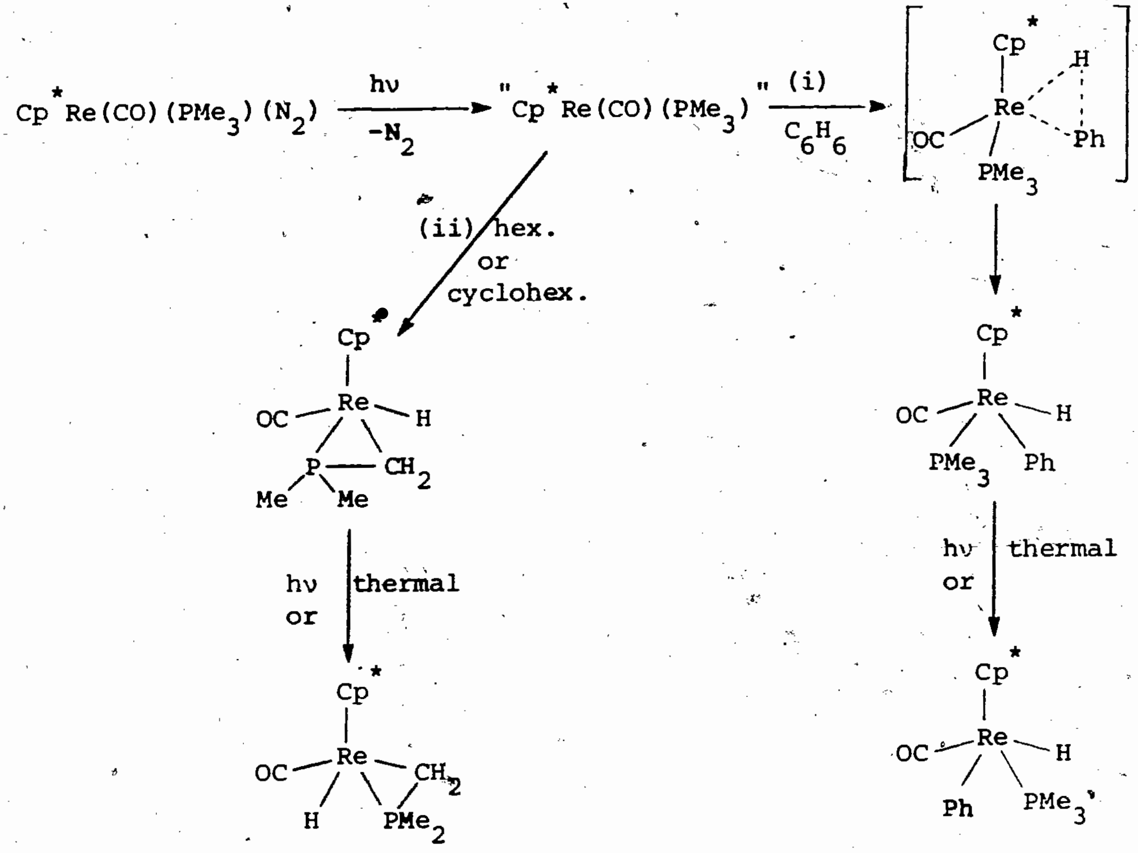
Compound 18 is very air-sensitive. It is very soluble in hexane and cyclohexane, and quite stable under N_2 at low temperature in those solvents. However, it reacted slowly with benzene in the dark to form the hydridophenyl complex (17). Likewise, it reacted with N_2 under 2000 psi of pressure to produce quantitatively the parent dinitrogen complex 13b. However, it did not react with CH_4 (500 psi) at room temperature. The ^1H NMR spectrum of compound 18 shows a doublet at δ -9.92, $^2J_{PH}$= 38.2 Hz with a relative intensity of 1H, which is assigned to the hydride resonance. Two doublets of doublets at δ -0.57 and 0.57 (each integrating for 1H) are assigned to the two non-equivalent methylene protons. Likewise, the two doublets at δ 1.37 (3H) and 1.55 (3H) are assigned to the two non-equivalent methyl groups. The resonance for the Cp^* protons appears at δ 2.02 with a relative intensity of 15H. The instability of this compound in C_6D_6 and cyclohexane-d_{12} over the time required for data collection has so far precluded accurate measurement of the ^{13}C NMR spectrum. By analogy with 17, and on the basis of ^1H NMR and NOE results, we believe that 18 possesses a trans stereochemistry, that is the hydride is trans to the methylene carbon and cis to P. NOE experiments have allowed us to assign the non-equivalent methyl groups and methylene protons of the cyclometalated fragment in 18. The NOE results are summarized as follows: irradiation of Me_b enhanced H_b more strongly than H_a; irradiation of Me_a enhanced H_a more strongly than H_b; irradiation of Cp^* enhanced H_b and Me_b much more strongly than it did H_a and Me_a. Irradiation of either Me_a or Me_b gave enhancement of hydride (more strongly with Me_a), as did irradiation of H_a, but not H_b. This suggests that the hydride is cis to PMe_2 and trans to CH_2.

Compound 18 could also be characterized by electron-impact MS at 12 eV, which exhibits the molecular ion at m/z 426 as the highest mass peak. As with the hydridophenyl complex, the spectrum at 70 eV shows peaks at m/z 502, 474 and 426.

Irradiation of 13b in hexane, in the presence of methane or molecular hydrogen did not give the expected hydridomethyl $Cp^*Re(CO)(PMe_3)(H)(Me)$ or dihydride $Cp^*Re(CO)(PMe_3)H_2$ complexes. Instead, 18 was the only product. ~~This result~~ contrasts with the formation of the known dihydride complex trans-$Cp^*Re(CO)_2H_2$[193] when the dicarbonyldinitrogen complex 13a was irradiated in hexane with H_2 purge. Irradiation of 13a in hexane with CH_4 purge gave a mixture of $Cp^*{}_2Re_2(CO)_3$ and $Cp^*{}_2Re_2(CO)_5$.

7.3. Discussion

The most straightforward mechanism for both intra and intermolecular oxidative addition reactions using the phosphine dinitrogen complex 13b as a photochemical precursor is shown in Scheme XV.



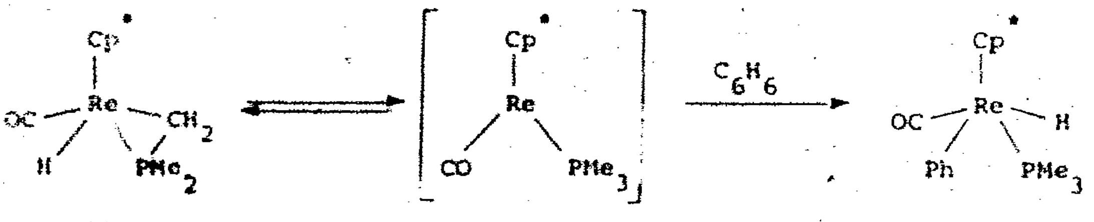
SchemeXV

A similar scheme has been proposed by Bergman using Cp*Re(CO)$_2$(PMe$_3$) or Cp*Re(CO)(PMe$_3$)$_2$ as photoprecursors.

We assume, based on extensive precedents,[178-181] that the irradiation of 13b leads primarily to the loss of N_2, forming the coordinatively unsaturated complex "$Cp^*Re(CO)(PMe_3)$" as a transient intermediate. The reactive 16-electron metal center in this intermediate then undergoes oxidative addition to the C-H bond of a benzene molecule (route (i)) presumably via a three-centered transition state leading to the cis-phenylhydrido (cis-17) (kinetic product) which isomerizes to the more stable trans isomer. The second possibility (route (ii)), which takes place in an inert solvent such as hexane or cyclohexane, is that the unsaturated fragment undergoes internal activation of the PMe_3 ligand to give the cyclometalated complex cis-18, which is converted to trans-18 thermally or by UV irradiation.

The generation of the unsaturated fragment $Cp^*Re(CO)(PMe_3)$ through the dinitrogen complex 13b and its subsequent oxidative addition to a C-H bond of benzene (intermolecular insertion) or to a C-H bond of the PMe_3 ligand (intramolecular insertion) is clearly much more effective than by using the Bergman photoprecursor $Cp^*Re(CO)_2(PMe_3)$, as can be observed in Fig.15. Furthermore, we were able to isolate the phenylhydrido complex 17 and the cyclometalated complex 18 and assign their stereochemistry. The trans stereochemistry of these insertion products was surprising but unambiguous. It is analogous to that observed by Hoyano and Graham in the hydrido complexes $CpRe(CO)_2H_2$[194] and $Cp^*Re(CO)_2H_2$.[193] The latter was produced photochemically from $Cp^*Re(CO)_3$ in the presence of H_2. Hoyano and Graham proposed that the reaction proceeds via photodissociation of CO and oxidative addition of H_2, but offered no comment about the stereochemistry.[193] It is expected that the production of the dihydrido complex trans-$Cp^*Re(CO)_2H_2$ occurs in an analogous manner to our trans complexes 17 and 18, i.e., the cis insertion product is primarily formed (in agreement with a concerted mechanism) and is then transformed to the more stable trans products.

There are other important features related to the phenylhydrido 17 and the cyclometalated 18 complexes which should be emphasized. Firstly, the slow dark reaction of 18 with C_6H_6 to form 17, suggests that reversible formation of the unsaturated fragment "$Cp^*Re(CO)(PMe_3)$" from 18 occurs and that 17 results from the thermal reaction of this intermediate with benzene (Eq.36).



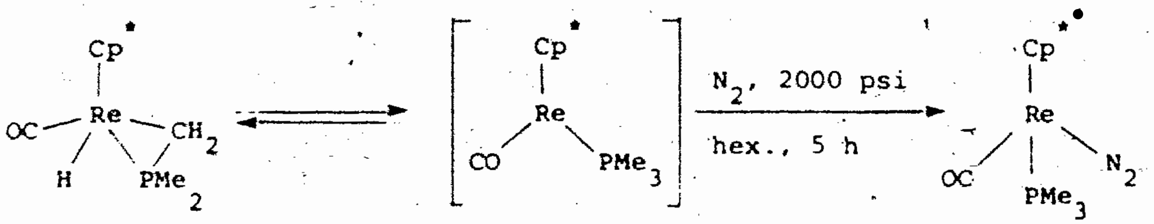
18

17

Eq.36.

The stereochemistry of the phenylhydride complex obtained by this route was not confirmed by ^1H NMR but the IR spectrum in C_6H_6 or hexane is identical to that observed for the same compound prepared photochemically. Therefore, if we assume a concerted mechanism for the insertion of the rhenium center into the benzene C-H bond, the cis to trans isomerization of the phenylhydride complex must proceed thermally.

Consistent with Eq.36, when benzene-d_6 was employed the hydride resonance was totally absent in the NMR spectrum, proving that the product was exclusively $Cp^*Re(CO)(PMe_3)(D)(C_6D_5)$ and that the hydride of 18 was reincorporated wholly into the PMe_3 group of 17. The incorporation of C_6D_6 was confirmed by the MS (12 eV) of the perdeuterated phenylhydride complex which showed m/z 510 (based on ^{187}Re), which corresponds to the molecular ion of 17-d_6. The reversible formation of "$Cp^*Re(CO)(PMe_3)$" from 18 was further indicated by the quantitative regeneration of the dinitrogen complex 13b when 18 is pressurized with N_2 (Eq.37).

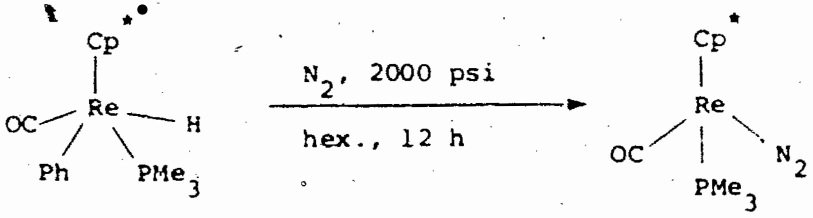


18

13b

Eq.37.

Even more surprising is the observation that the phenylhydrido complex 17 in hexane is also transformed essentially quantitatively (but more slowly) to the parent dinitrogen complex 13b under N_2 pressure (Eq.38).

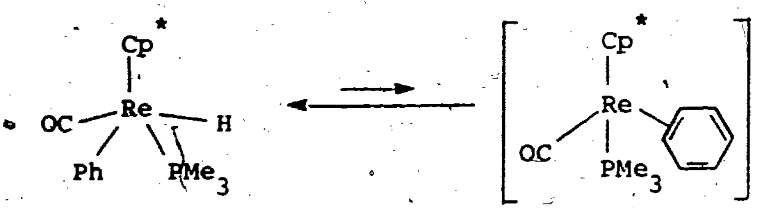


17

13b

Eq.38.

This may indicate that, in solution, 17 is partly dissociated into benzene and "$Cp^*Re(CO)(PMe_3)$" possibly via a benzene π-complex intermediate as shown in Eq.39.

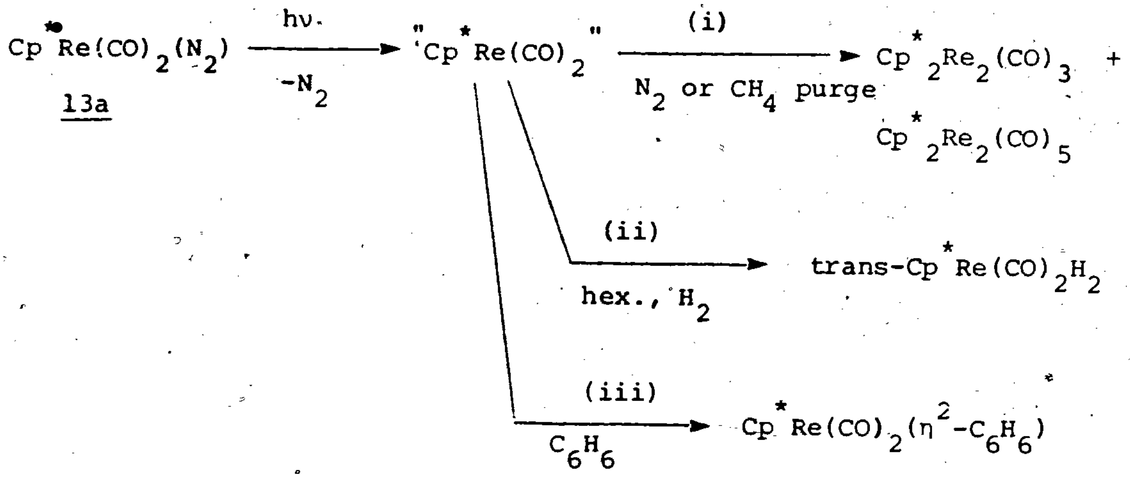


17

Eq. 39.

This suggestion is supported by Pasman and coworkers[192] and also by our results on the photolysis of 13a in benzene (see below). Furthermore, the ^{1}H NMR and MS of 17 indicated about 20% conversion to 17-d_6 in C_6D_6 at 80°C over six days.

Photochemical reactions of the less electron rich Cp*Re(CO)$_2$(N$_2$) (13a) (compared with the phosphine 13b) resulted in the photoextrusion of N$_2$ and presumably the formation of the unsaturated fragment "Cp*Re(CO)$_2$". These reactions are shown in Scheme XVI.



Scheme XVI

The products of reactions (i) and (ii) are the same as those obtained by Graham and coworkers using $Cp^*Re(CO)_3$ as a photochemical precursor.[144,193] Even though the same products are obtained from the tricarbonyl complex, 13a is a much better photoprecursor. For example, trans-$Cp^*Re(CO)_2H_2$ was produced quantitatively (by IR) according to route (ii) in 5-10 min, whereas Hoyano and Graham using $Cp^*Re(CO)_3$ as photoprecursor took more than 1 h to produce the dihydride complex in only 50% IR yield.[193]

No reaction with the methane C-H bonds occurred when 13a was irradiated in hexane with CH_4 purge (reaction (i) in Scheme XVI). Instead, the rhenium dimers $Cp^*_2Re_2(CO)_3$ and $Cp^*_2Re_2(CO)_5$ were obtained. This result is a further indication that the unsaturated fragment "$Cp^*Re(CO)_2$" is unreactive towards saturated hydrocarbon C-H bonds.

Irradiation of 13a in benzene also produced efficiently a dicarbonyl-containing compound (by IR) which we believe to be the η^2-benzene complex $Cp^*Re(CO)_2(\eta^2-C_6H_6)$ by comparison of the IR and ^1H NMR data with those reported by Pasman and coworkers for this compound.[192]

The differences in reactivity of the unsaturated fragments "$Cp^*Re(CO)_2$" and "$Cp^*Re(CO)(PMe_3)$" clearly indicate that the presence of the more electron-donating PMe_3 ligand plays an important role in the reactivity of the rhenium center towards C-H bonds. It has been suggested[182-184] that at least one of the factors which enhances the reactivity of the metal fragment toward C-H bonds is the presence of an electron-rich metal center. This suggestion is in agreement with our experimental results.

The trimethylphosphinedinitrogen complex 13b is the first example of a dinitrogen complex capable of giving isolable C-H bond activation products when irradiated in saturated and unsaturated hydrocarbons. The utilization of dinitrogen complexes as efficient photoprecursors for the activation of C-H bonds is an area of great promise for future investigations and is completely undeveloped at the present time.

7.4 Experimental Section

Photochemical reactions were carried out as described in Chapter II. Benzene, hexane and cyclohexane were dried over sodium and distilled directly into the reaction quartz tubes under oxygen-free nitrogen (Linde-Union Carbide). High pressure reactions were carried out in a Parr bomb, at room temperature using oxygen-free nitrogen. Spectroscopic measurements were done as described in Chapter II.

Preparation of trans-$Cp^*Re(CO)(PMe_3)(H)(Ph)$ (17)

A solution of the phosphinedinitrogen complex 13b (100 mg, 0.220 mmol) in about 15 mL of freshly distilled benzene was degassed twice from liquid N_2 and then irradiated for 10 min at 10°C. During the photolysis a slow flux of N_2 was maintained. The IR spectrum of the slightly yellow solution indicated a quantitative conversion of 13b into a monocarbonyl containing compound (Fig.15b). After removal of the solvent under vacuum at room temperature, the residual oily solid was redissolved in about 2 mL of benzene and carefully transferred to an air-free neutral alumina column and eluted with a mixture benzene/hexane 2:1. Evaporation of the solvent under vacuum gave **17** as a white solid which was recrystallized from freshly distilled hexane at -78°C. M.p. slow decomposition above 75°C. IR (C_6H_6): 1872 s, ν(CO), cm^{-1} (1899 cm^{-1} in hexane). ^1H NMR (C_6D_6): δ -9.18 d ($^2J_{PH}$= 66.7, 1H, Re-H), 1.08 d ($^2J_{PH}$= 8.9, 9H, PMe_3), 1.81 s (15H, Cp*), 7.16 m (3H, *m*-Ph and *p*-Ph), 7.96 m (2H, *o*-Ph). ^{13}C NMR (C_6D_6): δ 11.47 q (J_{CH}= 127.0, $C_5\underline{Me}_5$), 22.56 q of d ($^1J_{CH}$= 128.9, $^2J_{CP}$= 34.9, PMe_3), 95.97 s ($\underline{C}_5Me_5$), 123.34 d ($^1J_{CH}$= 157.2, *p*-Ph), 126.94 d ($^1J_{CH}$= 154.0, *m*-Ph), 144.87 d ($^2J_{CP}$= 23.3, i-Ph), 147.31 d of d ($^1J_{CH}$= 160.7, $^3J_{CP}$= 5.41, *o*-Ph), 209.02 d ($^2J_{CH}$= 10.8 [singlet in $^{13}C\{^1H\}$ NMR] CO). MS (EI, 12 eV): m/z 504 (M^+), 426 ($M-C_6H_6$)$^+$ base peak. Anal. Calcd. for **17**: C, 47.62; H, 5.95. Found: C, 47.88; H, 6.20.

Preparation of Cp*Re(CO)(η^2-PMe_2CH_2)(H) (**18**)

Cp*Re(CO)(PMe_3)(N_2) (**13b**) (20 mg, 0.044 mmol) was dissolved in about 10 mL of freshly distilled hexane or cyclohexane and degassed twice. This solution was then irradiated for 8 min through a quartz tube with N_2 purge. The IR spectrum of the resulting light-brown solution (Fig.16b) showed only the presence of **18**. Evaporation of the solvent under vacuum gave a brown solid which was redissolved in about 3 mL of hexane and filtered through a short neutral alumina column and stored at -78°C for two or three days. After this period a white microcrystalline solid was obtained, and isolated by decanting the supernatant solution and drying under vacuum at -78°C for 3 h. Estimated yield 60% based on 13b. M.p. decomposed above 50°C. IR (cyclohexane) (Fig.2b): 1878 s, ν(CO) cm^{-1}. ^{1}H NMR (cyclohexane-d_{12}): δ -9. 92 d($^2J_{CH}$= 38.2, 1H, Re-H), -0.57 d of d ($^2J_{HH}$= 7.3, $^2J_{PH}$= 3.0, 1H, H_b), 0.57 d of d ($^2J_{HH}$= 7.3, $^2J_{PH}$= 4.3, 1H, H_b), 1.37 d ($^2J_{PH}$= 11.8, 3H, Me_b), 1.55 d ($^2J_{PH}$= 12.9, 3H, Me_a), 2.02 s (15H, Cp*). MS (EI, 12 eV): m/z 426 (M^+) (at 70 eV only a spectrum with prominent peaks at m/z 502, 474 and 426 was observed).

Photochemical Reactions of $Cp^*Re(CO)_2(N_2)$ (13a)

(a) In hexane or cyclohexane

The dicarbonyldinitrogen complex 13a (prepared according to method 1) (10 mg, 0.024 mmol) was dissolved in 5-10 mL of hexane or cyclohexane (freshly distilled) and UV-irradiated for about 5 to 10 min at room temperature with N_2 purge. After this time, the IR spectrum of the orange-yellow solution indicated the complete disappearance of 13a and the formation of a mixture of $Cp^*_2Re_2(CO)_3$ and $Cp^*_2Re_2(CO)_5$ in about 5:2 ratio. These compounds were separated by column chromatography and identified by IR and MS to be identical with those reported by Hoyano and Graham.[144]

(b) In hexane in presence of molecular H_2

This reaction was carried out similarly to that described above but H_2 was used instead of N_2. From 10 mg of 13a, 9 mg (97%) of the dihydrido complex $Cp^*Re(CO)_2H_2$ was obtained as a pale yellow solid. No further purification was attempted, and it was characterized as the trans isomer on the basis of the relative intensity of the ν(CO) absorptions in the IR spectrum. IR (hexane): 2008 m, 1938s, ν(CO) cm^{-1}. These ν(CO) values are identical with those reported by Hoyano and Graham.[193]

(c) In benzene

This reaction was carried out under similar conditions used for the photoreaction of <u>13b</u> in benzene. After 10-12 min of irradiation a clear yellow solution resulted. An IR spectrum of this solution showed two strong ν(CO) absorptions at 1937 and 1872 cm^{-1} of approximately equal intensity. A ^1H NMR spectrum of this solution with 25% of C_6D_6 added after the irradiation and recorded with solvent null, showed resonances at δ 1.45 and 1.64 in a 2:3 ratio and δ 5.98. The resonances at δ 1.64 and 5.98 are tentatively assigned to the η^2-benzene complex $Cp^*Re(CO)_2(\eta^2-C_6H_6)$.

High Pressure Reactions under Nitrogen

(a) $Cp^*Re(CO)(\eta^2-PMe_2CH_2)(H)$ (<u>18</u>)

Compound <u>18</u> (about 10 mg, 0.019 mmol) was dissolved in freshly distilled hexane (ca. 8 mL) at 0°C under nitrogen. This solution was carefully transferred to a Parr bomb under nitrogen and pressurized to 2000 psi with oxygen-free nitrogen for 5 h at room temperature. After this time, complete generation of the dinitrogen complex <u>13b</u> was observed by IR. Evaporation of the solvent gave 9mg (~ 95% yield) of the dinitrogen complex <u>13b</u>.

(b) $Cp^*Re(CO)(PMe_3)(H)(Ph)$ (<u>17</u>)

This reaction was carried out as described in (a). An IR spectrum after 5 h showed the presence of complex 17 and complex 13b in about 1:1 ratio. Additional 7 h under 2000 psi of N_2 gave almost quantitative conversion. From 10 mg of 17 , 7.8 mg (96%) of 13b were isolated.

APPENDIX I

The Rhenium Trioxo Complex Cp^*ReO_3

(a) Introduction

In this appendix we describe the reaction of the dicarbonyltetrahydrofuran complex $Cp^*Re(CO)_2(THF)$ with O_2 at 450 psi which gave the air-stable Re(VII) complex Cp^*ReO_3 (19). At the time that this work was submitted for publication[195] an analogous synthesis for this compound was reported by Herrmann et al.[196] Since then several reports including one review[197] have been published by Herrmann's group describing chemical reactions of this complex and structural studies of its derivatives.[198,199] Even so, metal complexes containing carbon-rhenium bonds with a VII oxidation state for rhenium are still very rare and as far as we know, only two other complexes of this type have been previously described. These are Me_3ReO_2[200] and $MeReO_3$.[201] Conversely, cyclopentadienyl or pentamethylcyclopentadienyl rhenium compounds are numerous, but are typically found with low oxidation states. It will be noted that this complex combines the maximum rhenium oxidation state VII with a typical 18-electrons count for an organometallic compound.

(b) Synthesis

Cp^*ReO_3 (19) was first observed by us serendipitously in an attempt to replace the MeCN ligand in $Cp^*Re(CO)(MeCN)(p\text{-}N_2C_6H_4OMe)^+$

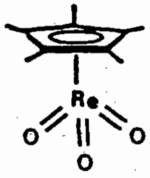
(11a) with dinitrogen and was identified readily from its elemental analysis, IR, mass spectrum and ^{1}H NMR spectrum. The MeCN complex in THF was pressurized with 1500 psi of undeoxygenated nitrogen for 3 days. IR spectroscopy then showed the absence of any carbonyl complexes and 19 was isolated after chromatography on neutral alumina as the only rhenium compound which eluted. It was similarly produced as a coproduct in the synthesis of Cp*Re(CO)$_2$(N$_2$) (13a) from Cp*Re(CO)$_2$(THF) in THF using undeoxygenated nitrogen at 1500 psi pressure (method 2), and in the reactions of the dicarbonylaryldiazenido cation 1a with halides (X$^-$) in THF-water under unpurified nitrogen (see Chapter IV).

Reaction of these carbonyl complexes with dioxygen impurity in the dinitrogen was implicated and was confirmed by the direct synthesis of 19 in 55% yield from Cp*Re(CO)$_2$(THF) in THF under 450 psi of dioxygen for 1 day. Chromatography on silica gel first eluted organic products (see below) using hexane, then a yellow band of 19 using ether, which was recrystallized as yellow needles that melt without decomposition at 192°C.

In all of the reactions giving 19 (above) where THF was the solvent organic oxidation products were observed, except in the reaction of 1a with halides where these products were not detected by IR because the presence of water in this reaction obscured the region of the spectrum where some of these products absorb (see below). These oxidation products were not formed when pure THF was pressurized with O$_2$ at 450 psi for 1 day alone or in the presence of the trioxo complex 19.

(c) Spectroscopic Characterization

The spectroscopic properties of 19 are simple indeed and in agreement with its formulation as a mononuclear complex as illustrated.



19

The 70 eV electron-impact mass spectrum gave the parent ion isotopic cluster in close to theoretical abundancies as the only prominent feature, with m/z values (theoretical % in parenthesis): 368 [56% (58.5%) ^{187}Re], 369 [8% (6.7%)], 370 [100% (100%) ^{187}Re], 371 [12.5% (11.5%)]. The IR spectrum (KBr) had bands at 910 s cm^{-1} (ν_{sym} ReO_3) and 881 vs cm^{-1} (ν_{asym} ReO_3) and the ^{1}H NMR ($CDCl_3$) had only a single resonance for the Cp* group at δ 2.16. It sublimes readily at 40°C and 10^{-2} torr, is insoluble in hexane but soluble in common organic solvents (ether, THF, C_6H_6, MeOH, CH_2Cl_2) and the solutions are air-stable. Although optically excellent crystals can be grown readily from, e.g., CH_2Cl_2/hexane, all thus far examined have been twinned and no X-ray structure is yet available.

The organic side-products, were identified by characteristic IR absorptions at 1776 vs and 1726 m, cm^{-1} in THF solution plus associated shoulders. From the reaction of Cp*Re(CO)$_2$(THF) with O_2, these products were separated from 19 by elution with hexane .

and the GC-MS spectrum showed at least five components, not all yet identified. The major one, and the only one identified so far, was γ-butyrolactone ($C_4H_6O_2$) (ν(CO) 1776 cm^{-1} in THF, m/z 86).

(d) **Experimental**

$Cp^*Re(CO)_3$ (400 mg, 0.988 mmol) was dissolved in about 300 mL of THF and irradiated as described in Chapter II. The resulting solution was concentrated to about 20 mL, placed inside a Parr bomb and pressurized under 450 psi of oxygen (Linde-Union Carbide) for 1 day. After this time oxygen was released and a bright-yellow solution remained. An IR spectrum of this showed only two absorptions at 1776 and 1726 cm^{-1}, respectively. THF was evaporated under vacuum and the yellow-oily residues were redissolved in 5 mL of THF and chromatographed on a neutral alumina column. Hexane eluted the compounds possessing the IR absorptions at 1776 and 1726 cm^{-1}. The trioxo complex (<u>19</u>) was eluted with ether. Evaporation of the ether under vacuum gave a bright-yellow solid which was recrystallized from CH_2Cl_2/hexane (1:1). Yield 200 mg (55% based on $Cp^*Re(CO)_3$)). The trioxo complex was characterized as described in section (c). Anal. Calcd. for <u>19</u>: C, 32.43; H, 4.05. Found: C, 32.31; H, 3.95. GC separation was obtained on a OV-1 capillary column (25 m x 0.25 mm) using a Hewlett-Packard Model 5880 Gas Chromatograph, and GC-MS on a Hewlett-Packard Model 5985 Mass Spectrometer. Analysis of the data: peak at 202 min (m/z 86) γ-butyrolactone (major peak); peak at 8.58 min (m/z 73); peak at 8.94 min (m/z 99); peak at 12.37 min (m/z 85); peak at 15.50 min (m/z 124).

References

1.- Chatt J., Dilworth J.R. and Richards R.L., Chem. Rev. (1977), 78, 589.

2.- Chatt J. and Richards R.L., J. Organomet. Chem. (1982), 239, 65.

3.- Parshall G.W., J. Am. Chem. Soc. (1965), 87, 2133; (1967), 89, 1822.

4.- Gilchrist A.B., Rayner-Canham G.W. and Sutton D., Nature (1972), 235, 42.

5.- Henderson R.A., Leigh G.J. and Pickett C.J., Adv. Inorg. Chem. and Radiochem. (1983), 27, 197.

6.- Nelson M.J., Lindahl P.A. and Orme-Johnson W.H., Adv. Inorg. and Biochem. (1982), 4, 1.

7.- Enemark J.H., "Nitrogen Fixation" (W.E. Newton and W.H. Orme-Johnson eds.) Vol.1, p.297. Univ. Park Press, Baltimore, 1980.

8.- Taqui Khan M.M. and Martell A.E., "Homogeneous Catalysis by Metal Complexes" Vol.1, p.181. Acad. Press, New York, 1974.

9.- Barrientos-Penna C.F., Einstein F.W.B., Sutton D. and Willis A.C., Inorg. Chem. (1980), 19, 2740.

10.- Barrientos-Penna C.F., Einstein F.W.B., Jones T. and Sutton D., Inorg. Chem. (1982), 21, 2578.

11.- Sutton D., Chem. Soc. Rev. (1975), 4, 443.

12.- Haymore B.L., Ph.D. Thesis, Northwestern Univ. (1975).

13.- Haymore B.L. and Ibers J.A., Inorg. Chem. (1975), 14, 2784.

14.- Cowie M., Haymore B.L. and Ibers J.A., J. Am. Chem. Soc. (1976), 24, 7608.

15.- Haymore B.L. and Ibers J.A., Inorg. Chem. (1975), 14, 3060.

16.- Dilworth J.R., Kan C.T., Richards R.L., Mason J. and Stenhouse I.A., J. Organomet. Chem. (1980), 201, C24.

17.- Schramm K.D. and Ibers J.A., Inorg. Chem. (1977), 16, 3287.

18.- Gaughan A.P. and Ibers J.A., Inorg. Chem. (1975), 14, 352.

19.- Dilworth J.R., Latham I.A., Leigh G.L., Huttner G. and Jibril I., J.C.S. Chem. Commun. (1983), 1368.

20.- Cobbledick R.E., Einstein F.W.B., Farrell N., Gilchrist A.B. and Sutton D., J.C.S. Dalton Trans. (1977), 373.

21.- Krogsrud S. and Ibers J.A., Inorg. Chem. (1975), 14, 2298.

22.- Butler G., Chatt J., Leigh G.J., Smith A.R.P. and Williams G., Inorg. Chim. Acta (1978), 28, L165.

23.- Cowie M., Haymore B.L. and Ibers J.A., Inorg. Chem. (1975), 14, 2617.

24.- Hillhouse G.L., Haymore B.L. and Herrmann W.A., Inorg. Chem. (1979), 18, 2423.

25.- Duckworth V.F., Douglas P.G., Mason R. and Shaw B.L., J.C.S. Chem. Commun. (1970), 1083.

26.- Mason J., Chem. Brit. (1983), 19, 654.

27.- Barrientos-Penna C.F., Ph.D. Thesis, Simon Fraser Univ. (1983).

28.- Fisher D.R. and Sutton D., Can. J. Chem. (1973), 51, 1697.

29.- Haymore B.L. and Ibers J.A., J. Am. Chem. Soc. (1973), 95, 3052.

30.- Connelly N.G. and Demidowicz Z., J. Organomet. Chem. (1974), 73, C31.

31.- Connelly N.G. and Gardner C., J. Organomet. Chem. (1978), 159, 179.

32.- Mason R., Thomas K.M., Zubieta J., Douglas P.G., Galbraith A.R. and Shaw B.L., J. Am. Chem. Soc. (1974), 96, 260.

33.- Barrientos-Penna C.F.,Gilchrist A.B. and Sutton D., Organometallics (1983), 2, 1265.

34.- Ittel S.D. and Ibers J.A., J. Am. Chem. Soc. (1974), 96, 4804.

35.- Haymore B.L. and Ibers J.A., J. Am. Chem. Soc. (1975), 97, 5369.

36.- Frost V.L. and Henderson R.A., J.C.S. Dalton Trans. (1985), 2059.

37.- Henderson R.A., J.C.S. Dalton Trans. (1985), 2067.

38.- Chatt J., Pure Appl. Chem. (1982), 54, 2545.

39.- Haymore B.L., personal communication.

40.- Nicholson T. and Zubieta J., J.C.S. Chem. Commun. (1985), 367.

41.- Hidai M, Komori K, Kodama T., Jin D-N, Takahashi T., Sugiura S., Uchida Y. and Mizobe Y., J. Organomet. Chem. (1984), 272, 155.

42.- March F.C., Mason R. and Thomas K.M., J. Organomet. Chem. (1975), 96, C43.

43.- Dilworth J.R., Harrison S.A., Walton D.R.M. and Schweda E., Inorg. Chem. (1985), 24, 2595.

44.- Chatt J., Fakley M.E., Mason J., Richards R.L. and Stenhouse I.A., J. Chem. Res. (1979), s, 322.

45.- Donovan-Mtunzi S., Richards R.L. and Mason J., J.C.S. Dalton Trans. (1984), 1329.

46.- Barrientos-Penna C.F., Campana C.F., Einstein F.W.B., Jones T., Tracey A.S. and Sutton D., Inorg. Chem. (1984), 23, 363.

47.- Allen A.D. and Senoff C.V., J.C.S. Chem. Commun. (1965), 621.

48.- Du Bois D.L. and Hoffman R., Nov. J. Chim. (1978), 1, 479.

49.- Yamabe T., Hori K, Minato T. and Fukui H., Inorg. Chem. (1980), 19, 2154.

50.- Pelikan P. and Boca R., Coord. Chem. Rev. (1984), 55, 55.

51.- Chatt J., Fakley M.E., Richards R.L., Mason J. and Stenhouse I.A., J. Chem. Res. (1979), s, 44.

52.- Donovan-Mtunzi S., Richards R.L. and Mason J., J.C.S. Dalton Trans. (1984), 469.

53.- Busetto C., D'Alfonso A., Maspero F., Perego G. and Zazzetta A., J.C.S. Dalton Trans. (1977), 1828.

54.- Thorn D.L., Tulip T.H. and Ibers J.A., J.C.S. Dalton Trans. (1979), 2022.

55.- Gynane M.J., Jeffery J. and Lappert M.F., J.C.S. Chem. Commun. (1978), 34.

56.- Allen A.D., Harris R.D., Loescher B.R., Stevens J.R. and Whiteley R.N., Chem. Rev. (1973), 73, 11.

57.- Carvalho M.F., Pombeiro A.J.L., Schubert V., Pickett C.J. and Richards R.L., J.C.S. Dalton Trans. (1985), 2079.

58.- Carmona E., Galindo A., Poveda M.L. and Rogers R.D., Inorg. Chem. (1985), 24, 4033.

59.- Chiu K.W., Howard C.G., Rzepa H.S., Sheppard R.N., Wilkinson G., Galas A.M.R. and Hursthouse M.B., Polyhedron (1982), 1, 441.

60.- Sato M., Tatsumi T., Kodama T., Hidai M., Uchida T. and Uchida Y., J. Am. Chem. Soc. (1979), 100, 4447.

61.- Quinby M.S. and Feltham R.D., Inorg. Chem. (1972), 11, 2468.

62.- Darensbourg D.J., Inorg. Chem. (1972), 11, 1436.

63.- (a) Chatt J., Crabtree R.H., Jeffery E.A. and Richards R.L., J.C.S. Dalton Trans. (1973), 1167.

(b) Chatt J., Leigh G.L., Neukomm H., Pickett C.J. and Stanley D.R., J.C.S. Dalton Trans. (1980), 121.

64.- Leigh G.L., Morris R.H., Pickett C.J., Stanley D.R. and Chatt J., J.C.S. Dalton Trans. (1981), 800.

65.- Hussain W., Leigh G.L., Ali H.M., Pickett C.J. and Rankin D.A., J.C.S. Dalton Trans. (1984), 1703.

66.- Dilworth J.R., Donovan-Mtuzi S., Kan C.T., Richards R.L. and Mason J., Inorg. Chim. Acta (1981), 53, L161.

67.- Archer L.J. and George T.A., J. Organomet. Chem. (1973), 54, C25.

68.- Chatt J., Leigh G.L. and Richards R.L., J.C.S. A (1970), 2243.

69.- Chatt J., Lloyd J.P. and Richards R.L., J.C.S. Dalton Trans, (1976), 565.

70.- Carmona E., Marin J.M., Poveda M.L., Atwood J.L. and Rogers R.D., J. Am. Chem. Soc. (1983), 105, 304.

71.- Chatt J., Dilworth J.R. and Leigh G.L., J.C.S. Dalton Trans. (1973), 612.

72.- Dadkhah H., Dilworth J.R., Fairman K., Kan C.T., Richards R.L. and Hughes D.L., J.C.S. Dalton Trans. (1985), 1523.

73.- Pombeiro A.J.L., Jeffery J.C., Pickett C.J. and Richards R.L., J. Organomet. Chem. (1984), 277, C7.

74.- Tatzumi T., Tominaga H., Hidai M. and Uchida Y., J. Organomet. Chem. (1980), 199, 63.

75.- Tatzumi T., Hidai M. and Uchida Y., Inorg. Chem. (1975), 14, 2530.

76.- Donovan-Mtunzi S., Richards R.L. and Mason J., J.C.S. Dalton Trans. (1984), 2729.

77.- Chatt J., Pearman A.J. and Richards R.L., J.C.S. Dalton Trans. (1977), 2139.

78.- Morris R.H., Ressner J.M., Sawyer J.F. and Shiralian M., J. Am. Chem. Soc. (1984), 106, 3683.

79.- Chatt J., Pearman A.J. and Richards R.L., J.C.S. Dalton Trans. (1977), 1852.

80.- Anderson S.N., Fakley M.E., Richards R.L. and Chatt J., J.C.S. Dalton Trans. (1981), 1973.

81.- Bossard G.E., George T.A. and Lester R.K., Inorg. Chim. Acta (1982), 64, L227.

82.- George T.A. and Tisdale R.C., J. Am. Chem. Soc. (1985), 107, 5157.

83.- Chatt J., Heath G.A. and Richards R.L., J.C.S. Dalton Trans. (1974), 2074.

84.- Hidai M., Kodama T., Harakawa M. and Uchida Y., Inorg. Chem. (1976), 15, 2694.

85.- Chatt J., Pearman A.J. and Richards R.L., J.C.S. Dalton Trans. (1976), 1520.

86.- Chatt J., Diamantis A.A., Heath G.A., Hooper N.E. and Leigh G.J., J.C.S. Dalton Trans. (1977), 688.

87.- Day V.W., George T.A. and Iske S.D.A., J. Am. Chem. Soc. (1975), 97, 4127.

88.- Bossard G.E., Busby D.C., Chang M., George T.A. and Iske S.D.A., J. Am. Chem. Soc. (1980), 102, 1001.

89.- Busby D.C., George T.A., Iske S.D.A. and Wagner S.D., Inorg. Chem. (1981), 20, 22.

90.- Chatt J., Head R.A., Leigh G.J. and Pickett C.J., J.C.S. Dalton Trans. (1978), 1638.

91.- Bevan P.C., Chatt J., Leigh G.J. and Leelamani E.G., J. Organomet. Chem. (1977), 139, C59.

92.- Sellmann D. and Weiss W., Angew. Chem. Int. Ed. Engl. (1978), 17, 269.

93.- Barrientos-Penna C.F., Gilchrist A.B., Klahn-Oliva A.H., Hanlan A.J.L. and Sutton D., Organometallics (1985), 4, 478.

94.- Heberhold M. and Bernhagen W., Z. Naturfosch., B: Anorg. Chem., Org. Chem. (1974). 293, 801.

95.- Sweet J.R. and Graham W.A.G., J. Am. Chem. Soc. (1982), 104, 2811.

96.- Patton A.J., Strouse C.E., Knobler C.B. and Gladysz J.A., J. Am. Chem. Soc. (1983), 105, 5804.

97.- King R.B. and Bisnette M.B., J. Organomet. Chem. (1967), 8, 278.

98.- Hoyano J.K. and Graham W.A.G., personal communication.

99.- Collman J.P., Accts. Chem. Res. (1975), 8, 342.

100.-Fisher E.O., Adv. Organomet. Chem. (1976), 14, 1.

101.-Gladysz J.A., Adv. Organomet. Chem. (1982), 20, 1.

102.-Ford P.C., Accts. Chem. Res. (1972), 5, 31.

103.-Angelici R.J., Accts. Chem. Res. (1972), 5, 335.

104.-Yoshida T., Ueda Y. and Otsuka S., J. Am. Chem. Soc. (1978), 100, 3941.

105.-Darensbourg D.J. and Rokicki A., Organometallics (1982), 1, 1685.

106.-Clark H.C. and Jacobs W.J., Inorg. Chem. (1970), 9, 1229.

107.-Sweet J.R. and Graham W.A.G., Organometallics (1982), 1, 982.

108.-Deeming A.J. and Shaw B.L., J.C.S. A (1969), 443.

109.-Gaice N., Kao S.C. and Pettit R., J. Am. Chem. Soc. (1979), 101, 1627.

110.-Gibson D.H. and Ong T-S., Organometallics (1984), 3, 1911.

111.-Tam W., Lin G.Y., Wong W.K., Kiel W.A., Wong V.K. and Gladysz J.A., J. Am. Chem. Soc. (1982), 104, 141.

112.-Bennett M.A. and Rokicki A., Organometallics (1985), 4, 180.

113.-Gibson D.H., Owens K. and Ong T-S., J. Am. Chem. Soc. (1984), 106, 1125.

114.-Catellani M. and Halpern J., Inorg. Chem. (1980), 19, 566.

115.-Merrifield T.H. and Gladysz J.A., Organometallics (1983), 2, 272.

116.-(a) Rivetti F. and Romano V., J. Organomet. Chem. (1979), 174, 221.

(b) Martin W.E. and Farona M.F., J. Organomet. Chem. (1981), 206, 393.

117.-Behrens H., Adv. Organomet. Chem. (1980), 18, 1.

118.-Darensbourg D.J. and Darensbourg M.Y., Inorg. Chem. (1970), 9, 1691.

119.-Lilga M.A. and Ibers J.A., Orgametallics (1985), 4, 590.

120.-Vasapollo G., Nobile C.F. and Sacco A., J. Organomet. Chem. (1985), 296, 435.

121.-Thorn D.L., Organometallics (1982), 1, 197.

122.-Angelici R.J. and Formanek T., Inorg. Chim. Acta. (1983), 76, L9.

123.-Barrientos-Penna C.F., Klahn-Oliva A.H. and Sutton D., Organometallics (1985), 4, 367.

124.-Junbaur A. and Behrens H., Z. Naturforsch., B: Anorg. Chem. Org. Chem. (1979), 34B, 1641.

125.-Jetz W. and Angelici R.J., J.Am. Chem. Soc. (1972), 94, 3799.

126.-Brink R.W. and Angelici R.J., Inorg. Chem. (1973), 12, 1062.

127.-Angelici R.J. and Busetto L., J. Am. Chem. Soc. (1969), 91, 3197.

128.-Alberts M.O. and Coville N.J., Coord. Chem. Rev. (1984), 33, 227.

129.-Sweet J.R. and Graham W.A.G., J. Organomet. Chem. (1983), 241, 45.

130.-Sweet J.R. and Graham W.A.G., Organometallics (1983), 2, 135.

131.-Pomeroy R.K. and Wijesekera K.S., Inorg. Chem. (1980),19, 3729.

132.-Busetto L. and Angelici R.J., Inorg. Chim. Acta (1968), 2, 391.

133.-Baker P.K., Bradley K. and Connelly N.G., J.C.S. Dalton Trans. (1982), 471.

134.-Naack K. and Calderazzo F., J. Organomet. Chem. (1967), 10, 101.

135.-Schardt B.C. and Hill G.L., Inorg. Chem. (1983), 22, 1563.

136.-Koelle V., J. Organomet. Chem. (1978), 155, 53.

137.-Webb M.J. and Graham W.A.G., J. Organomet. Chem. (1975), 93, 119.

138.-Casey C.P., Marder S.R., Colbron R.E. and Goodson P.A., Organometallics (1986), 5, 199.

139.-Catheline D. and Astruc D., J. Organomet. Chem. (1984), 272, 417.

140.-Martin G.P., Martin M.L. and Gouesnard J.P., "^{15}N-NMR Spectroscopy", p.158. Springer-Verlag, Berlin, 1981.

141.-Mason J., Chem. Rev. (1981), 81, 205.

142.-Becker W., Beck W. and Rieck R., Z. Naturforsch., B: Anorg. Chem., Org. Chem. (1970), 25B, 1332.

143.-(a) Sherman E.O. and Schreiner P.R., J.C.S. Chem. Commun. (1976), 27.

(b) Sherman E.O. and Olson M., J. Organomet. Chem. (1979), 172, C13.

144.-Hoyano J.K. and Graham W.A.G., J.C.S. Chem. Commun. (1982), 27.

145.-Tolman C.A., Chem. Rev. (1977), 77, 313.

146.-Bodner G.M., May M.P. and McKinney L.E., Inorg. Chem. (1980), 19, 1951.

147.-Bodner G.M., Inorg. Chem. (1974), 13, 2563.

148.-Saltzman H. and Sharefkin J.G., "Organic Synthesis" Vol.V, p.658. Wiley, New York Collect.

149.-Chatt J., Dilworth J.R. and Leigh G.J., J.C.S. Chem. Commun. (1969), 687.

150.-Tully M.E. and Ginsberg A.D., J. Am. Chem. Soc. (1973), 95, 2042.

151.-Sellmann D., J. Organomet.Chem. (1972), 36, C27.

152.-Sellmann D. and Kleinschmidt E., Z. Naturforsch., B: Anorg. Chem., Org. Chem. (1977), 32B, 795.

153.-Sellmann D. and Maisel G., Z. Naturforsch. (1972), 425.

154.-(a) Cobbledick R.E., Einstein F.W.B., Pomeroy R.K. and Spetch E.R., J. Organomet. Chem. (1980), 195, 77.
(b) Milbrath D.S., Springer J.P., Clardy J.C. and Verkade J.G., Inorg. Chem. (1975), 14, 2665.

155.-Burns R.J., Bulkowki P.B., Stevens S.C.V. and Baird M.C., J.C.S. Dalton Trans. (1974), 415.

156.-Faller J.W. and Johnson B.V., J. Organomet. Chem. (1975), 96, 99.

157.-Brown D.A., Lyons H.J. and Manning A.R., Inorg. Chim. Acta (1970), 4, 428.

158.-Isaacs E.E. and Graham W.A.G., J. Organomet. Chem. (1975), 90, 319.

159.-Brown J.M. and Mertis K., J. Organomet. Chem. (1973), 47, C5.

160.-Nesmeyanov A.N., Kolobova N.E., Makarov Yu. V. and Anisimov K.M., Izv. Akad. Nauk. SSSR, Sev. Khim. (1969), 1826.

161.-King R.B., Reimann R.H. and Darensbourg D.J., J. Organomet. Chem. (1975), 93, C23.

162.-Kolobova N.E., Valueva Z.P. and Kazimirchuck E.I., Izv. Akad. Nauk. SSSR, Sev. Khim. (1981), 408.

163.-Dong D.F., Hoyano J.K. and Graham W.A.G., Can. J. Chem. (1981), 59, 1455.

164.-King R.B., J. Inorg. Nucl. Chem. (1967), 29, 2119.

165.-King R.B. and Reimann R.H., Inorg. Chem. (1976), 15, 183.

166.-Einstein F.W.B., Klahn-Oliva A.H., Sutton D. and Tyers K.G., Organometallics (1986), 5, 53.

167.-Todd L.J., Wilkinson J.R., Hickey J.P., Beach D.L. and Barnett K.W., J. Organomet. Chem. (1978), 154, 151.

168.-Beach D.L. and Barnett K.W., J. Organomet. Chem. (1975), 97, C27.

169.-Flood T.C., Rosenberg E. and Sarhangi A., J. Am. Chem. Soc. (1977), 99, 4334.

170.-Faller J.W. and Anderson A.S., J. Am. Chem. Soc. (1970), 92, 5852.

171.-Pyshnograyeva N.I., Setkina V.N., Parrosyan G.A., Petrovoskii P.V., Makarov Yu. V., Kolobova N.E. and Kursanov D.N., J. Organomet. Chem. (1976), 108, 85.

172.-Chatt J., Crabtree R.H., Dilworth J.R. and Richards R.L., J.C.S. Dalton Trans. (1974), 2358.

173.-Blake D.M. and Kubota M., J. Am. Chem. Soc. (1970), 92, 2578.

174.-Ginzburg A.G., Setkina V.N. and Kursanov D.N., Izv. Akad. Nauk. SSSR, Sev. Khim. (1979), 894.

175.-Purcell K.F. and Kotz J.C., "Inorganic Chemistry" p.703. Saunders, Philadelphia, 1977.

176.-Appleton T.G., Clark H.C. and Manzer L.E., Coord. Chem. Rev. (1973), 10, 335.

177.-Jones W.D. and Maguire J.A., Organometallics (1986), 5, 590.

178.-Darensbourg D.J., Inorg. Nucl. Chem. Lett. (1972), 8, 529.

179.-Archer L.J. and George T.A., Inorg. Chim. Acta (1980), 44, L129.

180.-Hughes D.L., Pombeiro A.J.L., Pickett C.J. and Richards R.L., J. Organomet. Chem. (1983), 248, C26.

181.-Bradley M.G., Roberts D.A. and Geoffroy G.L., J. Am. Chem. Soc. (1981), 103, 379.

182.-Muetterties E.L., Chem. Soc. Rev. (1983), 12,283.

183.-Crabtree R.H., Chem. Rev. (1985), 85, 245.

184.-Janowicz A.H. and Bergman R.G., J. Am. Chem. Soc. (1983), 105, 3929.

185.-Bergman R.G., Science (1984), 223, 902.

186.-Crabtree R.H., Mihelcic J.M. and Quirk J.M.,J. Am. Chem.Soc. (1979), 101, 7738.

187.-Hoyano J.K., McMaster A.D. and Graham W.A.G., J. Am. Chem. Soc. (1983), 105, 7190.

188.-Graham W.A.G., J. Organomet. Chem. (1986), 300, 81.

189.-Jones W.D. and Feher F.J., J. Am. Chem. Soc. (1984), 106, 1650.

190.-Bergman R.G., Seidler P.F. and Wenzel T.T., J. Am. Chem. Soc. (1985), 107, 4358.

191.-Klahn-Oliva A.H., Singer R.D. and Sutton D., J. Am. Chem. Soc. (1986), 108, 0000.

192.-Heijden H., Orpen A.G. and Pasman P., J.C.S. Chem. Commun. (1985), 1576.

193.-Hoyano J.K. and Graham W.A.G., J. Am. Chem. Soc. (1982), 104, 3722.

194.-Hoyano J.K. and Graham W.A.G., Organometallics (1982), 1, 783.

195.-Klahn-Oliva A.H. and Sutton D., Organometallics (1984), 3, 1313.

196.-Herrmann W.A., Serrano R. and Bock H., Angew. Chem. Int. Ed. Engl. (1984), 23, 383.

197.-Herrmann W.A., J. Organomet. Chem. (1986), 300, 111.

198.-Herrmann W.A., Kusthardt V., Ziegler M.L. and Zahn T. Angew. Chem. Int. Ed. Engl. (1985), 24, 860.

199.-Herrmann W.A., Serrano R., Kustharst V., Guggolz E., Nuber B.and Ziegler M.L., J.Organomet. Chem. (1985), 287, 329.

200.-Mertis K. and Wilkinson G., J.C.S. Dalton Trans. (1976), 1488.

201.-Beattie I.R. and Jones P.J., Inorg. Chem. (1979), 18, 2318.